

*Supplementary Material for*

“Third-Body” Collision Efficiencies for Combustion Modeling:  
Hydrocarbons in Atomic and Diatomic Baths

Ahren W. Jasper\* and C. Melania Oana

*Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551, USA*

James A. Miller

*Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, USA*

*Proc. Combust. Inst. 35, 2015*

## Binary Lennard-Jones parameters and collision rates

As discussed in the main text, the “one-dimensional minimization” method [1] and the TB+exp/6 PES [2,3] were used to calculate Lennard-Jones collision parameters ( $\sigma$  and  $\epsilon$ ) that include the effect of local anisotropy in the interaction potential. This method was previously shown to predict binary Lennard-Jones collision rates,  $Z$ , typically within ~10% of collision rate coefficients based on tabulated values. Here we present a brief study of the dependence of the calculated Lennard-Jones parameters on the size and branching of the hydrocarbon target.

Binary Lennard-Jones collision parameters were calculated for 29 unimolecular reactants (including n-alkanes, *iso*-alkanes, *neo*-alkanes, cycloalkanes, and alkenes) and 7 baths (He, Ne, Ar, Kr, H<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub>). The 203 calculated pairs of  $\sigma$  and  $\epsilon$  are given in the Table S1 of the accompanying spreadsheet. Results for the n-alkanes were fit to

$$\sigma_x(\text{M}) = \sigma_1(\text{M})x^{n_\sigma} \quad (\text{S1})$$

$$\epsilon_x(\text{M}) = \epsilon_1(\text{M})x^{n_\epsilon(\text{M})}$$

where  $\sigma_1(\text{M})$  and  $\epsilon_1(\text{M})$  are the calculated parameters for CH<sub>4</sub>+M, and  $n_\sigma$  and  $n_\epsilon(\text{M})$  (Table S2) were fit to reproduce the results of the larger n-alkanes.

Table S2. Fitted parameters for Eq. (S1)

Parameter	M = He	Ne	Ar	Kr	H <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>
$\sigma_1, \text{\AA}$	3.329	3.308	3.534	3.644	3.184	3.557	3.666
$\epsilon_1, \text{cm}^{-1}$	21.32	46.74	112.9	138.6	78.27	106.0	100.2
$n_\sigma$	0.15	0.15	0.15	0.15	0.15	0.15	0.15
$n_\epsilon$	0.40	0.25	0.31	0.29	0.28	0.35	0.26

The parameterizations in Eq. (S1) reproduce the collision rates based on the explicitly calculated parameters within 5% for *all* of the collision partners considered here, including the branched, cyclic, and unsaturated species. Specifically, the Lennard-Jones parameters for the *iso*- and *neo*-  $C_xH_{2x+2}$  species differ from those of their normal isomers by less than 4% and typically by only 1%, and those for the cyclic and 1-ene  $C_xH_{2x}$  species show similarly close agreement with one another for a given  $x$  and bath gas. The predicted values of  $\sigma$ ,  $\varepsilon$ , and  $Z$  for the normal alkanes differ from those of the 1-ene alkenes by approximately 2%, 25%, and 5%, respectively. A similar trend in  $Z$  was observed previously for  $C_3$  species, with  $Z$  decreasing by  $\sim 7\%$  per pair of H atoms lost [1].

One can further simplify things by assuming simple combining rules (the arithmetic and geometric means for  $\sigma$  and  $\varepsilon$ , respectively), assuming a set of pure bath gas parameters (we used the parameters given in Table 1 of Ref. 2), and generating pure gas parameters for the normal alkanes. The resulting *pure gas* Lennard-Jones parameters for the normal hydrocarbons (averaged over the seven baths) can be fit to

$$\begin{aligned}\sigma_x(\text{M}) &= 3.721x^{0.25} \text{ \AA} \\ \varepsilon_x(\text{M}) &= 139.3x^{0.59} \text{ cm}^{-1}.\end{aligned}\tag{S2}$$

Equation (S2), along with simple combining rules and the tabulated pure gas parameters for the bath gases, reproduces the calculated binary collision rates for *all* the species considered here within a few percent. Of course, this final simplification is similar to the usual procedure of using tabulated pure gas Lennard-Jones parameters, assuming values based on similar species when the species of interest have not been tabulated, and generating binary parameters via simple combining rules. Here we have quantified the error associated with this procedure, which, as discussed above, is only a few percent.

## References

- <sup>1</sup> Jasper, A. W.; Miller, J. A. Lennard-Jones Parameters for Combustion and Chemical Kinetics Modeling from Full-Dimensional Intermolecular Potentials. *Combust. Flame*, 2014, 161, 101.
- <sup>2</sup> Jasper, A. W.; Miller, J. A. Theoretical Unimolecular Kinetics for  $\text{CH}_4 + \text{M} \rightleftharpoons \text{CH}_3 + \text{H} + \text{M}$  in Eight Baths,  $\text{M} = \text{He, Ne, Ar, Kr, H}_2, \text{N}_2, \text{CO, and CH}_4$ . *J. Phys. Chem. A* 2011, 115, 6438–6455.
- <sup>3</sup> Jasper, A. W.; Miller, J. A.; Klippenstein, S. J. Collision Efficiency of Water in the Unimolecular Reaction  $\text{CH}_4 (+\text{H}_2\text{O}) \rightleftharpoons \text{CH}_3 + \text{H} (+\text{H}_2\text{O})$ : One-Dimensional and Two-Dimensional Solutions of the Low-Pressure-Limit Master Equation, *J. Phys. Chem. A* 2013, 117, 12243–12255.