FINAL REPORT

Project Title: "Theoretical Investigation of Kinetic Processes in Small Radicals of Importance in Combustion", DOE Project Identifier DESC0002323.

This project identifier was unchanged from that assigned to the previously funded (2009) project, entitled "SISGR: Investigation of Non-adiabatic Effects in Reactive and Inelastic Collisions of Molecular Combustion Intermediates".

The final report that follows below summarizes work done in the period May 2014 – Jun 2017.

Program Scope

Our group studies inelastic and reactive collisions of small molecules, focusing on radicals important in combustion environments. The goal is the better understanding of kinetic processes that may be difficult to access experimentally. An essential component is the accurate determination and fitting of potential energy surfaces (PESs). After fitting [1] the *ab initio* points to obtain global PESs, we treat the dynamics using time-independent (close-coupling) methods. Cross sections and rate constants for collisions of are determined with our Hibridon program suite [2].

We have studied energy transfer (rotationally, vibrationally, and/or electronically inelastic) in small hydrocarbon radicals (CH_2 and CH_3) and the CN radical. We have made a comparison with experimental measurements of relevant rate constants for collisions of these radicals.

Also, we have calculated accurate transport properties using state-of-the-art PESs and to investigate the sensitivity to these parameters in 1-dimensional flame simulations. Of particular interest are collision pairs involving the light H atom.

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Research Summary

Collisional Relaxation

We have carried out an extensive study of the collisional relaxation of methylene (CH_2), a system studied extensively at Brookhaven by the group of Hall and Sears [3]. We determined determined potential energy surfaces (PES's) for the interaction of CH_2 in both its ground X^3B_1 [4] and singlet excited a^1A_1 [1] electronic states with the He atom. Through quantum scattering calculations we determined state-to-state integral cross sections for rotationally inelastic transitions and rate constants for total removal of given rotational levels [1, 4]. The latter agreed well with the Brookhaven results. In particular, in the 2009-2014 period we studied:

A. Rovibronic collisional relaxation of methylene

Vibrational relaxation [5] of the bending mode of $CH_2(X)$ in collisions with He is ~ 50 times less efficient than rotational relaxation [1,4]. As a prerequisite to our recently published investigation of the rotational relaxation of CH_2 in its ground (X^3B_1) state, we determined [4] the dependence of the CH_2–He PES on the bending vibration of the molecule. By then averaging over the product of wavefunctions for two different bending vibrational levels, we can model ro-vibrational relaxation. As shown in Fig. 1, in addition to the inefficiency of rovibrational relaxation, as shown in Fig. 1, here is no clear-cut dependence on the energy gap. Our investigation [5] was one of the first ever fully-quantum calculations of cross sections for vibrational relaxation of a small molecule.

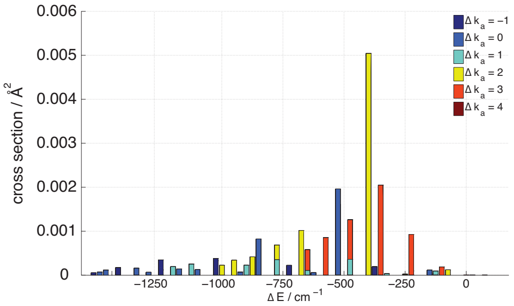

Fig. 1. Cross sections for relaxation out of the $NK_aK_c=5_{15}$ rotational level of the (0,1,0) vibrational manifold of $CH_2(X)$ into rotational levels of the ground (0,0,0) vibrational manifold (from Ref. 5). The colors differentiate transitions into different K stacks. *Note the extremely small size of the cross sections*.

B. Electronic collisional relaxation of methylene

The first excited ($^1\tilde{a}$) state of CH_2 lies close enough to the ground state that there exist several near-degeneracies between rotational levels, as shown in Fig. 2. Bley and Temps [6] suggested that spin-orbit mixing of these near degenerate levels could result in substantial collisional coupling. This "gateway" mechanism for collision-induced intersystem crossing (CIIC) was first proposed by Gelbart and Freed [7].

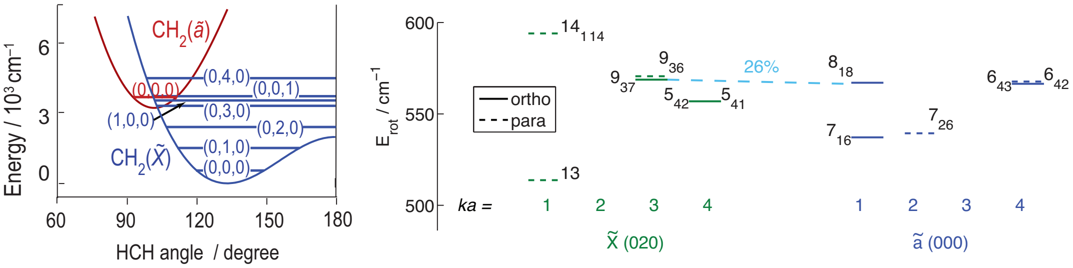

Fig. 2. (Left panel) relative positions of bend-stretch levels of the ground and first excited states of CH_2. (Right panel) High resolution illustration of the near degeneracy between the $\tilde{a}(000)$ 8_{18} and $X(020)$ 9_{37} rotational levels of o-CH_2.

In our use of the "gateway" model, CIIC is facilitated by coherent mixing of the scattering T-matrix elements for collisional transitions involving a few accidentally degenerate rotational states [8]. These accidental degeneracies are shown by the light blue dashed line in Fig. 2 (connecting the 9_{36} and 8_{18} levels). We then used our calculated CIIC and pure-rotational rate constants in a kinetic simulation of the collisional relaxation of $CH_2(X,a)$ in collisions with He.

Figure 3 presents snapshots, following the relaxation of the 8_{18} mixed, nominal *a* state, studied at Brookhaven. Relaxation proceeds in three steps: (1) rapid equilibration of the two mixed-pair levels [*a*(0,0,0)8_{18} and *X*(0,2,0)9_{37}, in Fig. 1.3], (2) fast relaxation within the *a* state, and (3) slower relaxation among the *X*-state levels.

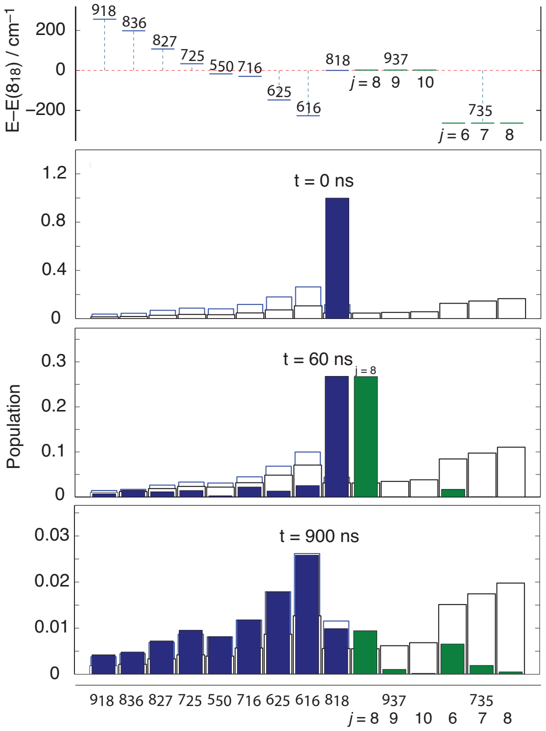

Fig. 3. Rotational distributions of selected singlet (blue) and triplet (green) levels at various times following initial population of the *a*(0,0,0) 8_{18} mixed level; $p = 2$ Torr, $T = 300$ K. The black rectangular empty boxes denote the relative $T = 300$ K Boltzmann populations. The upper panel indicates the energies of the levels.

C. *Collisional relaxation of the methyl radical*

Stimulated by our earlier theoretical work on rotational energy transfer in CH_3-He collisions [9], Orr-Ewing (Bristol, UK) applied molecular beam and velocity map imaging to the determination of differential cross sections for scattering of a photolytically generated beam of CD_3 with a number of collision partners. REMPI detection of the scattered CD_3 allowed resolution of the rotational angular momentum *n*, but averaged over a subset of the projection quantum numbers. In a series of studies, Orr-Ewing and his group have determined differential cross sections for collisions of CD_3 with He, H_2, Ar, and N_2. We have employed PES's determined by our group for the first three collision partners to compute differential cross sections. These agree well with experiment [10–12], as can be seen in Fig. 4. The dynamics of collision of the symmetric top CD_3 is richer than that of a diatomic. In collaborations with Orr-Ewing and van der Avoird (Nijmegen, Netherlands), [12–13] we compared the scattering of CD_3 with that of another (nonplanar) symmetric top ND_3.

D. *Rotational energy transfer in the CN radical*

We have worked with Hall and Sears on the study of rotational energy transfer (RET) of CN(*X*) in collisions with He and Ar. [14] These authors employed frequency modulated transient absorption in a double-resonance, depletion recovery experiment. We carried out quantum scattering calculations for RET of selected rotational levels. Our calculations agree well with measured thermal rate constants, as well as non-thermal Doppler-resolved rate constants. In the future we will investigate collisional depolarization of non-isotropic *m* distributions.

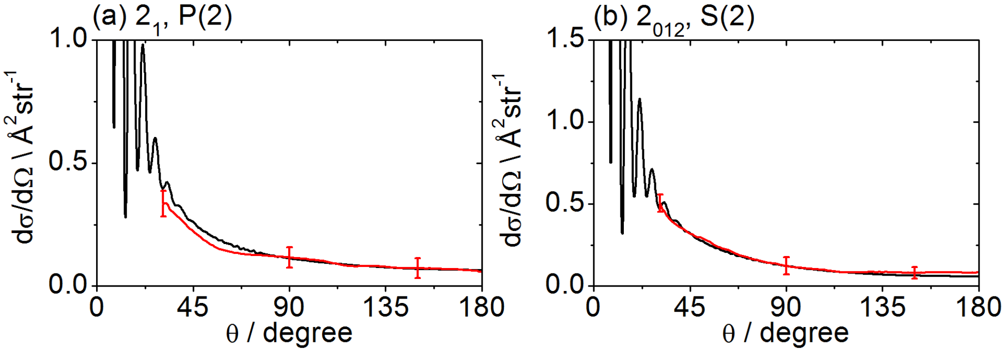

Fig. 4. DCSs for inelastic scattering of CD_3 radicals into (left panel) final rotational levels *nk*=21 and (right panel) 20+21+22. The REMPI line employed for detection is indicated, along with the range of *k′* projection levels contributing to the signal. Red curves: experiment; black curves: theory.

Transport properties and combustion modeling

A. Transport cross sections

Modeling combustion involves the prediction of the temporal and spatial dependence of the concentrations of all relevant species, as well as for the calculation of flame velocities. This requires knowledge of rate constants of all the relevant species, as well transport properties. Sensitivity analysis by several groups suggests that uncertainties in transport properties can be as significant as uncertainties in reaction rate constants. Present computational resources allow the accurate calculation of transport properties using state-of-the-art PESs. We have been computing accurate transport properties in quantum scattering calculations for collisions of various free radicals. Based on our recent work [15–18], we found that: (a) Retention of just the isotropic part of the potential results in errors in transport properties of only a few percent. (The exceptions involve species where the lowest unoccupied molecular orbital (LUMO) is low lying, as in $CH_2(a)$ and BH_3.) (b) Isotropic Lennard-Jones (LJ) 12-6 potentials yield diffusion coefficients with too steep a temperature dependence. This occurs because the repulsive walls of LJ 12-6 potentials are too steep. (c) Transport property calculations with LJ potentials for radical-radical systems disagree significantly with calculations using accurate potentials.

We have concentrated [16–18] on the calculation of transport properties for collision pairs involving the light H atom and have computed PESs when these are not available. We have also used these calculated properties to assess how a more accurate treatment of transport affects 1-dimensional laminar combustion simulations. In some cases accurate transport properties differ significantly from LJ estimates, as illustrated in Fig. 5 for the H–CO and H–CO_2 binary diffusion coefficients.

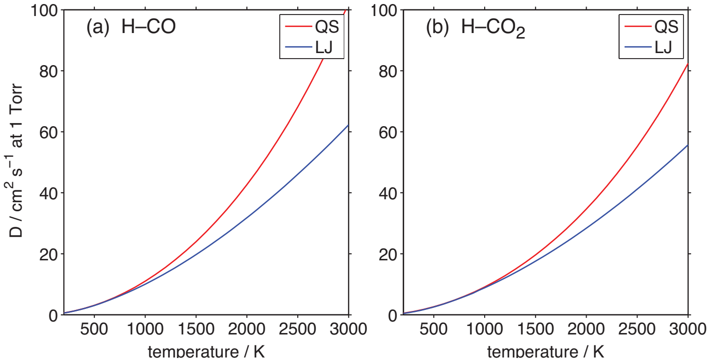

Fig. 5. Comparison of binary diffusion coefficients at 1 Torr for (a) H–CO and (b) H–CO_2. QS and LJ denote quantum scattering calculations and conventional calculations with LJ (12-6) potentials, respectively.

In recent calculations [18], we have computed a new RCCSD(T) PES for H–N_2 and have computed transport properties for comparison with the previous calculations by Stallcop *et al.* [J. Chem. Phys. **97**, 3431 (1992)], who used a spherically averaged potential. We have also computed a PES for H–CH_4 and computed transport properties using both the full anisotropic and spherically averaged potentials.

B. Flame Simulations

We have carried out 1-dimensional flame simulations of a freely propagating H_2/O_2/He flame with two sets of transport properties [19], We have extended our 1-dimensional flame simulations to the combustion of methane in both air and in oxygen. Two sets of calculations were carried out: The first set was based on the conventional parameterized LJ 12-6 potentials, while the second set incorporated exact transport properties for the available collision pairs. The calculated flame speeds as a function of the equivalence ratio are presented in Fig. 6.

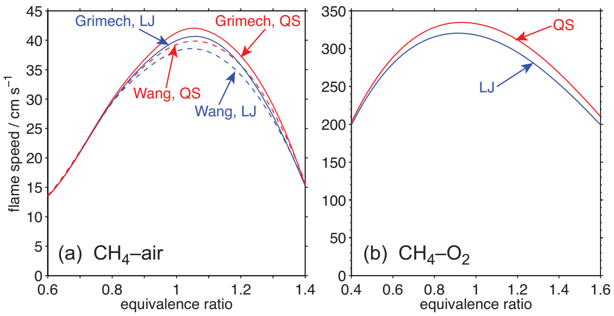

FIG. 6. Laminar flame speeds for (a) CH_4–air and (b) CH_4–O_2 at 1 atm. The blue and red curves denote calculations with LJ and accurate transport properties, respectively. Chemistry models employed for CH_4–air included Grimech 3.0 (solid lines) and USC Mech 3 (dashed lines). For CH_4–O_2 Grimech 3.0 was employed as the chemistry model.

It can be seen from Fig. 6(a) that the differences in flame speeds computed with conventional LJ and accurate transport properties are comparable to differences in flame speeds computed with different chemistry models. A sensitivity analysis indicates that for the air flame the flame speed is most strongly affected by the transport properties for H–N_2, while for the O_2 flame the most important transport properties are for the H–CO and H–CO_2 collision pairs.

Outreach and Interactions

Dagdigian and Alexander have published several review articles [20,21] outlining theoretical methods used in the calculations carried out under this project.

A. DOE Synergy

As mentioned above, Alexander and Dagdigian interact closely with Hall and Sears at Brookhaven. In addition to our collaborative work on the collisional relaxation of CH_2, we have collaborated on the Doppler-resolved kinetics and pressure broadening of the CN radical. Alexander has collaborated with Chandler at Sandia Livermore on inelastic scattering of the NO radical. Development of Dagdigian's 1-dimensional combustion simulations were facilitated by interactions with Sivaramakrishnan at Argonne.

B. Interaction with other groups

As discussed above, we collaborated with Orr-Ewing at Bristol UK on the determination of CD_3 differential cross sections in collisions with a number of species. We hope to compare recently-computed [22] pressure broadening calculations on the OH $A - X$ transition with measurements from the group of Ritchie at Oxford. Oxford, UK.

Figure 3 (above) was based on solution of a kinetic master equation following a method first described by Alexander, Dagdigian and Hall [23]. In work supported by another grant, this method has been recently used to interpret experiments carried out by Mullin [24].

In a collaboration with Lique [25], Dagdigian employed the PES for the interaction of $CH_2(X)$ with helium [4] to estimate collisional excitation rate constants between the fine-structure levels of $CH_2(X)$ induced by collisions with H_2. These data were employed in radiative transfer calculations to simulate the excitation of CH_2 in interstellar molecular clouds. Similar calculations [26] were also carried out for collisions of $O(^3P)$ with H atoms and H_2, using previously calculated PES's [17].

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