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Unimolecular Decomposition Kinetics of the Stabilised Criegee Intermediates CH_2OO and CD_2OO

Supplementary Information

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Determination of normalised Criegee Intermediate spectra and concentrations

The observed absorbance between wavelengths of 300 nm and 440 nm following photolysis of $CH_2I_2/O_2/He$ mixtures contains contributions from CH_2I_2, CH_2OO and IO (produced by secondary chemistry), with the total absorbance a particular time and wavelength, $A_{t,\lambda}$, given by Equation S1:

$$A_{t,\lambda} = \ln(I_{0,\lambda} / I_{t,\lambda}) = A_{CH2I2,t,\lambda} + A_{CH2OO,t,\lambda} + A_{IO,t,\lambda} \qquad \text{(Equation S1)}$$

where I_0 is the average light intensity at wavelength λ prior to photolysis, $I_{\lambda,t}$ is the light intensity at wavelength λ and time t following photolysis, $A_{CH2I2,t,\lambda}$ is the absorbance of CH_2I_2 at time t and wavelength λ, $A_{CH2OO,t,\lambda}$ is the absorbance of CH_2OO at time t and wavelength λ, and $A_{IO,t,\lambda}$ is the absorbance of IO at time t and wavelength λ.

From the Beer-Lambert law, $A_{t,\lambda}$ can be given in terms of the absorption cross-sections, concentrations and path length of the light

$$A_{t,\lambda} = \sigma_{CH2I2,\lambda}\, \Delta[CH_2I_2]\, l + \sigma_{CH2OO,\lambda}\, [CH_2OO]_t\, l + \sigma_{IO,\lambda}\, [IO]_t\, l \qquad \text{(Equation S2)}$$

where $\sigma_{CH2I2,\lambda}$ is the CH_2I_2 absorption cross-section at wavelength λ, $\Delta[CH_2I_2]$ is the change in CH_2I_2 concentration on photolysis, $\sigma_{CH2OO,\lambda}$ is the CH_2OO absorption cross-section at wavelength λ, $[CH_2OO]_t$ is the concentration of CH_2OO at time t, $\sigma_{IO,\lambda}$ is the IO absorption cross-section at wavelength λ, $[IO]_t$ is the concentration of CH_2OO at time t, and l is the path length of the light.

Absorption cross-sections for CH_2I_2 and IO are well characterised in the literature,[1-5] and there have been several recent studies of the absorption cross-sections for CH_2OO.[6-8] However, since the CH2OO kinetics under investigation are first-order, knowledge of the absolute CH2OO concentration, and thus absorption cross-section, is not required. The shape of the CH_2OO absorption spectrum can be determined from these experiments by subtraction of a spectrum recorded at a late time point after photolysis, after the CH_2OO has reacted and thus containing only contributions from CH_2I_2 and IO, from a spectrum recorded shortly after photolysis which contains contributions from

CH_2I_2, CH_2OO and IO, with the contribution from CH_2I_2 assumed to be constant and those from IO in each spectrum determined using the structured region of the spectrum. Since the absolute CH_2OO concentration is not required in this work, the CH_2OO absorption spectrum obtained is normalised to the maximum absorbance. A similar approach was taken to determine the normalised spectrum for CD_2OO, generated by photolysis of CD_2I_2/O_2/He mixtures. Figure 3 (main text) shows the normalised CH_2OO and CD_2OO spectra determined in this work.

The observed total absorbance is subsequently fitted to the absolute absorption cross-sections for CH_2I_2[1,2] and IO[3-5] and the normalised absorption cross-sections for CH_2OO (or CD_2OO) at wavelengths between 300 and 440 nm at each time point during the course of the reaction, using Equation S2, to determine the changes in CH_2OO (or CD_2OO) concentration throughout the reaction. Concentrations of CH_2OO and CD_2OO throughout are normalised to the maximum concentration in each experiment owing to uncertainties in the absolute absorption cross-sections.

Kinetic Fits to CH_2OO Time Profiles

Time profiles for CH_2OO were fit to an exponential decay convolved with a Gaussian instrument function (Figure 1, main text). The quality of the kinetic fits to the experimental data for CH_2OO was investigated as a function of the photolysis laser fluence and initial CH_2I_2 concentration to examine any dependence on the initial experimental conditions. Figure S1 shows the sum of the residuals for the fit to each CH2OO trace as a function of the laser fluence and initial CH_2I_2 concentration, showing that there is no dependence of the fit quality on the initial experimental conditions.

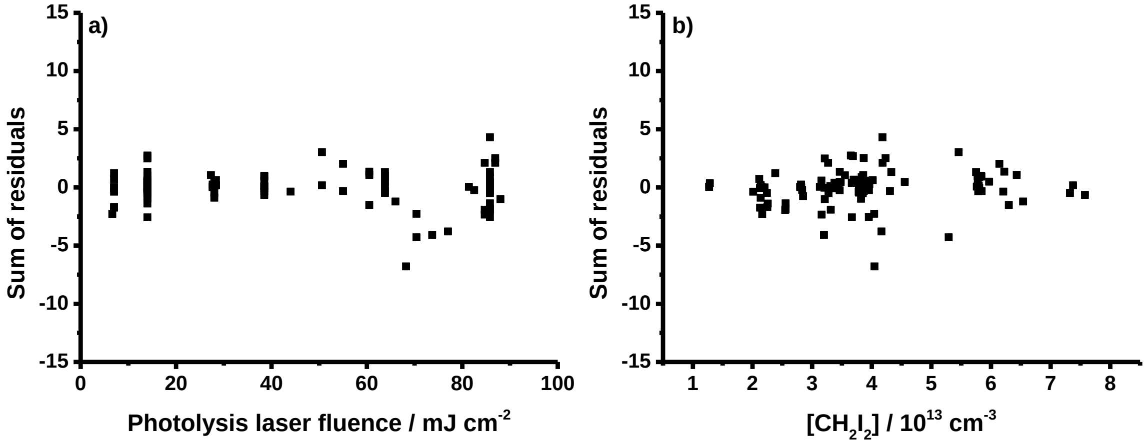

Figure S1: Dependence of the sum of residuals to fits to CH_2OO data on a) the photolysis laser fluence and b) the initial CH_2I_2 concentration.

$CH_2OO + CH_2I_2$

The observed rate coefficients describing the loss of CH_2OO in the UV experiments were found to contain contributions from a pressure- and temperature-dependent term, k(p,T), attributed to the decomposition of CH_2OO, and a pressure-independent temperature-dependent term, k(T), representing background losses in the system. At 450 K, the observed rate coefficients describing the loss of CH_2OO displayed little dependence on pressure, indicating the dominance of the background losses. The data at 450 K suggest a contribution to the background loss from reaction between CH_2OO and CH_2I_2, as shown in Figure S2, with a bimolecular rate coefficient of $(8.2 \pm 1.7) \times 10^{-12}$ cm^3 s^{-1}. The reaction has also recently been observed by Liu et al.,[9] with a rate coefficient of $(5.2 \pm 2.6) \times 10^{-14}$ cm^3 s^{-1} at 298 K. At temperatures above 450 K, concentrations of CH_2I_2 were not varied over a sufficient range to fully assess the role of $CH_2OO + CH_2I_2$.

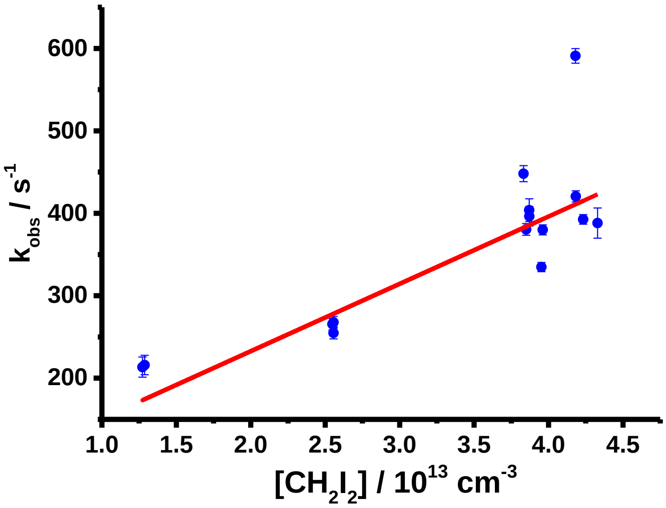

Figure S2: Variation of the observed rate coefficient describing the loss of CH_2OO with the concentration of the CH_2I_2 precursor at a temperature of 450 K. The slope indicates a bimolecular rate coefficient of $(8.2 \pm 1.7) \times 10^{-12}$ cm^3 s^{-1} for the reaction $CH_2OO + CH_2I_2$ at this temperature.

Kinetics of OH(v=1)

The kinetics of OH(v=1) collisional relaxation to OH(v=0) by O_2 were determined from the experiments monitoring OH(v=1) following photolysis of $CH_2I_2/O_2/N_2$. As described in the main text, the OH(v=1) LIF signal (Figure 7, main text) was observed to display a photolytic component, followed by a rapid growth owing to collisional relaxation from OH(v≥2) states produced photolytically, and a subsequent biexponential decay consisting of a genuine OH(v=1) decay perturbed by a slow growth of OH(v=1) owing to direct production from CH_2OO decomposition. Biexponential fits to the observed OH(v=1) signals therefore give the pseudo-first-order rate coefficients for collisional relaxation of OH(v=1) (k'_6 in the main text), which was dominated by O_2, and the rate coefficient describing CH_2OO decomposition (k_1 in the main text).

The values for k_6 determined in this work are shown in Figure S3 as a function of temperature, with the parameterisation of previous measurements obtained by McCabe et al.[10] in the range 204-371 K shown for comparison. The dependence of the OH(v=1) signal amplitudes (S_g and $S_{OH(v=0),t=0}$ in Equation 2, main text) on $[CH_2I_2]$ is shown in Figure S4, with the ratio of the signal amplitudes ($S_g/S_{OH(v=0),t=0}$) on $[CH_2I_2]$, $[O_2]$ and total pressure shown in Figure S5.

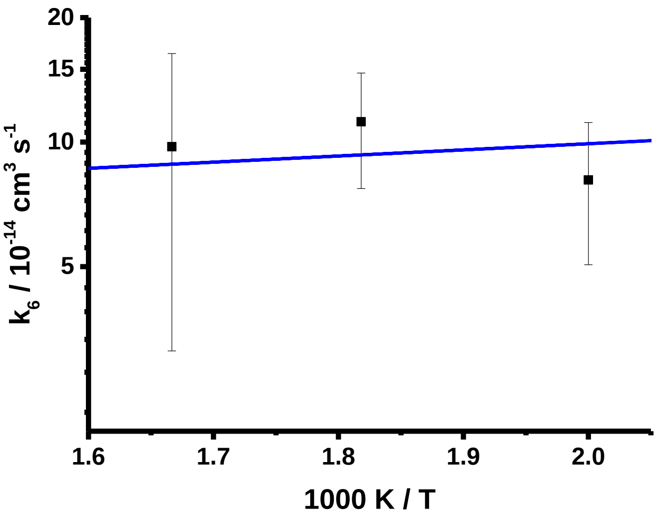

Figure S3: Bimolecular rate coefficients for collisional relaxation of OH(v=1) to OH(v=0) by O_2 (k_6) determined in this work (data points). The parameterisation of measurements by McCabe et al.[10] at temperatures between 204 and 371 K is shown for comparison (solid blue line).

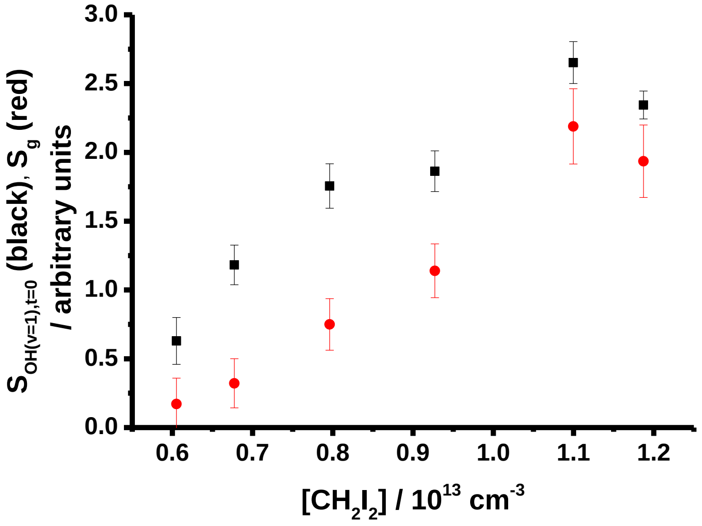

Figure S4: a) Dependence of $S_{OH(v=0),t=0}$ (black) and S_g (red) (Equation 2, main text) on the CH_2I_2 concentration. Data shown were taken at 570 K and 95 Torr.

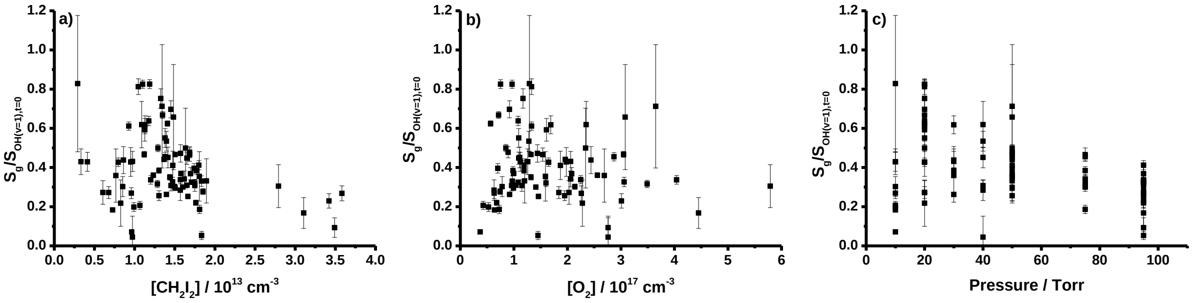

Figure S5: Dependence of the ratio of S_g:$S_{OH(v=0),t=0}$ (Equation 2, main text) on a) [CH_2I_2]; b) [O_2]; c) total pressure.

Uncertainties in fits to $k_{1,obs}$ and $k_{2,obs}$

The fits of Equation 1 (main text) to the observed decays for CH_2OO and CD_2OO indicate significant uncertainties in the individual fit parameters (A_0, E_0, A_∞, E_∞, A_{bg} and E_{bg} which determine k_0, k_∞, and k_{bg}, respectively) describing the total loss rate coefficients. However, inspection of the covariance matrices for the fits to $k_{1,obs}$ (Table S1) and $k_{2,obs}$ (Table S2) indicate that the fit parameters are highly correlated.

	A_0	E_0	A_∞	E_∞	A_{bg}	E_{bg}
A_0	1.697×10^{-15}	8.568×10^{-5}	-3.804×10^{3}	-1.042×10^{-4}	5.280×10^{-5}	1.048×10^{-6}
E_0	8.568×10^{-5}	4.334×10^{6}	-1.911×10^{14}	-5.250×10^{6}	3.351×10^{6}	7.562×10^{4}
A_∞	-3.804×10^{3}	-1.911×10^{14}	9.577×10^{21}	2.602×10^{14}	-9.682×10^{13}	-2.413×10^{12}
E_∞	-1.042×10^{-4}	-5.250×10^{6}	2.602×10^{14}	7.089×10^{6}	-3.350×10^{6}	-8.839×10^{4}
A_{bg}	5.280×10^{-5}	3.351×10^{6}	-9.682×10^{13}	-3.350×10^{6}	1.235×10^{8}	4.395×10^{6}
E_{bg}	1.048×10^{-6}	7.562×10^{4}	-2.413×10^{12}	-8.839×10^{4}	4.395×10^{6}	1.593×10^{5}

Table S1: Covariance matrix showing the correlations between the fit parameters determined by fitting to the observed rate coefficients describing the loss of CH_2OO ($k_{1,obs}$).

	A_0	E_0	A_∞	E_∞	k_{bg} 450 K	k_{bg} 500 K	k_{bg} 550 K	k_{bg} 600 K	k_{bg} 650 K
A_0	1.570×10^{-21}	7.108×10^{-8}	-1.218×10^{6}	-1.219×10^{-7}	-1.557×10^{-9}	-7.734×10^{-9}	-2.063×10^{-9}	2.060×10^{-8}	-3.328×10^{-9}
E_0	7.108×10^{-8}	3.229×10^{6}	-4.750×10^{19}	-4.854×10^{6}	-6.522×10^{4}	-3.191×10^{5}	-6.619×10^{4}	9.571×10^{5}	-1.034×10^{5}
A_∞	-1.218×10^{6}	-4.750×10^{19}	7.587×10^{33}	6.785×10^{20}	6.148×10^{18}	3.592×10^{19}	3.296×10^{19}	5.190×10^{19}	2.908×10^{19}
E_∞	-1.219×10^{-7}	-4.854×10^{6}	6.785×10^{20}	6.084×10^{7}	5.576×10^{5}	3.253×10^{6}	2.982×10^{6}	2.907×10^{5}	2.544×10^{6}
k_{bg} 450 K	-1.557×10^{-9}	-6.522×10^{4}	6.148×10^{18}	5.576×10^{5}	1.606×10^{5}	3.112×10^{4}	2.894×10^{4}	-3.068×10^{3}	2.067×10^{4}
k_{bg} 500 K	-7.734×10^{-9}	-3.191×10^{5}	3.592×10^{19}	3.253×10^{6}	3.112×10^{4}	4.554×10^{5}	1.841×10^{5}	9.785×10^{3}	1.170×10^{5}
k_{bg} 550 K	-2.063×10^{-9}	-6.619×10^{4}	3.296×10^{-19}	2.982×10^{6}	2.894×10^{4}	1.841×10^{5}	4.326×10^{5}	1.283×10^{5}	8.818×10^{4}
k_{bg} 600 K	2.060×10^{-8}	9.571×10^{5}	5.190×10^{18}	2.907×10^{5}	-3.068×10^{3}	9.785×10^{3}	1.283×10^{5}	5.488×10^{5}	8.244×10^{4}
k_{bg} 650 K	-3.328×10^{-9}	-1.034×10^{5}	2.908×10^{19}	2.544×10^{6}	2.067×10^{4}	1.170×10^{5}	8.818×10^{4}	8.244×10^{4}	4.293×10^{5}

Table S2: Covariance matrix showing the correlations between the fit parameters determined by fitting to the observed rate coefficients describing the loss of CD_2OO ($k_{2,obs}$).

Propagation of the uncertainties in the covariance matrices, according to Equation S3, enables a more detailed assessment of the true total uncertainty in the fits to the observed rate coefficients.

$$\begin{aligned}\sigma_k^2 = {} & \left|\frac{\partial k}{\partial A_0}\right|^2 \sigma_{A_0}^2 + \left|\frac{\partial k}{\partial E_0}\right|^2 \sigma_{E_0}^2 + \left|\frac{\partial k}{\partial A_\infty}\right|^2 \sigma_{A_\infty}^2 + \left|\frac{\partial k}{\partial E_\infty}\right|^2 \sigma_{E_\infty}^2 + \left|\frac{\partial k}{\partial A_{\mathrm{bg}}}\right|^2 \sigma_{A_{\mathrm{bg}}}^2 + \left|\frac{\partial k}{\partial E_{\mathrm{bg}}}\right|^2 \sigma_{E_{\mathrm{bg}}}^2 \\ & + 2\frac{\partial k}{\partial A_0}\frac{\partial k}{\partial E_0}\sigma_{A_0E_0} + 2\frac{\partial k}{\partial A_0}\frac{\partial k}{\partial A_\infty}\sigma_{A_0A_\infty} + 2\frac{\partial k}{\partial A_0}\frac{\partial k}{\partial E_\infty}\sigma_{A_0E_\infty} + 2\frac{\partial k}{\partial A_0}\frac{\partial k}{\partial A_{\mathrm{bg}}}\sigma_{A_0A_{\mathrm{bg}}} \\ & + 2\frac{\partial k}{\partial A_0}\frac{\partial k}{\partial E_{\mathrm{bg}}}\sigma_{A_0E_{\mathrm{bg}}} + 2\frac{\partial k}{\partial E_0}\frac{\partial k}{\partial A_\infty}\sigma_{E_0A_\infty} + 2\frac{\partial k}{\partial E_0}\frac{\partial k}{\partial E_\infty}\sigma_{E_0E_\infty} + 2\frac{\partial k}{\partial E_0}\frac{\partial k}{\partial A_{\mathrm{bg}}}\sigma_{E_0A_{\mathrm{bg}}} \\ & + 2\frac{\partial k}{\partial E_0}\frac{\partial k}{\partial E_{\mathrm{bg}}}\sigma_{E_0E_{\mathrm{bg}}} + 2\frac{\partial k}{\partial A_\infty}\frac{\partial k}{\partial E_\infty}\sigma_{A_\infty E_\infty} + 2\frac{\partial k}{\partial A_\infty}\frac{\partial k}{\partial A_{\mathrm{bg}}}\sigma_{A_\infty A_{\mathrm{bg}}} + 2\frac{\partial k}{\partial A_\infty}\frac{\partial k}{\partial E_{\mathrm{bg}}}\sigma_{A_\infty E_{\mathrm{bg}}} \\ & + 2\frac{\partial k}{\partial E_\infty}\frac{\partial k}{\partial A_{\mathrm{bg}}}\sigma_{E_\infty A_{\mathrm{bg}}} + 2\frac{\partial k}{\partial E_\infty}\frac{\partial k}{\partial E_{\mathrm{bg}}}\sigma_{E_\infty E_{\mathrm{bg}}} + 2\frac{\partial k}{\partial A_{\mathrm{bg}}}\frac{\partial k}{\partial E_{\mathrm{bg}}}\sigma_{A_{\mathrm{bg}}E_{\mathrm{bg}}}\end{aligned}$$

Equation S3

where σ_k is the uncertainty in k, the parameters σ_{A_0}, σ_{E_0}, σ_{A_∞}, σ_{E_∞}, $\sigma_{A_{\mathrm{bg}}}$ and $\sigma_{E_{\mathrm{bg}}}$ are the fit uncertainties in the Arrhenius parameters describing k_0, k_∞ and k_{bg} and are determined from the diagonals in the covariance matrix and the parameters such as $\sigma_{A_0E_0}$ described the correlations between the fit parameters are given by the off-diagonals in the covariance matrix. Partial derivatives were determined using the software Maple.[11]

For CH_2OO, the overall uncertainties range from 3 % at the highest temperatures and pressures to 17 % at the lowest temperatures and pressures, with a mean and median of 10 %. For CD_2OO, there is a greater range of uncertainties owing to fewer observations and the use of separate k_{bg} values at each temperature owing to poorer fits using an Arrhenius expression to describe k_{bg}. The mean total uncertainty in the fits for CD_2OO is 24 %, with a median of 21 %. The absolute uncertainties in the fits to $k_{1,\mathrm{obs}}$ and $k_{2,\mathrm{obs}}$ are given in the main text in Tables 1 and 2, respectively.

MESMER Input File

A sample MESMER input file used for fitting to CH2OO decomposition data is given below.

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  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">1.313 0.238 0.202 </array>
  </property>
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
   <scalar>1 </scalar>
  </property>
```

```
 </propertyList>
 <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>

<molecule id="IS1" description="IS1:IS1" >
 <atomArray>
  <atom id="a1" elementType="O" x3="1.176631" y3="0.200956" z3="0.000000"/>
  <atom id="a2" elementType="C" x3="0.000000" y3="0.385803" z3="0.000000"/>
  <atom id="a3" elementType="H" x3="-0.467516" y3="1.384109" z3="0.000000"/>
  <atom id="a4" elementType="O" x3="-0.893965" y3="-0.628426" z3="0.000000"/>
  <atom id="a5" elementType="H" x3="-1.793811" y3="-0.279168" z3="0.000000"/>
 </atomArray>
 <bondArray>
  <bond atomRefs2="a1 a2" order="2"/>
  <bond atomRefs2="a2 a3" order="1"/>
  <bond atomRefs2="a2 a4" order="1"/>
  <bond atomRefs2="a4 a5" order="1"/>
 </bondArray>
 <propertyList>
  <property title="program">
   <scalar>Gaussian 09, Revision C.01</scalar>
  </property>
  <property title="basis">
   <scalar>Aug-CC-pVTZ (5D, 7F)</scalar>
  </property>
  <property title="method">
   <scalar>b3lyp</scalar>
  </property>
  <property title="File Format">
   <scalar>g03</scalar>
  </property>
```

```
  <property title="Energy" dictRef="me:ZPE">
   <scalar units="kJ/mol">-465.7</scalar>
  </property>
  <property title="Vibrational Frequencies" dictRef="me:vibFreqs">
   <array units="cm-1">532.93 659.67 1032.25 1103.84 1268.31 1413.66 1855.80 2962.84 3781.65 </array>
  </property>
  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">2.910 0.390 0.344 </array>
  </property>
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
   <scalar>1 </scalar>
  </property>
  </propertyList>
  <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>

<molecule id="OH" description="OH radical">
 <atomArray>
  <atom id="a1" elementType="O" spinMultiplicity="2" x3="0.000000" y3="0.000000" z3="0.108368"/>
  <atom id="a2" elementType="H" x3="0.000000" y3="0.000000" z3="-0.866945"/>
 </atomArray>
 <bondArray>
  <bond atomRefs2="a2 a1" order="1"/>
 </bondArray>
 <propertyList>
  <property title="program">
   <scalar>Gaussian 09, Revision C.01</scalar>
  </property>
  <property title="basis">
   <scalar>Aug-CC-pVTZ (5D, 7F)</scalar>
  </property>
  <property title="method">
   <scalar>b3lyp</scalar>
```

```
  </property>
  <property title="File Format">
   <scalar>g03</scalar>
  </property>
  <property title="Energy" dictRef="me:ZPE">
  <scalar units="kJ/mol">-41.4</scalar>
  </property>
  <property title="SpinMultiplicity" dictRef="me:spinMultiplicity">
   <scalar>2.00 </scalar>
  </property>
  <property title="Vibrational Frequencies" dictRef="me:vibFreqs">
   <array units="cm-1">3694.92 </array>
  </property>
  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">18.679 </array>
  </property>
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
   <scalar>1 </scalar>
  </property>
 </propertyList>
 <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>

<molecule id="HCO">
 <atomArray>
  <atom id="a1" elementType="C" spinMultiplicity="2" x3="0.061652"
y3="0.583056" z3="0.000000"/>
  <atom id="a2" elementType="H" x3="-0.863122" y3="1.219369"
z3="0.000000"/>
  <atom id="a3" elementType="O" x3="0.061652" y3="-0.589713"
z3="0.000000"/>
 </atomArray>
 <bondArray>
  <bond atomRefs2="a1 a2" order="1"/>
  <bond atomRefs2="a1 a3" order="2"/>
 </bondArray>
```

```
 <propertyList>
  <property title="program">
   <scalar>Gaussian 09, Revision C.01</scalar>
  </property>
  <property title="basis">
   <scalar>Aug-CC-pVTZ (5D, 7F)</scalar>
  </property>
  <property title="method">
   <scalar>b3lyp</scalar>
  </property>
  <property title="File Format">
   <scalar>g03</scalar>
  </property>
  <property title="Energy" dictRef="me:ZPE">
   <scalar units="kJ/mol">0</scalar>
  </property>
  <property title="SpinMultiplicity" dictRef="me:spinMultiplicity">
   <scalar>2.00 </scalar>
  </property>
  <property title="Vibrational Frequencies" dictRef="me:vibFreqs">
   <array units="cm-1">1102.12 1929.87 2655.33 </array>
  </property>
  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">24.099 1.501 1.413 </array>
  </property>
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
   <scalar>1 </scalar>
  </property>
 </propertyList>
 <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>

<molecule id="TS5">
 <atomArray>
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  <atom id="a1" elementType="O" x3="-1.134007" y3="0.439000"
z3="0.000000"/>
  <atom id="a2" elementType="C" x3="0.000000" y3="0.155725"
z3="0.000000"/>
  <atom id="a3" elementType="H" x3="0.869079" y3="1.294050"
z3="0.000000"/>
  <atom id="a4" elementType="O" x3="0.848794" y3="-0.769388"
z3="0.000000"/>
  <atom id="a5" elementType="H" x3="1.412626" y3="0.414702"
z3="0.000000"/>
 </atomArray>
 <bondArray>
  <bond atomRefs2="a1 a2" order="2"/>
  <bond atomRefs2="a2 a3" order="1"/>
  <bond atomRefs2="a2 a4" order="1"/>
  <bond atomRefs2="a4 a5" order="1"/>
 </bondArray>
 <propertyList>
  <property title="program">
   <scalar>Gaussian 09, Revision C.01</scalar>
  </property>
  <property title="basis">
   <scalar>Aug-CC-pVTZ (5D, 7F)</scalar>
  </property>
  <property title="method">
   <scalar>b3lyp</scalar>
  </property>
  <property title="File Format">
   <scalar>g03</scalar>
  </property>
  <property title="Energy" dictRef="me:ZPE">
    <scalar units="kJ/mol" derivedFrom="TS1:ZPE" factor="1.0"
addand="-262.8">-190.7</scalar>
  </property>
  <property title="Vibrational Frequencies" dictRef="me:vibFreqs">
   <array units="cm-1">616.81 726.59 876.34 1039.68 1336.51 1734.07
2042.55 2095.29 </array>
```

```
  </property>
  <property title="ImaginaryFrequency" dictRef="me:imFreqs">
   <scalar units="cm-1">2206.30 </scalar>
  </property>
  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">3.274 0.381 0.341 </array>
  </property>
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
   <scalar>1 </scalar>
  </property>
 </propertyList>
     <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
 </molecule>


<molecule id ="TS3">
 <atomArray>
  <atom id="a1" elementType="C" x3="-0.157084" y3="0.377834"
z3="0.014004"/>
  <atom id="a2" elementType="O" x3="-1.155801" y3="-0.267509"
z3="0.007193"/>
  <atom id="a3" elementType="O" x3="1.102200" y3="-0.158796" z3="-
0.116713"/>
  <atom id="a4" elementType="H" x3="1.514899" y3="-0.333444"
z3="0.737164"/>
  <atom id="a5" elementType="H" x3="-0.143587" y3="1.476878"
z3="0.054969"/>
 </atomArray>
 <bondArray>
  <bond atomRefs2="a3 a1" order="1"/>
  <bond atomRefs2="a3 a4" order="1"/>
  <bond atomRefs2="a2 a1" order="2"/>
  <bond atomRefs2="a1 a5" order="1"/>
 </bondArray>
 <propertyList>
  <property title="program">
   <scalar>Gaussian 09, Revision C.01</scalar>
```

```
  </property>
  <property title="basis">
   <scalar>Aug-CC-pVTZ (5D, 7F)</scalar>
  </property>
  <property title="method">
   <scalar>b3lyp</scalar>
  </property>
  <property title="File Format">
   <scalar>g03</scalar>
  </property>
  <property title="Energy" dictRef="me:ZPE">
   <scalar   units="kJ/mol"   derivedFrom="TS1:ZPE"   factor="1.0"
addand="-507.1">-435.1</scalar>
  </property>
  <property title="Vibrational Frequencies" dictRef="me:vibFreqs">
   <array units="cm-1">674.33 903.87 1070.11 1188.86 1388.58 1829.25
2996.38 3803.61 </array>
  </property>
  <property title="ImaginaryFrequency" dictRef="me:imFreqs">
   <scalar units="cm-1">628.57 </scalar>
  </property>
  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">2.691 0.382 0.344 </array>
  </property>
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
   <scalar>1 </scalar>
  </property>
 </propertyList>
 <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
 </molecule>

<molecule id ="TS4">
 <atomArray>
  <atom id="a1" elementType="C" spinMultiplicity="3" x3="0.435474"
y3="0.455837" z3="-0.029068"/>
```

```
   <atom id="a2" elementType="O" spinMultiplicity="2" x3="1.307902"
y3="-0.277418" z3="0.017583"/>
   <atom id="a3" elementType="H" x3="-0.545293" y3="1.020708" z3="-
0.226868"/>
   <atom id="a4" elementType="O" spinMultiplicity="2" x3="-1.367897"
y3="-0.097246" z3="0.103555"/>
   <atom id="a5" elementType="H" x3="-1.587587" y3="-0.758418" z3="-
0.567830"/>
  </atomArray>
  <bondArray>
   <bond atomRefs2="a5 a4" order="1"/>
   <bond atomRefs2="a3 a1" order="1"/>
   <bond atomRefs2="a1 a2" order="1"/>
  </bondArray>
  <propertyList>
   <property title="program">
    <scalar>Gaussian 09, Revision C.01</scalar>
   </property>
   <property title="basis">
    <scalar>Aug-CC-pVTZ (5D, 7F)</scalar>
   </property>
   <property title="method">
    <scalar>b3lyp</scalar>
   </property>
   <property title="File Format">
    <scalar>g03</scalar>
   </property>
   <property title="Energy" dictRef="me:ZPE">
    <scalar units="kJ/mol" derivedFrom="TS1:ZPE" factor="1.0"
addand="-276.3">-204.2</scalar>
   </property>
   <property title="SpinMultiplicity" dictRef="me:spinMultiplicity">
    <scalar>5.00 </scalar>
   </property>
   <property title="Vibrational Frequencies" dictRef="me:vibFreqs">
    <array units="cm-1">309.93 361.47 570.17 739.03 1034.42 1961.46
2622.39 3765.84 </array>
```

```
  </property>
  <property title="ImaginaryFrequency" dictRef="me:imFreqs">
   <scalar units="cm-1">1594.78 </scalar>
  </property>
  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">2.794 0.268 0.248 </array>
  </property>
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
   <scalar>1 </scalar>
  </property>
 </propertyList>
 <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
 </molecule>

<molecule id ="IS2">
 <atomArray>
  <atom id="a1" elementType="O" x3="1.158555" y3="0.117298" z3="0.000000"/>
  <atom id="a2" elementType="C" x3="0.000000" y3="0.421046" z3="0.000000"/>
  <atom id="a3" elementType="H" x3="-0.383191" y3="1.447910" z3="0.000000"/>
  <atom id="a4" elementType="O" x3="-1.028198" y3="-0.446105" z3="0.000000"/>
  <atom id="a5" elementType="H" x3="-0.659665" y3="-1.343733" z3="0.000000"/>
 </atomArray>
 <bondArray>
  <bond atomRefs2="a1 a2" order="2"/>
  <bond atomRefs2="a2 a3" order="1"/>
  <bond atomRefs2="a2 a4" order="1"/>
  <bond atomRefs2="a4 a5" order="1"/>
 </bondArray>
 <propertyList>
  <property title="program">
   <scalar>Gaussian 09, Revision C.01</scalar>
```

```
  </property>
  <property title="basis">
   <scalar>Aug-CC-pVTZ (5D, 7F)</scalar>
  </property>
  <property title="method">
   <scalar>b3lyp</scalar>
  </property>
  <property title="File Format">
   <scalar>g03</scalar>
  </property>
  <property title="Energy" dictRef="me:ZPE">
  <scalar units="kJ/mol">-482.4</scalar>
  </property>
  <property title="Vibrational Frequencies" dictRef="me:vibFreqs">
   <array units="cm-1">628.62 676.98 1051.71 1121.40 1298.15 1401.81
1811.42 3048.91 3717.51 </array>
  </property>
  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">2.601 0.402 0.348 </array>
  </property>
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
   <scalar>1 </scalar>
  </property>
 </propertyList>
 <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>


<molecule id ="H2O">
 <atomArray>
  <atom id="a1" elementType="O" x3="0.000000" y3="0.000000"
z3="0.116992"/>
  <atom id="a2" elementType="H" x3="0.000000" y3="0.763646" z3="-
0.467967"/>
  <atom id="a3" elementType="H" x3="0.000000" y3="-0.763646" z3="-
0.467967"/>
 </atomArray>
```

```
 <bondArray>
  <bond atomRefs2="a2 a1" order="1"/>
  <bond atomRefs2="a3 a1" order="1"/>
 </bondArray>
 <propertyList>
  <property title="program">
   <scalar>Gaussian 09, Revision C.01</scalar>
  </property>
  <property title="basis">
   <scalar>Aug-CC-pVTZ (5D, 7F)</scalar>
  </property>
  <property title="method">
   <scalar>b3lyp</scalar>
  </property>
  <property title="File Format">
   <scalar>g03</scalar>
  </property>
  <property title="Energy" dictRef="me:ZPE">
  <scalar units="kJ/mol">-0.0</scalar>
  </property>
  <property title="Vibrational Frequencies" dictRef="me:vibFreqs">
   <array units="cm-1">1627.08 3795.01 3897.81 </array>
  </property>
  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">27.503 14.332 9.422 </array>
  </property>
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
   <scalar>2 </scalar>
  </property>
 </propertyList>
 <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
 </molecule>

<molecule id ="CO">
 <atomArray>
```

```
  <atom id="a1" elementType="C" spinMultiplicity="3" x3="0.000000"
y3="0.000000" z3="-0.643343"/>
  <atom  id="a2"  elementType="O"  x3="0.000000"  y3="0.000000"
z3="0.482508"/>
 </atomArray>
 <bondArray>
  <bond atomRefs2="a1 a2" order="2"/>
 </bondArray>
 <propertyList>
  <property title="program">
   <scalar>Gaussian 09, Revision C.01</scalar>
  </property>
  <property title="basis">
   <scalar>Aug-CC-pVTZ (5D, 7F)</scalar>
  </property>
  <property title="method">
   <scalar>b3lyp</scalar>
  </property>
  <property title="File Format">
   <scalar>g03</scalar>
  </property>
  <property title="Energy" dictRef="me:ZPE">
  <scalar units="kJ/mol">-465.7</scalar>
  </property>
  <property title="SpinMultiplicity" dictRef="me:spinMultiplicity">
   <scalar>3.00 </scalar>
  </property>
  <property title="Vibrational Frequencies" dictRef="me:vibFreqs">
   <array units="cm-1">2207.19 </array>
  </property>
  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">1.938 </array>
  </property>
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
   <scalar>1 </scalar>
```

```
  </property>
 </propertyList>
 <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>


<molecule id ="H2">
 <atomArray>
  <atom   id="a1"   elementType="H"   x3="0.000000"   y3="0.000000"
z3="0.371435"/>
  <atom id="a2" elementType="H" x3="0.000000" y3="0.000000" z3="-
0.371435"/>
 </atomArray>
 <propertyList>
  <property title="program">
   <scalar>Gaussian 09, Revision C.01</scalar>
  </property>
  <property title="basis">
   <scalar>Aug-CC-pVTZ (5D, 7F)</scalar>
  </property>
  <property title="method">
   <scalar>b3lyp</scalar>
  </property>
  <property title="File Format">
   <scalar>g03</scalar>
  </property>
  <property title="Energy" dictRef="me:ZPE">
   <scalar units="kJ/mol">-0.0</scalar>
  </property>
  <property title="Vibrational Frequencies" dictRef="me:vibFreqs">
   <array units="cm-1">4417.64 </array>
  </property>
  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">60.578 </array>
  </property>
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
```

```
    <scalar>2 </scalar>
   </property>
  </propertyList>
  <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
 </molecule>

 <molecule id ="CO2">
  <atomArray>
   <atom   id="a1"   elementType="C"   x3="0.000000"   y3="0.000000"
 z3="0.000000"/>
   <atom   id="a2"   elementType="O"   x3="0.000000"   y3="0.000000"
 z3="1.160479"/>
   <atom  id="a3"  elementType="O"  x3="0.000000"  y3="0.000000"  z3="-
 1.160479"/>
  </atomArray>
  <bondArray>
   <bond atomRefs2="a3 a1" order="2"/>
   <bond atomRefs2="a1 a2" order="2"/>
  </bondArray>
  <propertyList>
   <property title="program">
    <scalar>Gaussian 09, Revision C.01</scalar>
   </property>
   <property title="basis">
    <scalar>Aug-CC-pVTZ (5D, 7F)</scalar>
   </property>
   <property title="method">
    <scalar>b3lyp</scalar>
   </property>
   <property title="File Format">
    <scalar>g03</scalar>
   </property>
   <property title="Energy" dictRef="me:ZPE">
    <scalar units="kJ/mol">-500.41</scalar>
   </property>
   <property title="Vibrational Frequencies" dictRef="me:vibFreqs">
```

```
   <array units="cm-1">673.82 673.82 1369.12 2400.29 </array>
  </property>
  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">0.391 </array>
  </property>
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
   <scalar>2 </scalar>
  </property>
 </propertyList>
 <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>

<molecule xmlns="http://www.xml-cml.org/schema" id="TS2D">
 <atomArray>
  <atom id="a1" elementType="C" spinMultiplicity="2" x3="0.895751" y3="-0.283101" z3="0.003878"/>
  <atom id="a2" elementType="H" isotope="2" x3="1.784593" y3="-0.123719" z3="0.618403"/>
  <atom id="a3" elementType="H" isotope="2" x3="0.764277" y3="-1.188149" z3="-0.578331"/>
  <atom id="a4" elementType="O" x3="0.063367" y3="0.651519" z3="-0.083827"/>
  <atom id="a5" elementType="O" spinMultiplicity="2" x3="-1.053789" y3="-0.275211" z3="0.075909"/>
 </atomArray>
 <bondArray>
  <bond atomRefs2="a3 a1" order="1"/>
  <bond atomRefs2="a4 a1" order="1"/>
  <bond atomRefs2="a4 a5" order="1"/>
  <bond atomRefs2="a1 a2" order="1"/>
 </bondArray>
 <propertyList>
  <property title="program">
   <scalar>Gaussian 09, Revision D.01</scalar>
  </property>
  <property title="basis">
```

```
   <scalar>CC-pVTZ (5D, 7F)</scalar>
  </property>
  <property title="File Format">
   <scalar>g03</scalar>
  </property>
  <property title="Energy" dictRef="me:ZPE">
   <scalar units="kJ/mol" lower="78" upper="79"
stepsize="1">78.68</scalar>
  </property>
   <property title="SpinMultiplicity"
dictRef="me:spinMultiplicity">
   <scalar>3.00 </scalar>
  </property>
  <property title="Vibrational Frequencies" dictRef="me:vibFreqs">
    <array units="cm-1">638.99 800.82 843.84 964.12 1074.96 1554.37
2251.28 2422.51 </array>
  </property>
  <property title="ImaginaryFrequency" dictRef="me:imFreqs">
   <scalar units="cm-1">746.12 </scalar>
  </property>
  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">1.249 0.459 0.359 </array>
  </property>
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
   <scalar>1 </scalar>
  </property>
 </propertyList>
</molecule>


<molecule id ="TS2">
 <atomArray>
  <atom id="a1" elementType="C" spinMultiplicity="2" x3="-0.902569"
y3="-0.288490" z3="0.003408"/>
  <atom id="a2" elementType="H" x3="-0.779893" y3="-1.179098" z3="-
0.600782"/>
  <atom id="a3" elementType="O" spinMultiplicity="2" x3="1.063702"
y3="-0.280379" z3="0.075532"/>
```

```
  <atom id="a4" elementType="O" x3="-0.067083" y3="0.662384" z3="-0.082967"/>
  <atom id="a5" elementType="H" x3="-1.777640" y3="-0.146000" z3="0.639815"/>
 </atomArray>
 <bondArray>
  <bond atomRefs2="a2 a1" order="1"/>
  <bond atomRefs2="a4 a1" order="1"/>
  <bond atomRefs2="a4 a3" order="1"/>
  <bond atomRefs2="a1 a5" order="1"/>
 </bondArray>
 <propertyList>
  <property title="program">
   <scalar>Gaussian 09, Revision C.01</scalar>
  </property>
  <property title="basis">
   <scalar>Aug-CC-pVTZ (5D, 7F)</scalar>
  </property>
  <property title="method">
   <scalar>b3lyp</scalar>
  </property>
  <property title="File Format">
   <scalar>g03</scalar>
  </property>
  <property title="Energy" dictRef="me:ZPE">
   <scalar units="kJ/mol" lower="70" upper="90" stepsize="1">78.24</scalar>
 </property>
  <property title="SpinMultiplicity" dictRef="me:spinMultiplicity">
   <scalar>3.00 </scalar>
  </property>
  <property title="Vibrational Frequencies" dictRef="me:vibFreqs">
   <array units="cm-1">756.60 779.09 1044.11 1208.78 1408.96 1560.53 3050.95 3202.38 </array>
  </property>
  <property title="ImaginaryFrequency" dictRef="me:imFreqs">
```

```
   <scalar units="cm-1">700.26 </scalar>
  </property>
  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">1.459 0.516 0.398 </array>
  </property>
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
   <scalar>1 </scalar>
  </property>
 </propertyList>
 <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>

<molecule id ="IS3">
 <atomArray>
  <atom id="a1" elementType="C" x3="0.731359" y3="0.000000" z3="0.000000"/>
  <atom id="a2" elementType="H" x3="1.301663" y3="0.000001" z3="0.926430"/>
  <atom id="a3" elementType="O" x3="-0.436968" y3="0.749154" z3="0.000000"/>
  <atom id="a4" elementType="O" x3="-0.436967" y3="-0.749155" z3="0.000000"/>
  <atom id="a5" elementType="H" x3="1.301663" y3="0.000001" z3="-0.926430"/>
 </atomArray>
 <bondArray>
  <bond atomRefs2="a5 a1" order="1"/>
  <bond atomRefs2="a1 a3" order="1"/>
  <bond atomRefs2="a1 a4" order="1"/>
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  <bond atomRefs2="a3 a4" order="1"/>
 </bondArray>
 <propertyList>
  <property title="program">
   <scalar>Gaussian 09, Revision C.01</scalar>
  </property>
```

```
  <property title="basis">
   <scalar>Aug-CC-pVTZ (5D, 7F)</scalar>
  </property>
  <property title="method">
   <scalar>b3lyp</scalar>
  </property>
  <property title="File Format">
   <scalar>g03</scalar>
  </property>
  <property title="Energy" dictRef="me:ZPE">
   <scalar units="kJ/mol">-107.5</scalar>
  </property>
  <property title="Vibrational Frequencies" dictRef="me:vibFreqs">
   <array units="cm-1">818.98 892.47 1030.85 1177.47 1263.86 1307.81
1545.18 3058.88 3151.86 </array>
  </property>
  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">0.961 0.856 0.499 </array>
  </property>
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
   <scalar>1 </scalar>
  </property>
  <property dictRef="me:deltaEDown">
   <me:deltaEDown units="cm-1" bathGas="He"
derivedFrom="CH2OO:deltaEDown:He" factor="1.0"
addand="0.0">350.0</me:deltaEDown>
  </property>
 </propertyList>
 <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>


<molecule xmlns="http://www.xml-cml.org/schema" id="IS3D">
 <atomArray>
  <atom id="a1" elementType="C" x3="0.731331" y3="-0.000024"
z3="0.000020"/>
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```
  <atom id="a2" elementType="H" isotope="2" x3="1.297711" y3="-
0.000035" z3="-0.927075"/>
  <atom id="a3" elementType="H" isotope="2" x3="1.297661" y3="-
0.000044" z3="0.927146"/>
  <atom id="a4" elementType="O" x3="-0.436486" y3="-0.732049" z3="-
0.000016"/>
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0.000008"/>
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  <bond atomRefs2="a2 a1" order="1"/>
  <bond atomRefs2="a4 a5" order="1"/>
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  <bond atomRefs2="a5 a1" order="1"/>
  <bond atomRefs2="a1 a3" order="1"/>
 </bondArray>
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  </property>
  <property title="basis">
   <scalar>CC-pVTZ (5D, 7F)</scalar>
  </property>
  <property title="File Format">
   <scalar>g03</scalar>
  </property>
  <property title="Energy" dictRef="me:ZPE">
   <scalar units="kJ/mol">-107.5</scalar>
  </property>
  <property title="Vibrational Frequencies" dictRef="me:vibFreqs">
   <array units="cm-1">779.63 898.15 904.98 927.40 1033.75 1090.69
1399.64 2250.72 2392.45 </array>
  </property>
  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">0.818 0.740 0.462 </array>
  </property>
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```
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
   <scalar>1 </scalar>
  </property>
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 <me:energyTransferModel xsi:type="me:ExponentialDown">
  <me:deltaEDown units="cm-1" bathGas="He"
derivedFrom="CD2OO:deltaEDown:He" factor="1.0"
addand="0.0">350.0</me:deltaEDown>
 </me:energyTransferModel>
</molecule>


<molecule id ="TS6">
 <atomArray>
  <atom id="a1" elementType="C" x3="0.000142" y3="0.543416" z3="-
0.000024"/>
  <atom id="a2" elementType="H" x3="-0.001437" y3="1.192013"
z3="0.899398"/>
  <atom id="a3" elementType="O" spinMultiplicity="2" x3="1.009185"
y3="-0.352829" z3="0.000111"/>
  <atom id="a4" elementType="O" spinMultiplicity="2" x3="-1.009233"
y3="-0.352825" z3="-0.000156"/>
  <atom id="a5" elementType="H" x3="0.000960" y3="1.192722" z3="-
0.898903"/>
 </atomArray>
 <bondArray>
  <bond atomRefs2="a5 a1" order="1"/>
  <bond atomRefs2="a4 a1" order="1"/>
  <bond atomRefs2="a1 a3" order="1"/>
  <bond atomRefs2="a1 a2" order="1"/>
 </bondArray>
 <propertyList>
  <property title="program">
   <scalar>Gaussian 09, Revision C.01</scalar>
  </property>
  <property title="basis">
   <scalar>Aug-CC-pVTZ (5D, 7F)</scalar>
```

```
  </property>
  <property title="method">
   <scalar>ub3lyp</scalar>
  </property>
  <property title="File Format">
   <scalar>g03</scalar>
  </property>
  <property title="Energy" dictRef="me:ZPE">
   <scalar units="kJ/mol" derivedFrom="TS2:ZPE" factor="1.0" addand="-99.6">-3.3</scalar>
  </property>
  <property title="SpinMultiplicity" dictRef="me:spinMultiplicity">
   <scalar>3.00 </scalar>
  </property>
  <property title="Vibrational Frequencies" dictRef="me:vibFreqs">
   <array units="cm-1">848.50 992.27 1072.24 1143.09 1204.06 1349.84 2853.84 2875.34 </array>
  </property>
  <property title="ImaginaryFrequency" dictRef="me:imFreqs">
   <scalar units="cm-1">563.19 </scalar>
  </property>
  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">1.416 0.492 0.393 </array>
  </property>
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
   <scalar>1 </scalar>
  </property>
 </propertyList>
 <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>

<molecule id ="TS6D">
 <atomArray>
  <atom id="a1" elementType="C" x3="0.000142" y3="0.543416" z3="-0.000024"/>
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```
  <atom id="a2" elementType="H" x3="-0.001437" y3="1.192013" z3="0.899398"/>
  <atom id="a3" elementType="O" spinMultiplicity="2" x3="1.009185" y3="-0.352829" z3="0.000111"/>
  <atom id="a4" elementType="O" spinMultiplicity="2" x3="-1.009233" y3="-0.352825" z3="-0.000156"/>
  <atom id="a5" elementType="H" x3="0.000960" y3="1.192722" z3="-0.898903"/>
 </atomArray>
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  <bond atomRefs2="a5 a1" order="1"/>
  <bond atomRefs2="a4 a1" order="1"/>
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  <bond atomRefs2="a1 a2" order="1"/>
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  </property>
  <property title="basis">
   <scalar>Aug-CC-pVTZ (5D, 7F)</scalar>
  </property>
  <property title="method">
   <scalar>ub3lyp</scalar>
  </property>
  <property title="File Format">
   <scalar>g03</scalar>
  </property>
  <property title="Energy" dictRef="me:ZPE">
   <scalar units="kJ/mol" derivedFrom="TS2D:ZPE" factor="1.0" addand="-99.6">-3.3</scalar>
  </property>
  <property title="SpinMultiplicity" dictRef="me:spinMultiplicity">
   <scalar>3.00 </scalar>
  </property>
  <property title="Vibrational Frequencies" dictRef="me:vibFreqs">
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```
   <array units="cm-1">848.50 992.27 1072.24 1143.09 1204.06 1349.84
2853.84 2875.34 </array>
  </property>
  <property title="ImaginaryFrequency" dictRef="me:imFreqs">
   <scalar units="cm-1">563.19 </scalar>
  </property>
  <property title="Rotational Constants" dictRef="me:rotConsts">
   <array units="cm-1">1.416 0.492 0.393 </array>
  </property>
  <property title="Symmetry Number" dictRef="me:symmetryNumber">
   <scalar>1 </scalar>
  </property>
 </propertyList>
 <me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>

<molecule id="He">
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 <propertyList>
  <property dictRef="me:epsilon">
   <scalar>10.2</scalar>
  </property>
  <property dictRef="me:sigma">
   <scalar>2.55</scalar>
  </property>
  <property dictRef="me:MW">
   <scalar units="amu">4.0</scalar>
  </property>
 </propertyList>
</molecule>

<molecule id="N2">
 <atom elementType="N"/>
 <propertyList>
  <property dictRef="me:epsilon">
```

```
   <scalar>48.0</scalar>
  </property>
  <property dictRef="me:sigma">
   <scalar>3.90</scalar>
  </property>
  <property dictRef="me:MW">
   <scalar units="amu">28.0</scalar>
  </property>
 </propertyList>
</molecule>

</moleculeList>

<reactionList>

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<reaction id="R1D">
 <reactant>
  <molecule ref="CD2OO" role="modelled" />
 </reactant>
 <product>
  <molecule ref="IS3D" role="modelled" />
 </product>
 <me:transitionState>
  <molecule ref="TS2D" role="transitionState" />
 </me:transitionState>
 <me:tunneling>Eckart</me:tunneling>
 <me:MCRCMethod name="SimpleRRKM"/>
</reaction>
-->

<reaction id="R1">
 <reactant>
  <molecule ref="CH2OO" role="modelled" />
 </reactant>
```

```
 <product>
  <molecule ref="IS3" role="modelled" />
 </product>
 <me:transitionState>
 <molecule ref="TS2" role="transitionState" />
 </me:transitionState>
 <me:MCRCMethod name="SimpleRRKM"/>
</reaction>

<!--
<reaction id="R1D">
 <reactant>
  <molecule ref="IS3D" role="modelled" />
 </reactant>
 <product>
  <molecule ref="H2" role="sink" />
 </product>
 <product>
  <molecule ref="CO2" role="sink" />
 </product>
 <me:transitionState>
  <molecule ref="TS6D" role="transitionState" />
 </me:transitionState>
 <me:MCRCMethod name="SimpleRRKM"/>
</reaction>
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<reaction id="R5">
 <reactant>
  <molecule ref="IS3" role="modelled" />
 </reactant>
  <product>
   <molecule ref="H2" role="sink" />
  </product>
  <product>
```

```
    <molecule ref="CO2" role="sink" />
   </product>
   <me:transitionState>
    <molecule ref="TS6" role="transitionState" />
   </me:transitionState>
   <me:MCRCMethod name="SimpleRRKM"/>
  </reaction>

</reactionList>

<me:conditions>

  <me:bathGas>He</me:bathGas>

  <me:PTs>

   <me:PTpair units="Torr" P=" 150  " T= "    500  "  precision="d">
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ref2= "CH2OO" error="    16.88594  ">   295.6875571
     </me:experimentalRate></me:PTpair>
   <me:PTpair units="Torr" P=" 200  " T= "    500  "  precision="d">
<me:bathGas>He   </me:bathGas>   <me:experimentalRate   ref1="CH2OO"
ref2= "CH2OO" error="    779.5365247    ">   465.1580571
     </me:experimentalRate></me:PTpair>
   <me:PTpair units="Torr" P=" 300  " T= "    500  "  precision="d">
<me:bathGas>He   </me:bathGas>   <me:experimentalRate   ref1="CH2OO"
ref2= "CH2OO" error="    415.1522907    ">   42.7040571
     </me:experimentalRate></me:PTpair>
   <me:PTpair units="Torr" P=" 300  " T= "    500  "  precision="d">
<me:bathGas>He   </me:bathGas>   <me:experimentalRate   ref1="CH2OO"
ref2= "CH2OO" error="    96.4216   ">   189.4825571
     </me:experimentalRate></me:PTpair>
   <me:PTpair units="Torr" P=" 50   " T= "    525  "  precision="d">
<me:bathGas>He   </me:bathGas>   <me:experimentalRate   ref1="CH2OO"
ref2= "CH2OO" error="    7.56916   ">   138.4034828
     </me:experimentalRate></me:PTpair>
   <me:PTpair units="Torr" P=" 100  " T= "    525  "  precision="d">
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ref2= "CH2OO" error="    12.22836  ">   388.9104828
     </me:experimentalRate></me:PTpair>
   <me:PTpair units="Torr" P=" 150  " T= "    525  "  precision="d">
<me:bathGas>He   </me:bathGas>   <me:experimentalRate   ref1="CH2OO"
```

```
ref2= "CH2OO" error="    19.8218   ">   681.8914828
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  <me:PTpair units="Torr" P=" 200  " T= "    525  "  precision="d">
<me:bathGas>He   </me:bathGas>   <me:experimentalRate   ref1="CH2OO"
ref2= "CH2OO" error="    31.1452   ">   1090.241483
     </me:experimentalRate></me:PTpair>

  <me:PTpair units="Torr" P=" 20   " T= "    550  "  precision="d">
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ref2= "CH2OO" error="    111.9873294    ">   41.08322455
     </me:experimentalRate></me:PTpair>

  <me:PTpair units="Torr" P=" 50   " T= "    550  "  precision="d">
<me:bathGas>He   </me:bathGas>   <me:experimentalRate   ref1="CH2OO"
ref2= "CH2OO" error="    186.8883223    ">   502.6127245
     </me:experimentalRate></me:PTpair>

  <me:PTpair units="Torr" P=" 100  " T= "    550  "  precision="d">
<me:bathGas>He   </me:bathGas>   <me:experimentalRate   ref1="CH2OO"
ref2= "CH2OO" error="    669.4179897    ">   1045.062725
     </me:experimentalRate></me:PTpair>

  <me:PTpair units="Torr" P=" 150  " T= "    550  "  precision="d">
<me:bathGas>He   </me:bathGas>   <me:experimentalRate   ref1="CH2OO"
ref2= "CH2OO" error="    1423.066539    ">   1543.007725
     </me:experimentalRate></me:PTpair>

  <me:PTpair units="Torr" P=" 200  " T= "    550  "  precision="d">
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ref2= "CH2OO" error="    1262.543821    ">   1798.224391
     </me:experimentalRate></me:PTpair>

  <me:PTpair units="Torr" P=" 250  " T= "    550  "  precision="d">
<me:bathGas>He   </me:bathGas>   <me:experimentalRate   ref1="CH2OO"
ref2= "CH2OO" error="    1120.658182    ">   1460.362725
     </me:experimentalRate></me:PTpair>

  <me:PTpair units="Torr" P=" 5    " T= "    600  "  precision="d">
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ref2= "CH2OO" error="    244.5675962    ">   136.685336
     </me:experimentalRate></me:PTpair>

  <me:PTpair units="Torr" P=" 10   " T= "    600  "  precision="d">
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ref2= "CH2OO" error="    448.1077094    ">   460.4726693
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  <me:PTpair units="Torr" P=" 20   " T= "    600  "  precision="d">
<me:bathGas>He   </me:bathGas>   <me:experimentalRate   ref1="CH2OO"
ref2= "CH2OO" error="    552.909414     ">   759.0160026
     </me:experimentalRate></me:PTpair>

  <me:PTpair units="Torr" P=" 50   " T= "    600  "  precision="d">
<me:bathGas>He   </me:bathGas>   <me:experimentalRate   ref1="CH2OO"
ref2= "CH2OO" error="    541.79673 ">   2241.770169
     </me:experimentalRate></me:PTpair>

  <me:PTpair units="Torr" P=" 100  " T= "    600  "  precision="d">
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```

```
ref2= "CH2OO" error="    1303.80712     ">   2558.679336
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<me:bathGas>He   </me:bathGas>   <me:experimentalRate   ref1="CH2OO"
ref2= "CH2OO" error="    1172.34528     ">   2829.010169
     </me:experimentalRate></me:PTpair>

  <me:PTpair units="Torr" P=" 200  " T= "    600  "  precision="d">
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ref2= "CH2OO" error="    2141.94312     ">   3690.617669
     </me:experimentalRate></me:PTpair>

  <me:PTpair units="Torr" P=" 2.2  " T= "    650  "  precision="d">
<me:bathGas>He   </me:bathGas>   <me:experimentalRate   ref1="CH2OO"
ref2= "CH2OO" error="    9.560083682    ">   304.3100001
     </me:experimentalRate></me:PTpair>

  <me:PTpair units="Torr" P=" 5    " T= "    650  "  precision="d">
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ref2= "CH2OO" error="    129.3439724    ">   645.2700001
     </me:experimentalRate></me:PTpair>

  <me:PTpair units="Torr" P=" 10   " T= "    650  "  precision="d">
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ref2= "CH2OO" error="    300.1552001    ">   1420.153333
     </me:experimentalRate></me:PTpair>

  <me:PTpair units="Torr" P=" 20   " T= "    650  "  precision="d">
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ref2= "CH2OO" error="    728.1982209    ">   2942.086667
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  <me:PTpair units="Torr" P=" 50   " T= "    650  "  precision="d">
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ref2= "CH2OO" error="    1504.965328    ">   5087.55
     </me:experimentalRate></me:PTpair>

  <me:PTpair units="Torr" P=" 100  " T= "    650  "  precision="d">
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ref2= "CH2OO" error="    2616.391278    ">   7332.173333
     </me:experimentalRate></me:PTpair>

  <me:PTpair units="Torr" P=" 150  " T= "    650  "  precision="d">
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ref2= "CH2OO" error="    7145.837283    ">   11297.325
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  <me:PTpair units="Torr" P=" 2    " T= "    450  "
precision="dd"/>

  <me:PTpair units="Torr" P=" 5    " T= "    450  "
precision="dd"/>

  <me:PTpair units="Torr" P=" 10   " T= "    450  "
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  <me:PTpair units="Torr" P=" 20   " T= "    450  "
precision="dd"/>
```

```
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</me:mesmer>
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