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Combustion simulations with accurate transport properties for reactive intermediates

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ABSTRACT

The effect of employing accurate transport properties in simulations of freely propagating H_2/O_2/He and CH_4/O_2 flames is investigated. Transport properties for the collision pairs H_2–H_2, H–H_2, and H–H are computed from published tables of collision integrals. Previous calculations in our group of transport properties for OH–He, H–H_2O and H–O_2 have been extended to higher temperatures. In addition, new calculations on H–He, O–He, H_2–He, and H_2O–He are reported. Flame simulations with two sets of transport data were compared. The first set contained transport properties obtained with the conventional method of employing parameterized Lennard-Jones (12-6) potentials, while in the second set transport properties for the above collision pairs were substituted. A modest increase in laminar flame speeds, comparable to differences found when employing different chemistry models, was found for both flames.

1. Introduction

There has been great interest and activity on computationally simulating combustion in spatially inhomogeneous environments, such as internal combustion engines [1]. A significant effort has been invested by many groups on the development of chemical combustion models to describe reliably the temperature, and also pressure, dependence of the rate constants for relevant chemical reactions (see, for example, [2–6]).

The use of accurate transport properties is also essential in the reliable modeling of combustion in flames and other media. Sensitivity analyses by several groups suggest that the uncertainties in the transport properties can be as significant as the uncertainties in measured reaction rate constants [7–10]. Brown et al. [11] have extensively reviewed the methods that have been employed for the estimation of transport properties for combustion modeling.

The conventional approach for the estimation of transport properties has usually involved the use of isotropic Lennard-Jones (LJ) (12-6) potentials with the well and depth and length parameters ϵ and σ, respectively, determined through combination rules for the like pairs. In recent work, Jasper, Miller, and co-workers [12,13] have fit LJ parameters to suitably spherically averaged ab initio potentials for alkane–helium and H, H_2, alkane–N_2 interactions. As noted by Paul and Warnatz [14], the repulsive wall of a LJ (12-6) is generally steeper than the true potential, and this can lead to an incorrect computed temperature dependence of the transport properties.

Several groups [15–24], including our own [25–28], have computed transport properties for a number of collision pairs through quantum or classical scattering calculations employing ab initio potentials. Our particular interest has centered on the calculation of transport properties of collision pairs involving small transient species such as atoms and diatomic radicals for which accurate potential energy surfaces (PES's) are available or are calculated. We have found that the repulsive walls of PES's involving radical species are less steep than that of the LJ (12-6) potential. In some cases, for example CH_2–He [26] and H–O_2 [26], the accurately computed transport properties are quite significantly different than those computed using assumed LJ (12-6) potentials, especially in their temperature dependence. These are systems for which the PES is strongly anisotropic or has a deep potential well.

It is worthwhile to go beyond sensitivity analyses of the importance of reliable transport properties and the comparison of accurate and LJ (12-6) computed transport properties. Dong et al. [8] have carried out combustion simulations of premixed H_2/air flames with updated diffusion coefficients to investigate their effect on computed extinction strain rates.

In the present study, we probe the effect of employing accurate transport properties in simulations of H_2/O_2/He flames. Here, the chemistry is quite simple as there are only 9 chemical species that need to be included: H_2, O_2, H_2O, H, O, OH, HO_2, H_2O_2, and He. With such a simple chemical system, it has been possible to include accurate transport properties for a significant fraction of the collision pairs, particularly those involving radical species. We have

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also investigated the effect of employing accurate transport properties on simulations of CH_4/O_2 flames, in which many more chemical species are present. Here, we compare laminar flame speeds in freely propagating flames, using different sets of transport properties. We find that the use of accurate transport properties has a noticeable effect on the computed flame properties.

This paper is organized as follows: The calculation of transport properties through quantum scattering calculations is briefly reviewed in the next section. The results of previous calculations are summarized, and transport properties for newly computed systems are presented. Section 3 describes our combustion simulations, and Section 4 presents computed flame speeds for freely propagating flames. The paper concludes with a discussion.

2. Calculation of transport properties

In our work [25–28], we have computed transport properties through quantum scattering calculations. We present a brief review of the methodology employed.

In previous papers, we considered the full anisotropic atom–molecule PES's and computed collision integrals $\Omega^{(n,s)}$ for specific collision pairs, from which transport properties can be determined. The collision integrals are computed as Boltzmann averages of integrals of transport cross sections over the molecular rotational levels [27,29–32]:

$$\Omega^{(n,s)}(T) = \frac{1}{q_R}\sum_{j_i}(2j_i+1)\exp(-\varepsilon_i/k_BT)\Omega_{j_i}^{(n,s)}(T) \tag{1}$$

where j_i and ε_i are the rotational angular momentum and energy, respectively, of the ith molecular rotational level, q_R is the rotational partition function, and k_B is the Boltzmann constant.

The state-specific collision integrals $\Omega_{j_i}^{(n,s)}(T)$ in Eq. (1) are computed by integration over the collision energy E of state-specific transport cross sections:

$$\Omega_{j_i}^{(n,s)}(T) = \frac{1}{2}\left(\frac{k_BT}{2\pi\mu}\right)^{1/2}\frac{1}{(k_BT)^{s+2}}\int_0^\infty E^{s+1}\exp(-E/k_BT)Q_{j_i}^{(n)}(E)dE \tag{2}$$

where μ is the atom–molecule reduced mass. The state-specific transport cross section $Q_{j_i}^{(n)}(E)$ in Eq. (2) is a sum of state-to-state cross transport sections over the final levels:

$$Q_{j_i}^{(n)}(E) = \sum_{j_f}Q_{j_i\to j_f}^{(n)}(E) \tag{3}$$

In Eq. (3), we have restricted the inelastic transitions to changes in the rotational level, and not vibrational transitions. Cross sections for the latter are much smaller than for rotational transitions.

The state-to-state transport cross sections in Eq. (3) are angle weighted averages of state-to-state differential cross sections:

$$Q_{j_i\to j_f}^{(n)}(E) = \int\left(\frac{d\sigma}{d\Omega}\right)_{j_i\to j_f}\Phi_n(E)d\widehat{R} \tag{4}$$

where $\widehat{R}$ is the orientation of the Jacobi vector $\mathbf{R}$. The weighting factors $\Phi_n(E)$ for $n = 1$ and 2, as well as expressions for the state-to-state transport cross sections in terms of the T-matrix elements from time-independent quantum scattering calculations, have been given previously [26,30].

It is customary to employ reduced collision integrals $\Omega^{(n,s)*}$ in the calculation of transport properties. These are related to the collision integrals given in Eq. (1) by [29,11]

$$\sigma^2\Omega^{(n,s)*}(T^*) = \frac{F(n,s)\Omega^{(n,s)}(T)}{(k_BT/2\pi\mu)^{1/2}} \tag{5}$$

where $T^* = k_BT/\epsilon$ and the factor $F(n,s)$ equals

$$F(n,s) = \frac{4(n+1)}{\pi(s+1)![2n+1-(-1)^n]} \tag{6}$$

The binary diffusion coefficient is related to the (1, 1) reduced collision integral through the relation

$$D = \frac{3\left(2\pi k_B^3T^3/\mu\right)^{1/2}}{16N\sigma^2\Omega^{(n,s)*}} \tag{7}$$

where N is the number density of the gas. The following ratios of collision integrals are required for the calculation of thermal diffusion coefficients [33]:

$$A^* = \Omega^{(2,2)}/(2\Omega^{(1,1)}) \tag{8}$$

$$B^* = (5\Omega^{(1,2)} - \Omega^{(1,3)})/(3\Omega^{(1,1)}) \tag{9}$$

$$C^* = \Omega^{(1,2)}/(3\Omega^{(1,1)}) \tag{10}$$

We have employed literature values, where available, for calculated collision integrals. Specifically, we have taken reduced collision integrals for H_2–H_2, H–H_2, and H–H interactions from the work of Stallcop and co-workers [16,18]. We have extended our published [25,27,28] collision integral calculations on the OH–He, H_2O–H, and H–O_2 systems to higher collision energies so that collision integrals, including $\Omega^{(n,s)}$ for $(n,s) = (1,2)$ and (1, 3), can be computed to higher temperatures than 1500 K, reported in these papers.

The subsections below describe new calculations we have carried out on several other collision pairs involving radical species. The collision integrals $\Omega^{(n,s)}$ for $(n,s) = (1,1)$, (1,2), (1,3), and (2,2) for all the collision pairs considered are presented in the Supplementary Material (see Appendix A). We compare diffusion coefficients calculated with our collision integrals with those computed previously in Section 2.5. Plots of the collision integral ratios A^*, B^*, and C^* ratios are presented in the Supplementary Material.

2.1. H–He

Middha et al. [22] have computed the temperature-dependent diffusion coefficient for the H–He interaction through quantum scattering calculations employing an ab initio calculated potential energy curve. Since we would like to have collision integrals beyond just the (1, 1) term (see Eq. (7)) needed for the diffusion coefficient, we have computed a new H–He potential energy curve and calculated the collision integrals needed for the transport properties discussed above.

We employed the MOLPRO 2010.1 suite of computer codes [34] to compute the HHe potential energy curve by means of restricted coupled-cluster calculations with inclusion of single, double, and (perturbatively) triple excitations [RCCSD(T)] [35,36]. An atom-centered avqz basis set was used [37], with the addition of a set of mid-bond functions located midway between the atoms. A counterpoise correction was applied to correct for basis set superposition error [38].

2.2. O(^3P)–He

We have employed the OHe $^3\Sigma^-$ and $^3\Pi$ potential energy curves computed by Krems et al. [39] for the calculation of collision integrals for this system. The Hamiltonian for the interaction of an atom in a ^3P state with a closed-shell atom was taken from Alexander et al. [40]. We have considered the individual spin–orbit levels of the O(^3P_j) collision partner and carried out the Boltzmann state average in Eq. (1). The O(^3P) spin–orbit constant as assumed