

Appendix A. Supporting Information

Table SI Species thermodynamics data: enthalpy of formation, ΔH_f^0 in kcal mol⁻¹ at 298.15 K; entropy S^0 in cal mol⁻¹K⁻¹ at 298.15 K; and specific heat, c_p in cal mol⁻¹K⁻¹ at a number of temperatures in Kelvin

Species	ΔH_f^0 (298)	S^0 (298)	c_p (300)	c_p (800)	c_p (1000)	c_p (1500)	c_p (2000)	c_p (2500)
N ₂	0.000	45.792	6.961	7.512	7.811	8.309	8.606	8.772
Ar	0.000	37.006	4.968	4.968	4.968	4.968	4.968	4.968
H	52.102	27.416	4.968	4.968	4.968	4.968	4.968	4.968
H ₂	0.000	31.229	6.895	7.078	7.209	7.734	8.173	8.541
O	59.554	38.491	5.234	5.016	5.001	4.983	4.976	4.984
O ₂	0.000	49.028	7.024	8.066	8.337	8.725	9.048	9.321
OH	8.915	43.910	7.141	7.150	7.336	7.885	8.297	8.609
HO ₂	2.939	54.753	8.348	10.771	11.380	12.483	13.330	13.954
H ₂ O	-57.797	45.127	8.030	9.257	9.870	11.313	12.351	13.081
H ₂ O ₂	-32.475	56.051	10.154	13.990	14.947	16.592	17.678	18.381

Table SII. Values of the active variables of the trial, x_0 , and optimized, x_{opt} , reaction models

	Reactions	x_0	x_{opt}
1	H+O ₂ =O+OH	0	0.79
2	O+H ₂ =H+OH	-0.01	-0.01
3	OH+H ₂ =H+H ₂ O	0	-0.95
4	OH+OH=O+H ₂ O	-0.01	-0.01
5	H+H+M=H ₂ +M	0	0
	H+H+H ₂ =H ₂ +H ₂		
	H+H+H ₂ O=H ₂ +H ₂ O		
6	O+O+M=O ₂ +M	0	0
7	O+H+M=OH+M	0	0
8	H+OH+M=H ₂ O+M	0	0
9	H+O ₂ +M=HO ₂ +M	0	0
	H+O ₂ =HO ₂		
10	H+HO ₂ =O+H ₂ O	0	0
11	H+HO ₂ =H ₂ +O ₂	0	0
12	H+HO ₂ =OH+OH	0.07	-0.39
13	O+HO ₂ =OH+O ₂	0	0
14	OH+HO ₂ =H ₂ O+O ₂	0	0
15	HO ₂ +HO ₂ =H ₂ O ₂ +O ₂	0	0
	HO ₂ +HO ₂ =H ₂ O ₂ +O ₂		0
16	OH+OH+M=H ₂ O ₂ +M	-0.4	-0.88
	OH+OH=H ₂ O ₂		
17	H+H ₂ O ₂ =H ₂ O+OH	0	0
18	H+H ₂ O ₂ =HO ₂ +H ₂	0	-0.56
19	O+H ₂ O ₂ =HO ₂ +OH	0	0
20	OH+H ₂ O ₂ =H ₂ O+HO ₂	0	0
	OH+H ₂ O ₂ =H ₂ O+HO ₂	0	0
21	O+OH+M=HO ₂ +M	-0.1	-0.1

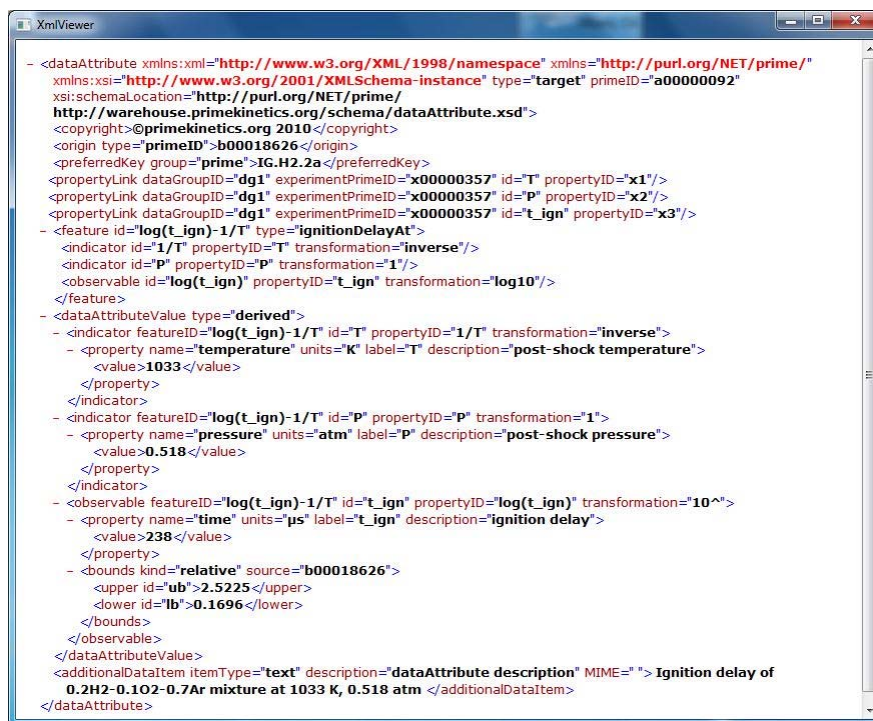


Figure S1. An example of a *dataAttribute* XML file.

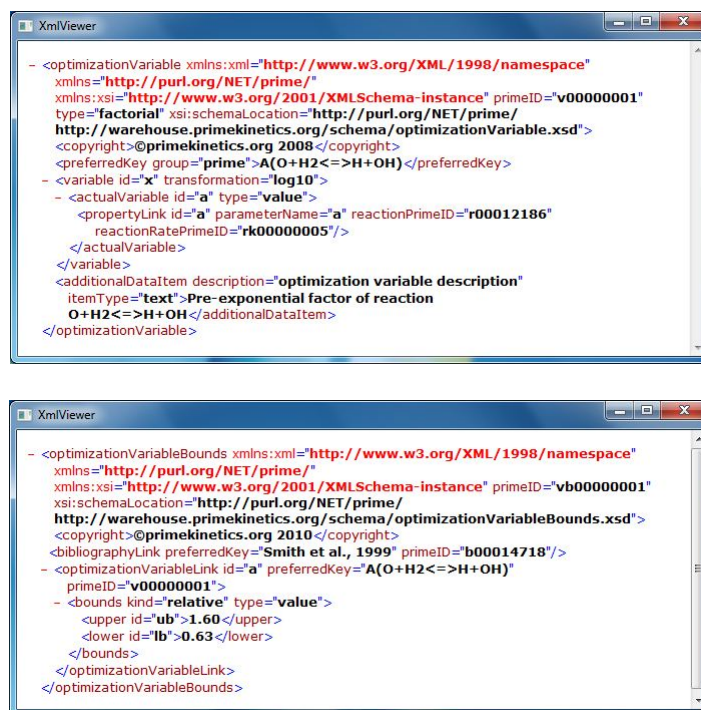


Figure S2. An examples of *optimizationVariable* and *optimizationVariableBounds* XML files.

```

<surrogateModel xmlns:xm1="http://www.w3.org/XML/1998/namespace" xmlns="http://purl.org/NET/prime/"
  xmlns:xsi="http://www.w3.org/2001/XMLSchema-instance" primeID="sm00000001" type="quadratic"
  xsi:schemaLocation="http://purl.org/NET/prime/ http://warehouse.primekinetics.org/schema/surrogateModel.xsd">
  <copyright>©primekinetics.org 2010</copyright>
  <preferredKey group="prime">IG.H2.2a</preferredKey>
  <dataAttributeLink preferredKey="IG.H2.2a" primeID="a00000092" transformation="log10" weight="1"/>
  <datasetLink preferredKey="Prime H2 1.0 dataset" primeID="d00000002"/>
  <optimizationVariables>
    <optimizationVariableLink boundsPrimeID="vb00000001" id="1" preferredKey="A(O2 + H <=> OH + O)"
      primeID="v00000014"/>
    <optimizationVariableLink boundsPrimeID="vb00000001" id="2" preferredKey="A(H2 + O <=> OH + H)"
      primeID="v00000001"/>
    <optimizationVariableLink boundsPrimeID="vb00000001" id="3" preferredKey="A(HO2 + H <=> H2 + O2)"
      primeID="v00000132"/>
    <optimizationVariableLink boundsPrimeID="vb00000001" id="4" preferredKey="A(H2 + OH <=> H2O + H)"
      primeID="v00000033"/>
    <optimizationVariableLink boundsPrimeID="vb00000001" id="5" preferredKey="A(O + H2O2 <=> OH + HO2)"
      primeID="v00000126"/>
    <optimizationVariableLink boundsPrimeID="vb00000001" id="6" preferredKey="A(OH + H <=> H2O)"
      primeID="v00000120"/>
    <optimizationVariableLink boundsPrimeID="vb00000001" id="7" preferredKey="A(O2 + H <=> HO2)"
      primeID="v00000118"/>
    <optimizationVariableLink boundsPrimeID="vb00000001" id="8" preferredKey="A(O + O <=> O2)"
      primeID="v00000128"/>
    <optimizationVariableLink boundsPrimeID="vb00000001" id="9" preferredKey="A(H + O <=> OH)"
      primeID="v00000129"/>
    <optimizationVariableLink boundsPrimeID="vb00000001" id="10" preferredKey="A(2 H <=> H2)"
      primeID="v00000119"/>
    <optimizationVariableLink boundsPrimeID="vb00000001" id="11" preferredKey="A(O + OH <=> HO2)"
      primeID="v00000133"/>
  </optimizationVariables>
  <coefficient>
    <variables>
      <variableLink>0</variableLink>
      <variableLink>0</variableLink>
    </variables>
    <value>2.53610742</value>
  </coefficient>

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Figure S3. An example of a *surrogateModel* XML file.

```

<chemicalModel xmlns:xm1="http://www.w3.org/XML/1998/namespace" xmlns="http://purl.org/NET/prime/"
  xmlns:xsi="http://www.w3.org/2001/XMLSchema-instance" primeID="m00000004"
  xsi:schemaLocation="http://purl.org/NET/prime/ http://warehouse.primekinetics.org/schema/model.xsd">
  <copyright>©primekinetics.org 2009-2010</copyright>
  <preferredKey group="prime">Prime H2 1.0</preferredKey>
  <bibliographyLink preferredKey="You et al., 2010" primeID="b00018992"/>
  <speciesSet>
    <speciesLink preferredKey="Ar" primeID="s00000049">
      <thermodynamicDataLink preferredKey="L 6/88" primeID="thp00000002"/>
    </speciesLink>
    <speciesLink preferredKey="N2" primeID="s00010231">
    <speciesLink preferredKey="H" primeID="s00009800">
    <speciesLink preferredKey="H2" primeID="s00009809">
    <speciesLink preferredKey="O" primeID="s00010285">
    <speciesLink preferredKey="O2" primeID="s00010295">
    <speciesLink preferredKey="OH" primeID="s00010102">
    <speciesLink preferredKey="H2O" primeID="s00009881">
    <speciesLink preferredKey="HO2" primeID="s00010103">
    <speciesLink preferredKey="H2O2" primeID="s00009882">
  </speciesSet>
  <reactionSet>
    <reactionLink preferredKey="O + O = O2" reversible="true" primeID="r00013869">
      <reactionRateLink preferredKey="2O = O2" primeID="rk00000026"/>
    </reactionLink>
    <reactionLink preferredKey="O + H = OH" reversible="true" primeID="r00012023">
    <reactionLink preferredKey="O + H2 = H + OH" reversible="true" primeID="r00012186">
    <reactionLink preferredKey="O + HO2 = OH + O2" reversible="true" primeID="r00012138">
    <reactionLink preferredKey="O + H2O2 = OH + HO2" reversible="true" primeID="r00015825">
    <reactionLink preferredKey="H + O2 = HO2" reversible="true" primeID="r00011821">
    <reactionLink preferredKey="H + O2 = O + OH" reversible="true" primeID="r00012255">
    <reactionLink preferredKey="H + H = H2" reversible="true" primeID="r00009454">
    <reactionLink preferredKey="H + OH = H2O" reversible="true" primeID="r00013764">
    <reactionLink preferredKey="H + HO2 = O + H2O" reversible="true" primeID="r00013804">
    <reactionLink preferredKey="H + HO2 = O2 + H2" reversible="true" primeID="r00009509">
    <reactionLink preferredKey="H + HO2 = OH + OH" reversible="true" primeID="r00011866">
    <reactionLink preferredKey="H + H2O2 = HO2 + H2" reversible="true" primeID="r00009484">
    <reactionLink preferredKey="H + H2O2 = OH + H2O" reversible="true" primeID="r00013701">

```

Figure S4. An example of a *chemicalModel* XML file.

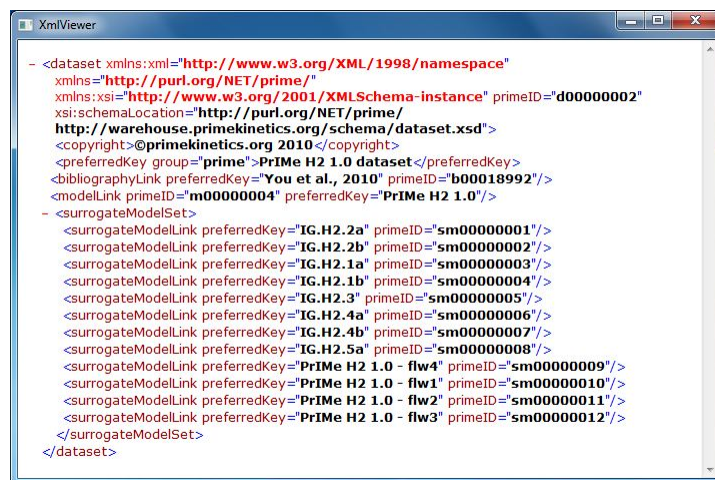


Figure S5. An example of a *dataset* XML file.

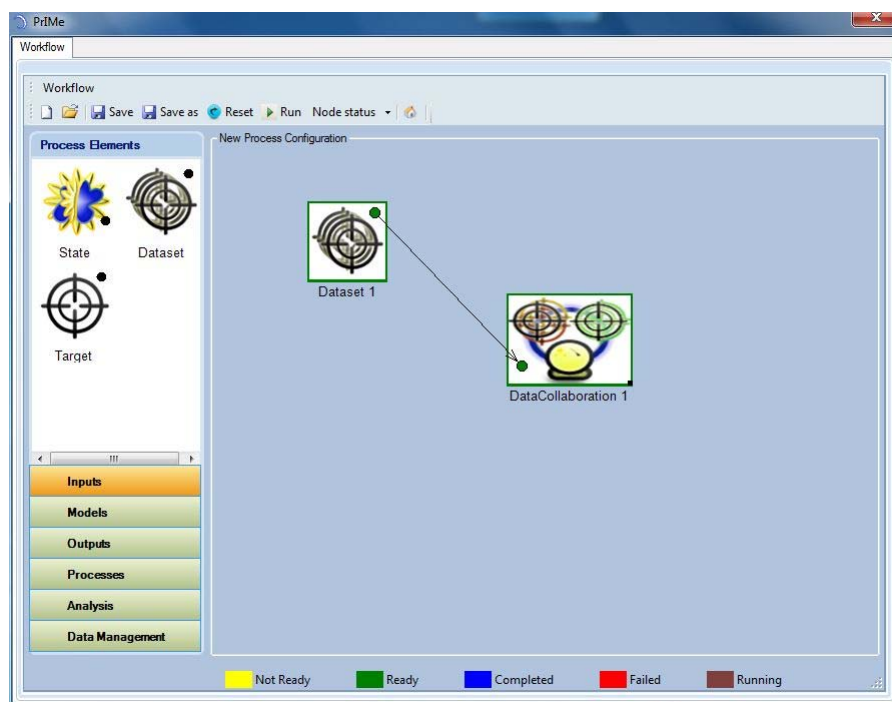


Figure S6. A snapshot of the PrIME Workflow Application.

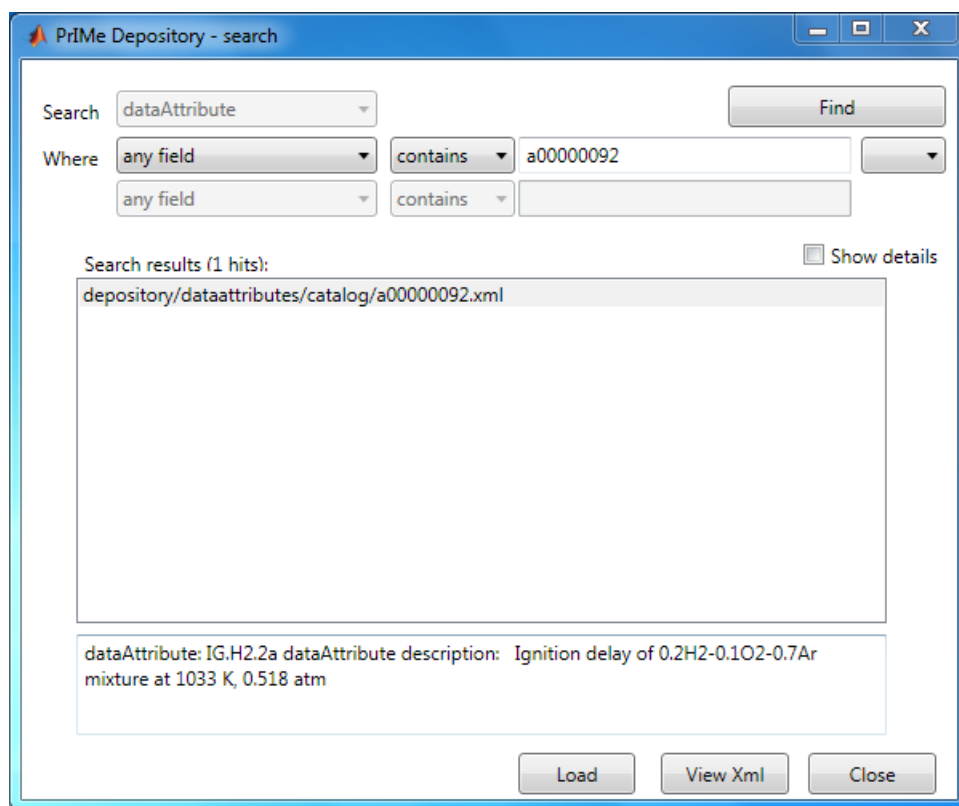


Figure S7. A snapshot of the PrIME Search-component window.

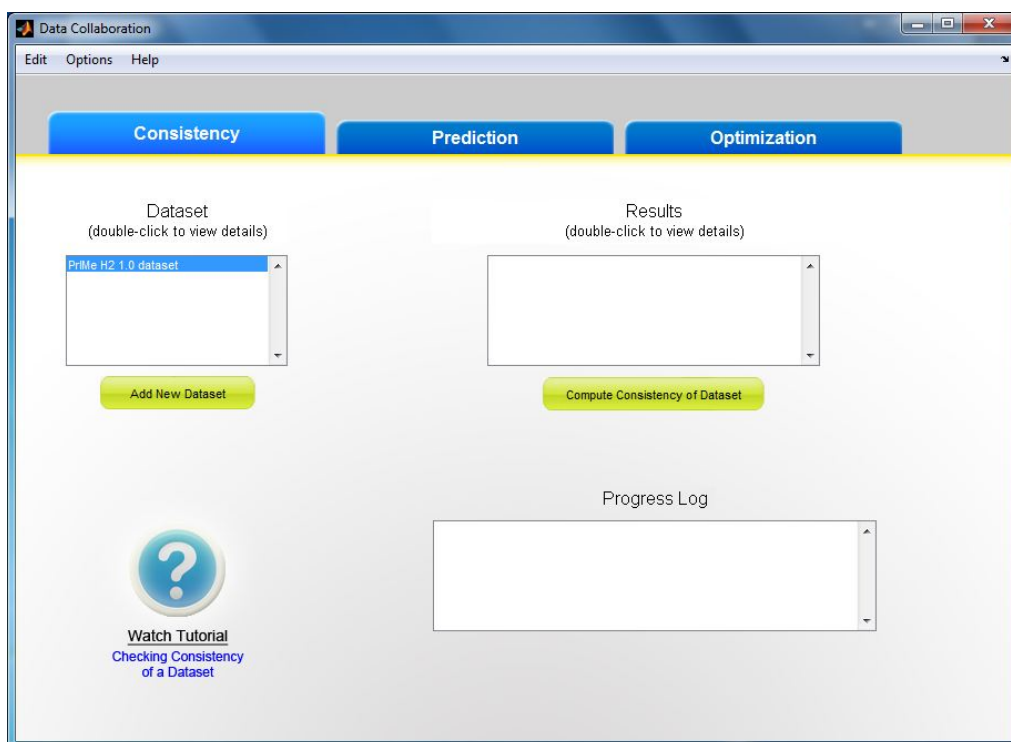


Figure S8. A snapshot of the DataCollaboration window.

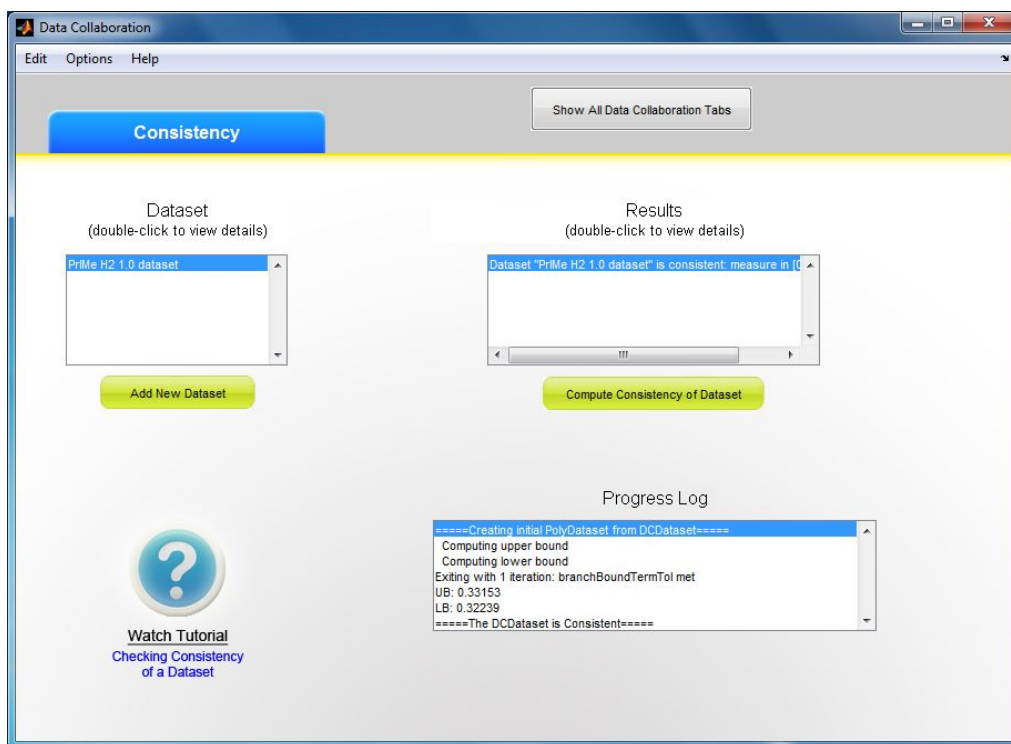


Figure S9. A snapshot of the DataCollaboration window initiating the Consistency analysis.

The screenshot shows the 'Initial State' window. The 'Equation of State' section has a dropdown menu set to 'Ideal Gas'. The 'Temperature' is 1500 K, 'Pressure' is 1 atm, and 'Flow Rate' is 1 cm3/s. The 'Mixture Composition' section has a table with the following data:

	Species	Mole Fract
1	H2	0.1
2	O2	0.1
3	H2O	0.1
4	Ar	0.7

Buttons for 'Add Species', 'Remove', 'Reset', 'Balance', and 'Done' are located to the right of the table.

Figure S10. A snapshot of the Initial State window form.

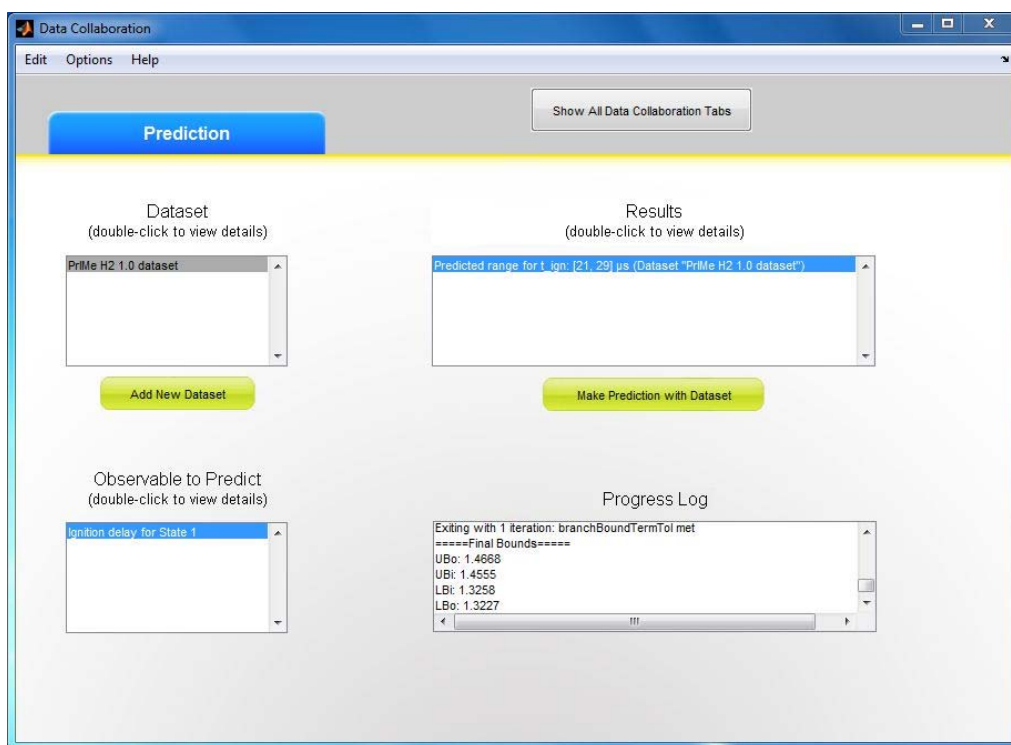


Figure S11. A snapshot of the DataCollaboration window initiating Prediction.

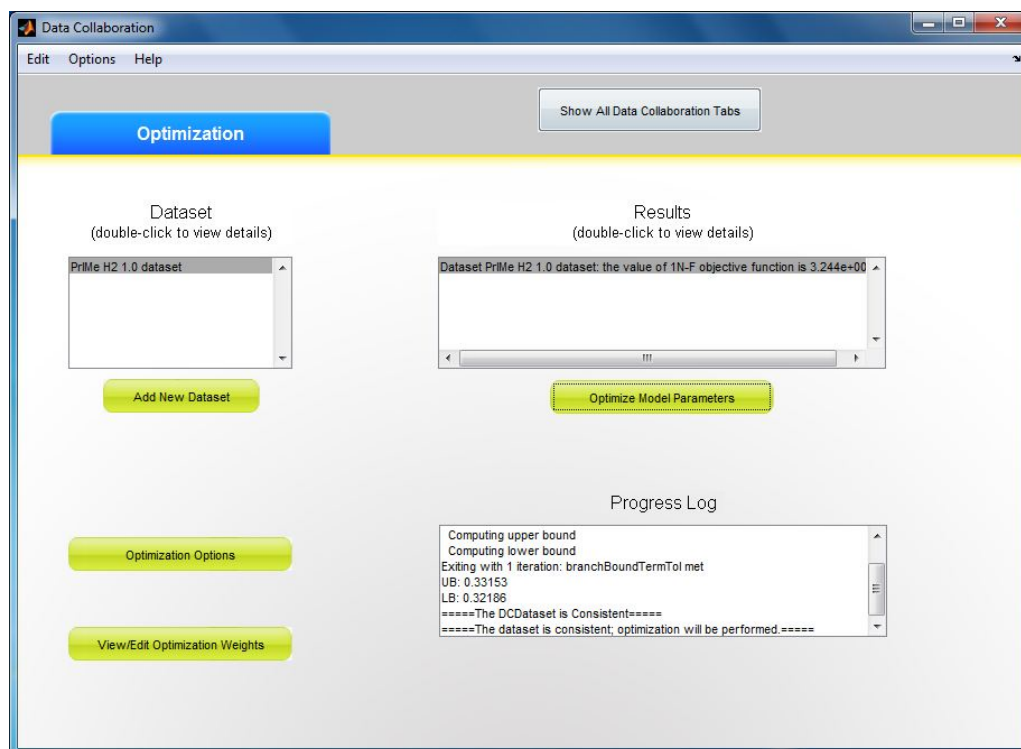


Figure S12. A snapshot of the DataCollaboration window initiating Model Optimization.

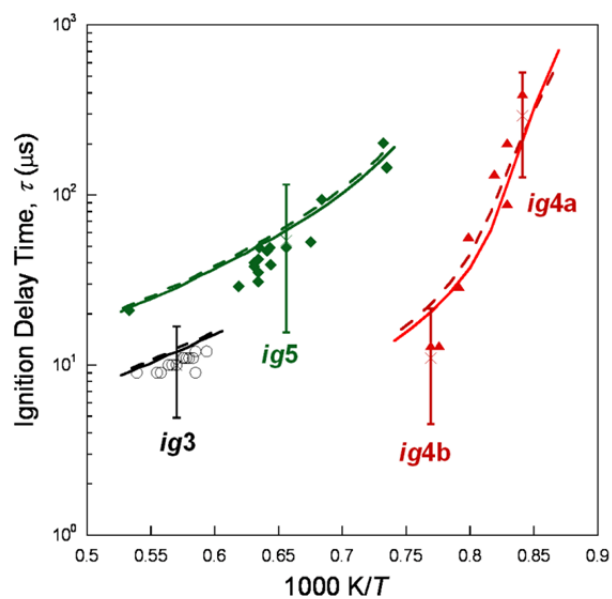


Figure S13. Ignition delay times for the $\text{H}_2/\text{O}_2/\text{Ar}$ mixtures: \circ 0.5% H_2 – 0.25% O_2 , 33 atm; \blacktriangle 2% H_2 – 1% O_2 , 33 atm; \blacklozenge 0.1% H_2 – 0.05% O_2 , 64 atm; – – – trial model; — optimized model; \times experimental targets with error bars.

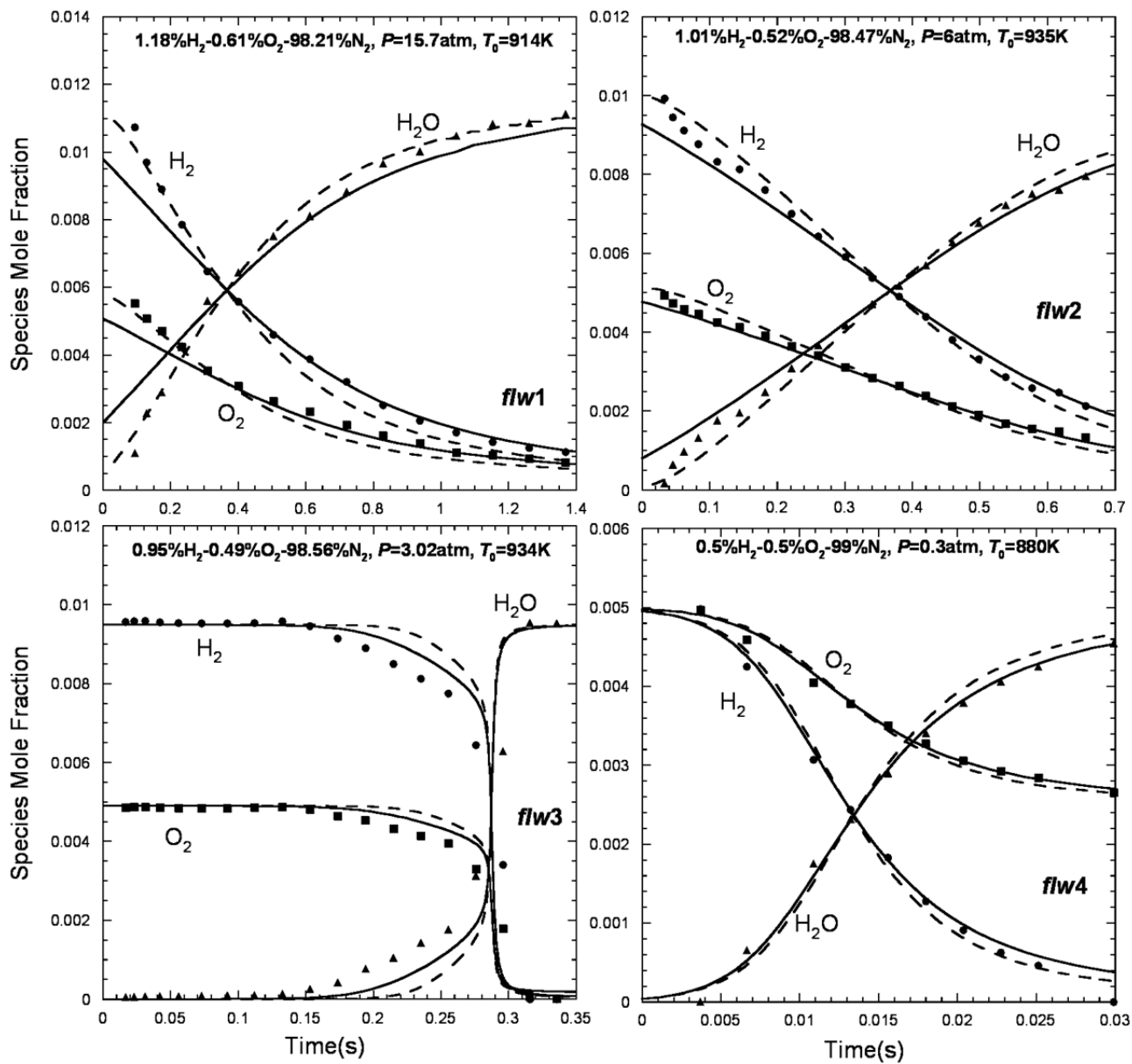


Figure S14. Experimental (symbols) and computed (lines) species mole fractions of hydrogen oxidation in a flow reactor. Solid lines: optimized model; dashed lines: trial model.