THERMODYNAMIC ANALYSIS OF BOUNDARY LAYER SPECIES DURING ABLATION

Maitreyee P. Sharma, Marco Panesi

University of Illinois Urbana-Champaign
Aerospace Engineering
Talbot Lab, 104 S Wright Street,
Room 306E, Urbana, IL-61801, USA

Richard L. Jaffe

NASA Ames Research Center
Aerothermodynamics Branch
Moffett Field,
CA-94035, USA

ABSTRACT

The focus of this work is on carbon clusters, hydrocarbons and other carbonaceous species which are constituents of pyrolysis gases injected into the boundary layer. Some of these molecules are observed to have absorption spectra in the VUV and UV region that match the emission spectra of atomic nitrogen and oxygen. Hence, they can potentially absorb the radiation impinging on the heat shield. Accurate thermodynamic data is not available for many of these species over the relevant temperature range for reentry. The objective of this work is to determine the thermochemical properties of potential radiation absorbing molecules using accurate ab initio quantum chemistry calculations. We have compiled a database of formation enthalpies, anharmonic vibrational frequencies and rotational constants for the ground and low-lying excited electronic states of these carbonaceous species. Using these thermochemical properties, we compute equilibrium mole fractions and observe that the mole fractions of some species of interest are significant, thus they could affect the radiative heat flux. Furthermore, comparisons of the formation enthalpies and mole fractions are made with data from literature.

Index Terms— Thermodynamics, carbon clusters, ablation, boundary layer chemistry

1. INTRODUCTION

Hyperbolic Earth entry at speeds of 10-13km/s causes the formation of a strong shock in the forebody region of a spacecraft. The radiation coming from the shock is predominantly due to atomic nitrogen (174.29 nm N(I) line) and atomic oxygen. In order to protect the spacecraft from this intense radiative heating, heat shields are used. One type of heat shields use ablating materials which help in attenuation of heating through ablation. These heat shields have an outer layer which undergoes sublimation and pyrolysis to form a gas layer that carries away some of the heat by convection. This layer of pyrolysis gases is predominantly composed of carbon compounds including carbon clusters, hydrocarbons and carbon oxides. It is known that the pyrolysis gases absorb some of the radiation coming from the shock layer. One must account for this absorption in the modeling and simulation of hypersonic flows around re-entry vehicles.

In a study by Prakash and Park [1], it was concluded that some species present in the boundary layer can potentially absorb radiation coming from the shock layer. They estimated the reduction in radiative flux could be as large as 12.5%. Among the species studied, C_3 is the predominant species released into the boundary layer [2, 3]. C_3 has a prominent spectral feature in the VUV region (centered at 160 nm [4]). This is close to the N(I) 174.29 nm emission line and hence can absorb the radiative heating coming from the shock layer [2]. Observations from experiments conducted in the temperature range of 3500-4000K and spectral range of 140-700nm with shock heated acetylene and methane showed strong absorption in the VUV region. These absorptions were attributed to C_3 [1] and C_2H [5]. A more recent study by Fujita et al. [6] suggests that the chemical models and reactions rates have a considerable effect on the radiative and convective heating rates. It was also observed that the presence of acetylene affects these heat transfer rates. In a similar study by Johnston et al. [7] it was found that depending on the spectral region being studied and the amount of ablation products, the radiative heating can be augmented or reduced. Finally, a more recent study by Martin et al. [8] compares various kinetic models used to study the chemistry around carbon-based phenolic ablative heat shields in air. The authors then suggest a new set of chemical reactions and reaction rate model selected based on sensitivity analysis of the boundary layer composition. The drawback in all the previous works is that they are limited to small carbon clusters, up to 3 carbon atoms. Observations and limitations of the previous studies motivate the investigation of thermodynamic and spectral properties of C_3, other carbon clusters and compounds consisting of C, H, O and N elements.

The thermodynamics for temperatures up to 10000K and spectral features of C_2, C_3 and C_2H are fairly well known, but thermodynamic, structural, energetic and spectroscopic data for other species are less well known. A previous study by the authors of this paper was focused on the thermodynamic

and spectral properties calculations of only carbon clusters and hydrocarbons [9]. It was concluded that C_4 and C_4H are other potential radiation absorbing molecules based on their absorption spectrum. In this paper, we lay our focus on molecules of the boundary layer composed of C, H, N and O elements. Thermodynamic properties of these molecules are computed based on the W1RO method [10, 11]. The error in the thermodynamic properties lies with 0.7-1.5 kcal/mol. After computing the thermodynamic properties, equilibrium mole fractions of the pyrolysis gases are estimated at the relevant temperature and pressure ranges in the boundary layer, namely 2000-5000K and 1 atm.

The paper is organized as follows. Section 2 discusses the quantum chemistry methods used to compute the thermodynamics properties. We also enumerate on the principles and methods of statistical mechanics used to compute the thermodynamic properties following the quantum chemistry calculations. Section 3 presents the results obtained using the thermodynamic properties computed in this work. These include the equilibrium mole fractions in the boundary layer at the conditions of interest during re-entry. The work is finally concluded in the Section 4.

2. THEORY AND METHODS

In this paper, we focus on ab initio calculation of thermochemical properties of molecules present in the boundary layer of an ablating heat shield. Primarily, our focus is on computation of enthalpies of formation, free energy, vibrational frequencies and rotational constants of molecules composed of C, H, N and O atoms. Partition functions are computed using the vibrational frequencies and rotational constants which in turn are used to calculate all thermodynamic properties of interest. For these large molecules, we use the rigid rotor and harmonic oscillator model. The second step following these ab initio calculations involve computing the mole fractions of the molecules at boundary layer conditions relevant to hypersonic re-entry of an ablating heat shield space craft.

2.1. Ab-initio Ground State Calculations

In an earlier paper by the authors [9], the focus lay on using the Gn methods proposed by Curtiss et al. in a series of papers [12, 13, 14]. These methods fall under the umbrella of composite methods. Composite methods determine the energies of molecules at their equilibrium geometries by combining results obtained from high-level correlation methods (like quadratic configuration interaction theory (QCISD) and coupled cluster theory (CCSD)) using small atomic orbital basis sets with results from lower level methods (like MP2 and MP4) using a much larger basis set. To increase the accuracy of the final result, an empirical additive correction term has been computed by comparing the results obtained from cal-

culations with those of experiments. This is done for a large set of test molecules for a specific property (e.g., atomization energy). The empirical term is the correction factor that bring the test set results into the best overall agreement with the experimental data.

The W1RO method [10] is a type of composite method used to compute the thermodynamics in this paper. This method is more accurate than the Gn methods and has a mean absolute error of approximately 0.3 kcal/mol for atomization energies. Unlike other methods, W1RO method includes only one empirical parameter. It has been developed for molecules composed of atoms from the first two rows of the periodic table which encompasses the molecules being studied in this work.

2.2. Thermodynamic Relations from Statistical Mechanics

The next step following the ab initio calculations, is utilizing the data to compute the thermodynamic properties. In order to study chemical reactions or even simple equilibrium compositions of individual species in a mixture, it is imperative to have knowledge regarding the formation enthalpy and entropy of each species in the temperature and pressure ranges of interest. These thermodynamic properties are obtained from molecular partition functions using the rigid-rotor harmonic oscillator model. The harmonic frequencies and rotational constants are computed for the equilibrium geometries of the molecule using the W1RO method described above. We also include a few low lying excited electronic states in the partition function which are computed using the time-dependent density functional theory [15]. These electronic states were computed by the authors in an earlier paper [9]. The enthalpy of formation is calculated using the atomization energies of the molecules. For Cn and CnH species, these values are given Table 1, [9].

The molecular partition function is a multiplication of partition functions for different modes of energy. The translation mode partition function (Q_{tr}) is a function of the mass of each species and the temperature and is given by [18],

$$Q_{tr} = \left(\frac{2\pi \, M \, k_B T}{N \, h^2} \right)^{\frac{3}{2}} \frac{RT}{P} \qquad (1)$$

where M is the molecular or atomic mass of the species, N is Avogadros number, h is Plancks constant, R is the gas constant and P is the pressure.

The molecular partition function for internal modes (vibration, rotation and electronic excitation) is given by [18],

$$Q_{int} = \sum_i g_i \exp(-E_i/k_B T) \qquad (2)$$

where the summation extends over all the energy levels of the atomic or molecular species. In the equation, E_i are the energy levels of the species, T is the temperature, g_i is the

Table 1. Comparison of $\Delta_f H$ at 0K with Existing Thermochemical Tables (in kcal mol^{-1})

Molecule	G4	W1RO	ATcT	JANAF [16]	Gurvich [17]
$C_2(^1\Sigma_g^+)$	192.50	196.09	196.04 ± 0.06	198.19	196.56
$C_3(^1\Sigma_g^+)$	192.91	194.73	194.68 ± 0.13	193.94	198.61
$C_4(^1A_g)$	248.10	251.57	250.34	230.43	244.98
$C_2H(^2\Sigma^+)$	133.84	134.79	134.77 ± 0.04	113.27	135.04
$CH\ (^2\Pi)$	140.50	141.61	141.68 ± 0.03	141.17	141.98
$C_2H_2(^1\Sigma_g^+)$	54.76	54.42	54.69 ± 0.03	54.32	54.48

degeneracy of the level 'i' and k_B is Boltzmann constant. It is common practice to factor Q_{int} into vibration, rotation and electronic components,

$$Q_{int} = Q_{rot} \times Q_{vib} \times Q_{elec}. \tag{3}$$

Often if the energy difference between the ground and first electronic states is much larger than $k_B T$, where T is the temperature, and the anharmonic effects are negligible, the harmonic oscillator-rigid rotor approximation (HO-RR) for Q_{rot} and Q_{vib} is a reasonable approximation. In this approximation, the same rotation and vibration partition function values are used for each electronic state. In case of the electronic partition function, the above summation in Eq. (2) is usually truncated after the second or third term depending on the temperature range of interest. At low temperatures, the exponential term becomes very small for higher electronic energy levels since the energy of these levels is several times larger than $k_B T$. Therefore, without foregoing much accuracy the summation can be truncated. Finally, we obtain the total partition function, Q_{TOT}, as the product of Q_{tr} and Q_{int}.

All thermodynamic properties can be derived from the molecular partition functions. The gaseous species in the shock and boundary layers are assumed to have ideal gas behavior and the thermodynamic functions are evaluated at the standard state. The standard state specific heat is given by [18],

$$C_P^{o_{INT}} = RT^2 \frac{\partial^2 \ln Q_{int}(T)}{\partial^2 T} + 2RT \frac{\partial \ln Q_{int}(T)}{\partial T} \tag{4}$$

The superscript o indicates standard state. The translation contribution to C_P^o is simply $\frac{5}{2}R$. Therefore, the total C_P is [18],

$$C_P^o = C_P^{o_{INT}} + \frac{5}{2}R \tag{5}$$

The methods mentioned in the previous subsection give the total electronic energy (ϵ_0), which along with zero-point vibration energy, is used to calculate the atomization energy, $D_0(M)$ at T = 0K, using,

$$D_0(M) = \sum x\,\epsilon_0(X) + \sum y\,\epsilon_0(Y) - \epsilon_0(M) \tag{6}$$

where x and y stand for number of X and Y atoms in molecule M and $\epsilon_0(M)$ includes the zero-point energy. The enthalpy of formation ($\Delta_f H^o$) of the molecules at 0K is related to the atomization energy as follows,

$$\begin{aligned} \Delta_f H^o(M,0K) &= x\,\Delta_f H^o(X,0K) + y\,\Delta_f H^o(Y,0K) \\ &- D_0(M) \end{aligned} \tag{7}$$

The enthalpy of formation ($\Delta_f H^o$) is the difference between the enthalpy of the molecule and its constituent atoms in their standard state. For standard state enthalpy [18],

$$H^o(T) = H^o(0) + RT^2 \frac{\partial \ln Q(T)}{\partial T} \tag{8}$$

$H^o(0)$ must include the formation enthalpy. Finally, the standard state entropy is given by [18],

$$S^o(T) = R \frac{\ln Q(T)}{N} + RT \frac{\partial \ln Q(T)}{\partial T} \tag{9}$$

It is convenient to use T = 0K as the reference temperature because only the lowest energy level of each species contribute to the thermodynamic functions.

The Gibbs free energy ($\Delta_f G^o$) and equilibrium constant is then obtained as [18],

$$\begin{aligned} \Delta_f G^o(M,0K) &= \Delta_f H^o(M,0K) - T[S^o(M,0K) \\ &- \sum_{atoms} S^o(X,0K)], \end{aligned} \tag{10}$$

$$K_{eq} = \exp\left(-\frac{\Delta G_r^o}{k_B\,T}\right). \tag{11}$$

The 'r' subscript represents the reaction being considered, for example,

$$a\,A + b\,B \rightarrow c\,C + d\,D \tag{12}$$
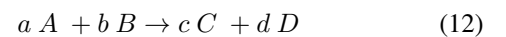
The equilibrium constant can also be expressed in terms of the partition functions as [18],

$$K_{eq} = \frac{Q_C^c\,Q_D^d}{Q_A^a\,Q_B^b} \tag{13}$$

It is important to note that while calculating the equilibrium constant using partition functions, the energies of all species should have a common reference energy.

3. RESULTS AND DISCUSSION

The W1RO method from Gaussian Software package [19, 20] is utilized to calculate the ab initio thermodynamic data. Using the computed ab intio thermodynamic properties, equilibrium composition of pyrolysis gas is estimated. The software PLATO [21, 22] is used to compute the thermochemical properties from the partition functions and equilibrium compositions. The equilibrium calculations are also carried for a range of boundary layer temperatures and pressures. A set of comparisons is made with the work of Fujita et al. [6] for the equilibrium composition of the pyrolysis gases. The species included are given in Table 2.

Many even numbered carbon clusters have triplet ground states and low lying singlet states. In general, the triplet states have linear structures and the singlet states have cyclic structures. Both these states are considered in this work. The T and S labels in the species list, Table 2, stand for these triplet and singlet states.

When studying the equilibrium mole fractions, we looked at three different mixtures. The first included species composed of C, H and N atoms (Figure 1), second one included molecules made of C, H and O atoms (Figure 2) and the last incorporated all the species give in the list (Figure 3). In the absence of O atom, Figure 1, the mole fractions of carbon clusters and hydrocarbons are significant in the temperature range of interest, i.e. 2500K - 5000K. The most abundant carbon cluster is C_3 which is expected (Black solid line with circles in Figure 1). C_4 triplet state (red solid line with circles) and C_4H linear isomer (brown dash dotted line) also have non-negligible mole fractions, thereby showing promise of radiation absorption. By non-negligible we mean mole fractions above 10^{-6}. Figure 2 introduces molecules containing O atom. In the case of abundance of C and O, the most abundant species is CO, another well-known and expected result. C_3 (red solid line with circles in Figure 2) again is an important species at slightly higher temperatures than seen in Figure 1. Although, with the inclusion of oxygen, C_4 triplet (brown solid line with circles) has a significant mole fraction, but the amount of C_4H is negligible.

The equilibrium composition in a mixture of all species listed in Table 2 is represented in Figure 3. The presence of both O and N containing molecules results in a significant decrease of the mole fractions of carbon clusters and hydrocarbons. The mixture is dominated by CO, N_2 and atomic oxygen.

Finally, Table 3 compared the equilibrium composition of pyrolysis gases with the results from the paper by Fujita et al. [6]. The first row in the table is the equilibrium composition from [6], the second row is the equilibrium composition
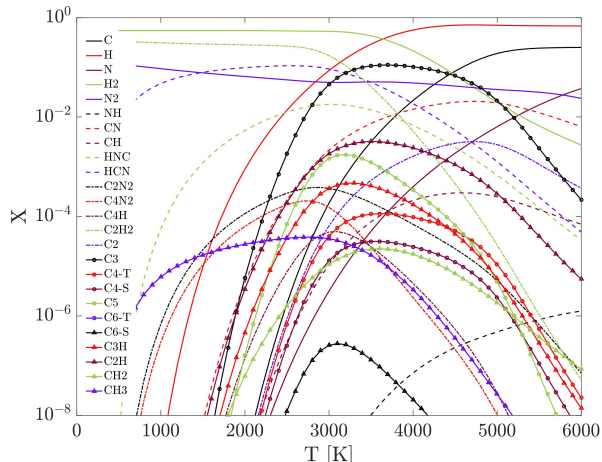
Fig. 1. Equilibrium Mole Fractions at 1 atm considering species composed of elements C, H and N

obtained using the thermodynamics calculated in this paper but using only the species considered in [6] and the last row represents the composition obtained using the entire species set given in Table 2. The equilibrium composition is computed at 3000 K, 1.47 atm pressure with 59.2% C, 13.1% H and 27.7% O by mass concentration [6]. The comparison shows some differences when looking at the first two rows of the table. However, these differences are in the second or third decimal place. When adding all the species considered, the differences between the second and third rows of the table are negligible. However, the importance of including all species lies in the study of the radiative heating attenuation. Since C_4 triplet and C_4H linear isomer have been observed to have favorable absorption spectra [9], it becomes necessary to include them as constituents of the pyrolysis gases. When considering all species, the mole fraction of C_4 triplet is observed to be 0.17e-04. However, C_4H has a negligible equilibrium mole fraction at these conditions.

4. CONCLUSIONS

Summarizing, this paper presents a new set of thermodynamic properties for carbon clusters, hydrocarbons and other species present in the boundary layer of an ablating heat shield. Properties are computed using ab initio quantum chemistry calculations. In this paper we use the W1RO method as implemented in the Gaussian Software package [19, 20]. Once we obtain the vibration frequencies and rotational constants, partition functions are computed and all thermodynamic properties are then obtained using the partition function. Using these properties, equilibrium mole fractions at conditions relevant to the boundary layer of an ablating heat shield are computed. These results give an approximate indication of the composition of the boundary layer.

Table 2. Species List

C	O	H	N	O_2	CO	H_2	N_2
NH	CN	OH	NO	CH	CO_2	H_2O	CON
NCO	CNO	HNC	HCN	HCO	HO_2	C_2N_2	C_4N_2
C_4H	C_2H_2	C_2	C_3	C_4-T	C_4-S	C_5	C_6-T
	C_6-S	C_3H	C_2H	CH_2	CH_3		

Table 3. Comparison of equilibrium composition of pyrolysis gases at 3,000K with Fujita et al. [6]

	H	H_2	C_2	CO	H_2O	C_2H	C_3	CO_2	C_2H_2
Fujita et al. [6]	0.09371	0.53371	0.00008	0.19922	0.0	0.00187	0.00185	0.0	0.17956
Current (Same Set)	0.07260	0.55804	0.00004	0.19789	1e-7	0.00125	0.02243	1e-8	0.14764
Current (All)	0.07266	0.55894	0.000035	0.19782	1e-7	0.00124	0.02205	1e-8	0.14624
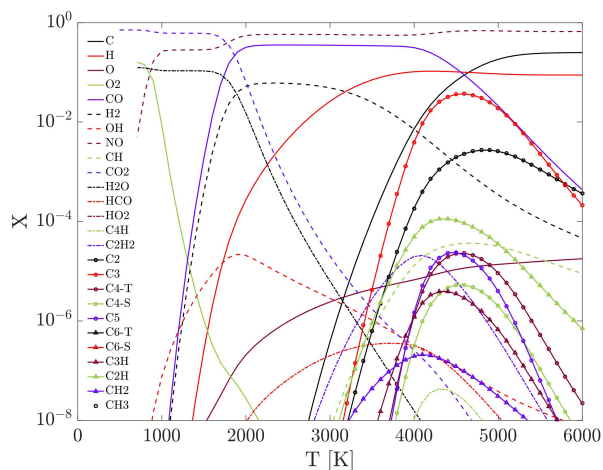
Fig. 2. Equilibrium Mole Fractions at 1 atm considering species composed of elements C, H and O

Fig. 3. Equilibrium Mole Fractions at 1 atm considering species composed of elements C, H, N and O

A comparison of the equilibrium mole fractions with literature values show some differences. These differences can be attributed to the different thermodynamic database used. We also studied the effect of adding various additional species not considered in literature and observed the differences due to these addition to be insignificant.

A previous paper by the authors [9] computed the spectral properties of these molecules of interest using Time Dependent Density Functional Theory (TD-DFT) method. Our future goal is to look at the absorption spectrum of these molecules using accurate quantum chemistry methods the like Equations of Motion Coupled Cluster Singles and Doubles (EOMCCSD) method. This along with the mole fractions data will be used to estimate the effect of these species on the radiative heat flux.

5. ACKNOWLEDGEMENT

6. REFERENCES

[1] S.G. Prakash and C. Park, "Shock tube spectroscopy of C_3+C_2H mixture in the 140-700 nm range," *AIAA Paper*, vol. 94, pp. 1979, 1979.

[2] R. L. Jaffe, G. Chaban, and D. Schwenke, "Theoretical determination of high-temperature absorption spectra for C_3 in the near-UV and VUV," in *43rd AIAA Thermophysics Conference*, p. 2743.

[3] C. Park, R. L. Jaffe, and H. Partridge, "Chemical-kinetic

parameters of hyperbolic earth entry," *Journal of Thermophysics and Heat transfer*, vol. 15, no. 1, pp. 76–90, 2001.

[4] G. Monninger, M. Förderer, P. Gürtler, S. Kalhofer, S. Petersen, L. Nemes, P. G. Szalay, and W. Krätschmer, "Vacuum ultraviolet spectroscopy of the carbon molecule C_3 in matrix isolated state: experiment and theory," *The Journal of Physical Chemistry A*, vol. 106, no. 24, pp. 5779–5788, 2002.

[5] J. L. Shinn, "Optical absorption of carbon and hydrocarbon species from shock-heated acetylene and methane in the 135-220 nm wavelength range," *Prog. Astron. Aeronaut.*, vol. 82, pp. 68–80, 1982.

[6] Kazuhisa Fujita, Tetsuya Yamada, and Nobuaki Ishii, "Impact of ablation gas kinetics on hyperbolic entry radiative heating," in *44th AIAA Aerospace Sciences Meeting and Exhibit*, 2006, p. 1185.

[7] Christopher O Johnston, Peter A Gnoffo, and Kenneth Sutton, "Influence of ablation on radiative heating for earth entry," *Journal of Spacecraft and Rockets*, vol. 46, no. 3, pp. 481–491, 2009.

[8] Alexandre Martin, Ioana Cozmuta, Michael J Wright, and Iain D Boyd, "Kinetic rates for gas-phase chemistry of phenolic-based carbon ablator in atmospheric air," *Journal of Thermophysics and Heat Transfer*, vol. 29, no. 2, pp. 222–240, 2015.

[9] Maitreyee Sharma Priyadarshini, Richard L Jaffe, Alessandro Munafò, and Marco Panesi, "Calculation of thermochemical properties of carbon-cluster ablation species," in *2018 Joint Thermophysics and Heat Transfer Conference*, 2018, p. 4179.

[10] Jan ML Martin and Glênisson de Oliveira, "Towards standard methods for benchmark quality ab initio thermochemistry-W1 and W2 theory," *The Journal of Chemical Physics*, vol. 111, no. 5, pp. 1843–1856, 1999.

[11] Ericka C Barnes, George A Petersson, John A Montgomery Jr, Michael J Frisch, and Jan ML Martin, "Unrestricted coupled cluster and brueckner doubles variations of W1 theory," *Journal of Chemical Theory and Computation*, vol. 5, no. 10, pp. 2687–2693, 2009.

[12] L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, "Gaussian-2 theory for molecular energies of first-and second-row compounds," *The Journal of Chemical Physics*, vol. 94, no. 11, pp. 7221–7230, 1991.

[13] L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, "Gaussian-3 (G3) theory for

molecules containing first and second-row atoms," *The Journal of Chemical Physics*, vol. 109, no. 18, pp. 7764–7776, 1998.

[14] L. A. Curtiss, P. C. Redfern, and K. Raghavachari, "Gaussian-4 theory," *The Journal of Chemical Physics*, vol. 126, no. 8, pp. 084108, 2007.

[15] A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *The Journal of Chemical Physics*, vol. 98, pp. 5648–5652, 1993.

[16] Daniel Richard Stull and Harold Prophet, "Janaf thermochemical tables," Tech. Rep., National Standard Reference Data System, 1971.

[17] Lev Veniaminovich Gurvich and I Veyts, *Thermodynamic Properties of Individual Substances: Elements and Compounds*, vol. 2, CRC press, 1990.

[18] Lev V Gurvich, IV Veits, and Ch B Alcock, "Thermodynamics properties of individual substances. Volume 1-Elements O, H/D, T/, F, Cl, Br, I, He, Ne, Ar, Kr, Xe, Rn, S, N, P, and their compounds. Part 1-Methods and computation. Part 2-Tables," *New York, Hemisphere Publishing Corp., 1989, p. Pt. 1, 577 p.; pt. 2, 352 p. Translation. No individual items are abstracted in this volume.*, 1989.

[19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al., "Official Gaussian 09 literature citation," vol. 9, 2014.

[20] MJ Frisch, GW Trucks, HB Schlegel, GE Scuseria, MA Robb, JR Cheeseman, G Scalmani, V Barone, GA Petersson, H Nakatsuji, et al., "Gaussian 16, Revision A. 03, Gaussian," *Inc., Wallingford CT*, 2016.

[21] A. Munafò, Y. Liu, and M. Panesi, "Physical models for dissociation and energy transfer in shock-heated nitrogen flows," *Phys. Fluids*, vol. 27, no. 12, pp. 127101, 2015.

[22] A. Munafò, N. N. Mansour, and M. Panesi, "A reduced-order NLTE kinetic model for radiating plasmas of outer envelopes of stellar atmospheres," *Astrophys. J.*, vol. 838, no. 2, pp. 126, 2017.