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A model of diamond growth in low pressure premixed flames

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Recognizing the potential importance of diamond thin film growth from combustion environments, a computational investigation of diamond synthesis in low pressure premixed flames has been conducted. The model employed solves the two-dimensional continuity, momentum, global energy, and species conservation equations in stagnation point flow geometry, and accounts for gas phase and surface reaction kinetics. The heterogeneous mechanism employed to describe diamond growth assumes that the methyl radical is the primary growth precursor. The gas phase mechanism includes elementary reaction pathways which generate methyl radicals from acetylene and in addition, includes a mechanism for cyclization (the formation of benzene) via acetylene and ethylene precursors. In this way, the pathway towards soot formation, which is believed to be a consequence of the formation of fused polycyclic aromatics, is shown to be a possible explanation for an eventual decrease in diamond growth rates at increasing fuel to oxygen flow ratios. A competition between oxidative pyrolysis of post flame hydrocarbons and cyclization establishes a criterion for optimum growth conditions.

I. INTRODUCTION

There has been a considerable level of interest recently, in the growth of diamond thin films by low pressure chemical vapor deposition (CVD).¹⁻³ This interest stems from the superior materials properties of diamond and its numerous technological applications in a variety of disciplines that include microelectronics, optics, and tribology. The synthesis of diamond, originally made possible at high temperature and pressures ($> 50\,000$ atm) is now possible at low pressures (< 1 atm) by CVD techniques that employ plasma activation (dc, rf, and microwave), thermal activation (filament-assisted methods), and combustion activation (traditionally with an oxygen-acetylene flame) of hydrogen-hydrocarbon-oxygen mixtures. Although a great deal of laboratory-scale research has been performed in these areas, increasing attention has been placed on methods that will produce diamond films at relatively high growth rates ($> 10\ \mu\text{m/h}$) with uniformity over larger areas, as CVD diamond synthesis still appears to be a very cost-sensitive technique.

It is generally believed that atomic hydrogen (and possibly OH^4 and oxygen atoms) plays an important role in hindering graphite growth kinetics, and promotes diamond growth by stabilizing sp^3 hybridized surface carbon bonds.¹⁻³ Any free sites created by the desorption or abstraction of surface chemisorbed hydrogen are believed to react with methyl radicals, giving rise to the addition of an sp^3 hybridized carbon atom and the extension of the diamond growth surface. An increased understanding of the diamond growth kinetics in a potentially high growth rate environment such as a combustion flame (an environment rich in reactive hydrocarbons and atomic hydrogen) can provide for the design optimization necessary to improve quality and lower manufacturing costs.

Diamond synthesis in premixed atmospheric pressure flames was originally reported by Hirose and colleagues^{5,6}

in 1988 and subsequently confirmed by others.^{4,7-11} Recent demonstration of high growth rate epitaxy in laminar oxygen-acetylene flames,¹² improved quality in turbulent flames,¹³ and growth over a larger area in highly stretched flames¹⁴ has made combustion synthesis of diamond one of the most promising methods for diamond growth. However, the atmospheric pressure growth of diamond has some limitations. Generally, the deposition area is small and the deposit is somewhat nonuniform. Furthermore, the high heat fluxes impose a number of practical problems associated with substrate thermal management.⁴ In some cases¹⁵ however, growth area can be extended by use of multiple flames and a rotating substrate. Cooper and Yarbrough¹⁶ have suggested circumventing many of these problems by using lower pressure flat flame burners, and have successfully demonstrated diamond synthesis in premixed oxygen-acetylene flames at reduced pressures. Similar experiments confirming these results are now underway at Caltech.¹⁷

Despite these previous studies and rapid advances in the technology of diamond thin film growth, it is not clear how the fundamental chemical processes influence the diamond growth, especially in view of the strong dependence of diamond film on the surface chemistry. Thus the primary objective in this investigation is to gain a fundamental understanding of the diamond growth in low pressure premixed oxygen-acetylene flames diluted in argon through theoretical modeling. Our present efforts are focused on using such a model for guiding low pressure flat flame operation that will optimize diamond growth conditions.

II. MODELING

A. Model formulation

A description of a low pressure flame in stagnation flow geometry requires, at the very least, a two-

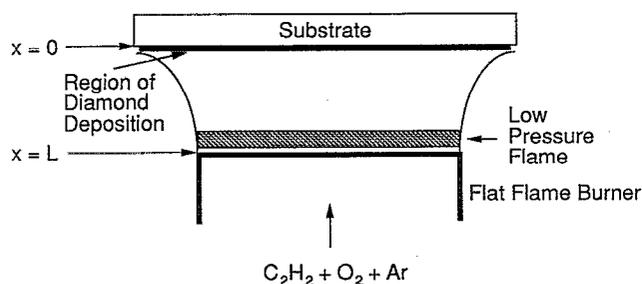


FIG. 1. Schematic for model of diamond synthesis in low pressure flames.

dimensional model that under certain constraints,^{18–20} can be reduced to one-dimension for computational purposes by a similarity transformation,¹⁹ provided that one conforms to the boundary condition that the incident free stream in stagnation is uniform and independent of the radial coordinate.¹⁹ Such a model has been used to successfully predict extinction limits in opposed stagnation flow, burner stabilized, premixed methane-air flames.¹⁹ In that geometry, the plane of symmetry between the two identical burners (source of premixed fuel and oxidizer) provides a zero flux boundary condition on species mole fractions and heat conduction. The flame is said to be burner stabilized when the flame speed exceeds the flow velocity and the primary flame is positioned near the burner surface within the region of maximum heat release and rapid rise in temperature. Under burner stabilized conditions, there is a finite conduction of heat back towards the burner.

To model low pressure combustion synthesis of diamond, we take a similar approach to that described in Kee *et al.*¹⁹ however, in our geometry (Fig. 1), a solid substrate (at $x=0$) is placed normal to a burner surface located at a distance $x=L$. As in the opposed flame configuration, this too is a stagnation point flow. The primary difference here is that the flame undergoes a significant cooling rate as it contacts a surface maintained at temperatures $T \sim 1200$ K, typically well below the adiabatic flame temperatures ($T_{ad} \sim 3000$ K). This results in a finite conduction of heat to the substrate ($\partial T / \partial x > 0$). Furthermore, the heterogeneous reactions involved at the growth surface result in a nonzero flux condition for reactive species.

The flow field is characterized by forced convection, which is taken to be purely axial as it emerges from the porous burner surface. The axial velocity is expected to immediately decrease due to the finite strain field, and subsequently increase as heat is released in the primary flame. Through numerical integration of the governing equations for overall mass, momentum, and energy conservation, as well as individual species conservation equations, we seek solutions for temperature, pressure, velocity, and species mole fraction profiles between the burner and the substrate. In this regard, the model is similar to that employed previously by Goodwin and Gavillet²¹ to predict diamond growth rates in hot filament environments. The primary difference of course, is that there is a substantial heat release due to combustion and the formation of a primary flame, and in addition, there may be additional important

reaction pathways that have not been included in previous flame synthesis calculations. For a review of the governing equations and stagnation flowfield description, the reader is directed to the paper by Kee *et al.*¹⁹

A numerical code similar to that described in Ref. 19 has been developed in our laboratory and is based primarily on a flame code originally designed for describing the chemistry in one-dimensional burner stabilized flames.²² Like the one-dimensional burner stabilized flame code, our stagnation flame code interfaces to a range of subroutines to facilitate the evaluation of thermodynamic properties and transport coefficients. To include gas phase reactions, we employ CHEMKIN,²³ which is used to compute the overall net reaction rate for the stable and radical species within the flow field, and SURFACE CHEMKIN²⁴ which in a similar manner, is used to compute the overall net reaction rates for active surface sites, thereby coupling surface sites to gas-phase radical reactivity. It is important to note here that subroutines such as CHEMKIN and SURFACE CHEMKIN are used only to facilitate the computation, and require data on reaction rates and thermochemical properties (to compute reverse reaction rates) as input. The thermochemical properties used here are that of the CHEMKIN thermodynamic data base.²⁵ The gas-phase mechanisms employed are described below.

B. Gas-phase mechanism

We employ two sets of gas phase reaction mechanisms. The first mechanism (from here on referred to as the non-sooting mechanism) and concomitant reaction rates are taken from Miller and Bowman²⁶ which has been found to describe reasonably well the structure of nonsooting oxygen-acetylene flames heavily diluted in argon (approximately 70% by mole fraction of reactants).²⁷ Our computational results described below also include argon as diluent, in that for this reaction mixture, there is a fair degree of confidence in the kinetics data, even though such a reaction mixture may not be optimized for diamond growth. The second reaction mechanism employed here is taken from that of Miller and Melius.²⁸ This later reaction mechanism (from here on referred to as the near-sooting mechanism) is an extension of that described in Refs. 26 and 27, in that it includes additional species and reaction pathways that lead to the formation of benzene. It is believed that the formation of cyclic aromatics such as benzene is an important step in the synthesis of polyaromatic hydrocarbons (PAH) and the formation of soot.²⁹ Basically, this near-sooting mechanism is similar to that proposed by others,^{30,31} in that it contains three general components: (i) the pyrolysis of acetylene to produce smaller hydrocarbon fragments some of which recombine to produce ethylene, (ii) the formation of larger hydrocarbons (containing three and four carbon members) through bimolecular recombination, and (iii) the reactions of these larger hydrocarbons with smaller ones (such as acetylene) to complete a six membered ring (typically benzene). The near-sooting mechanism provides additional pathways towards benzene formation not provided by the nonsooting mechanism for acetylene, ethylene, and smaller hydrocarbon fragments

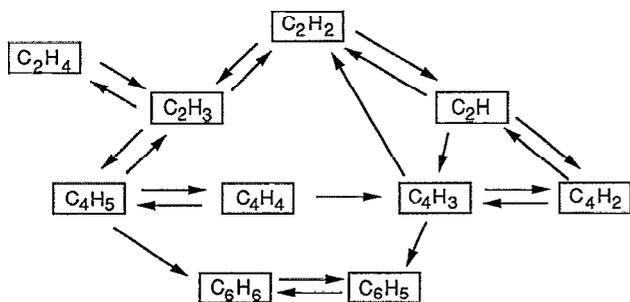
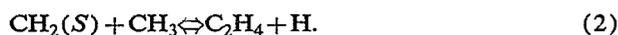
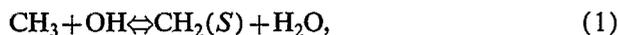


FIG. 2. Schematic of benzene forming pathways.

which would otherwise participate in diamond growth. Briefly, it includes some additional methyl radical formation and consumption reactions, given here as



Here, $\text{CH}_2(S)$ denotes the singlet state of CH_2 . A sensitivity analysis for the conditions of interest indicates that both of these elementary reactions consume the methyl radical (chemical shift is towards the right). More importantly, we find that reaction (2) dominates near the substrate surface. Ethylene (C_2H_4) is then readily converted to C_2H_3 by H atom abstraction (through reactions with H and OH), which is believed to be a very important precursor in the formation of benzene. Figure 2 displays a schematic diagram taken from Ref. 31, which illustrates this and alternate competing pathways towards benzene formation. Although an alternative pathway towards benzene formation is via the recombination reactions, $\text{C}_2\text{H}_2 + \text{C}_2\text{H} \Rightarrow \text{C}_4\text{H}_3$ and $\text{C}_4\text{H}_3 + \text{C}_2\text{H}_2 \Rightarrow \text{C}_6\text{H}_5$, we find that this pathway is not important under the conditions of interest here. Also, it has been shown³¹ that the formation of C_2H_3 is more likely a result of H abstraction from C_2H_4 rather than H addition to C_2H_2 . Based on our analysis of the near-sooting mechanism, we see diamond growth proceeding as a result of a balance between the oxidative pyrolysis of acetylene to form reactive hydrocarbons such as CH_3 and the recombination reactions to form precursors to benzene formation (which in turn will lead to soot formation at sufficiently high equivalence ratios). This balance should define an oxygen to acetylene volumetric flow ratio R where CH_3 radicals are at an optimum concentration, and hence where diamond growth is a maximum. We note here that Cooper and Yarbrough¹⁶ have found that low pressure flame synthesis of diamond is optimized at approximately $R=1.3$. We also note here that the unimolecular decomposition reactions and their associated recombination reactions exhibit a significant dependence on pressure. Both mechanisms (nonsooting and near-sooting) include pressure fall-off expressions^{23,32} for all unimolecular decomposition elementary reactions. In all, the nonsooting mechanism includes 34 species and 149 elementary reactions whereas the near-sooting mechanism employs a total of 50 species and 221 elementary reactions. We emphasize that neither

mechanisms are intended to model soot formation, but rather the chemistry leading up to larger hydrocarbon formation (i.e., C_6H_6), which may strongly influence the chemistry in flame synthesis of diamond.

C. Surface mechanism

To describe the growth of diamond, we employ a heterogeneous mechanism (and concomitant reaction rate coefficients) first proposed by Harris.³³ This mechanism takes bicyclononane (BCN), a nine-carbon species, as a model compound representing the fully hydrogenated, unreconstructed (100) diamond surface. It involves H_2 , H, and CH_3 as active gas-phase species which participate through a sequence of 12 elementary reactions that lead to the continuous incorporation of sp^3 hybridized carbon into the growth surface. Although the H-terminated unreconstructed (100) surface is believed to be thermodynamically unstable (the surface is likely to undergo a 2×1 dimer reconstruction³⁴), it is worth noting that the mechanism nonetheless has been found to predict the observed growth rates in such diverse CVD environments such as hot filaments,²¹ dc arcjets,³⁵ and rf plasma torches.³⁶ We emphasize here however, that we employ the mechanism simply to provide closure to our reactive gas-phase precursors (i.e., H, H_2 , and CH_3), and that the same general conclusions arrived at below are anticipated for other mechanisms that employ methyl radicals as the growth precursors. For the computational results presented here, we have assumed that all species other than H, H_2 , and CH_3 do not react with sites on the growing diamond surface. Calculations that include alternative mechanisms and growth on other crystallographic planes are presently underway.

It is noteworthy that a further consequence of growing diamond under conditions where sooting tendencies are strong is the possible incorporation of nondiamond carbon in the deposits. Glumac and Goodwin¹⁷ have shown that significant nondiamond carbon is deposited at conditions where $R < 1.3$. Growth of nondiamond carbon is not included in our heterogeneous mechanism.

D. Simulation conditions

The conditions employed in our calculation were selected to simulate conditions that are similar to (but not exactly) that employed by Cooper and Yarbrough.¹⁶ The primary difference is that we have added 66% argon by volume as diluent to our O_2 - C_2H_2 mixture, as we find that the gas phase reaction mechanisms employed have not been adequately tested without substantial dilution. We take the mean mass velocity of the mixture at the outlet of the burner surface to be 200–300 cm/s, the pressure is 50 Torr, and the burner surface and substrate temperatures are 300 and 1200 K, respectively. The reactant mixture is characterized by 66% argon (by initial mole fraction) in oxygen and acetylene. The oxygen to acetylene volumetric flow ratio is specified as R .

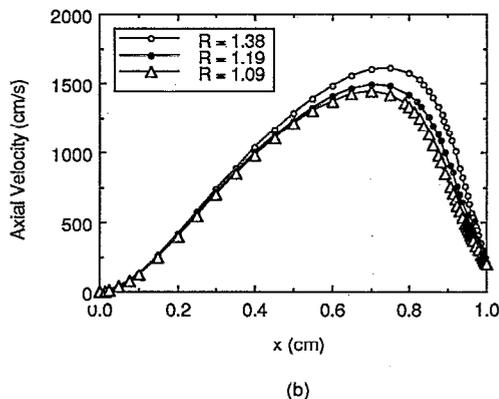
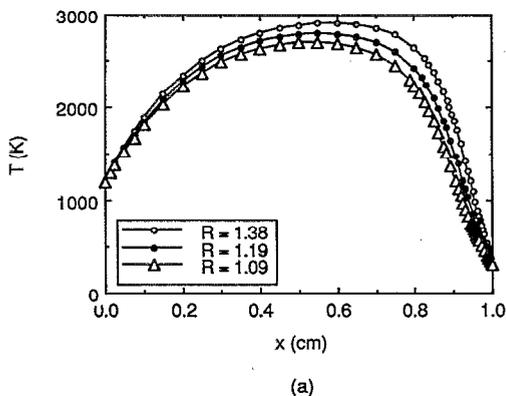


FIG. 3. Spatial variation of (a) the flame temperature and (b) axial velocity between the burner (located at $x=L=1$ cm) and the substrate ($x=0$).

III. RESULTS AND DISCUSSIONS

The spatial variation in temperature and axial velocity for a range of flow ratios R , as predicted by the model when using the near-sooting mechanism, is illustrated in Fig. 3. There is initially a rapid acceleration of the flow, coincident with the rise in temperature associated with the energy release from the primary flame. We note also that the flame temperature throughout the flow field decreases with decreasing R (as the mixture becomes more fuel rich) over the range of stoichiometries investigated.

The predicted spatial variations of H-atom and CH_3 -radical mole fractions and their sensitivity to volumetric flow ratios R are shown in Fig. 4. As expected, there is a rapid rise in radical species mole fraction concomitant with the rapid heat release in the primary flame. As the flame gradually cools to 1200 K due to the presence of the temperature controlled substrate, there is a subsequent drop in both the H-atom and CH_3 -radical mole fractions. We note that the CH_3 mole fraction in the post primary flame is especially sensitive to the value of R for $R > 1.3$. This rapid drop in CH_3 mole fraction with increasing R past values of approximately 1.3 is associated with the oxidative pyrolysis of remaining hydrocarbon fragments in the post flame region. We also note that CH_3 mole fractions in the post flame region "saturate" for values of $R < 1.2$ (in fact, the surface fluxes of both H and CH_3 begin to decrease for

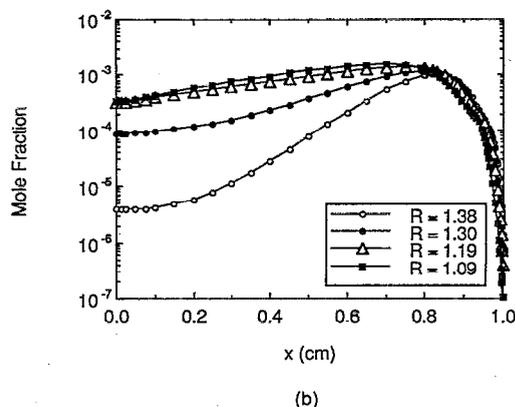
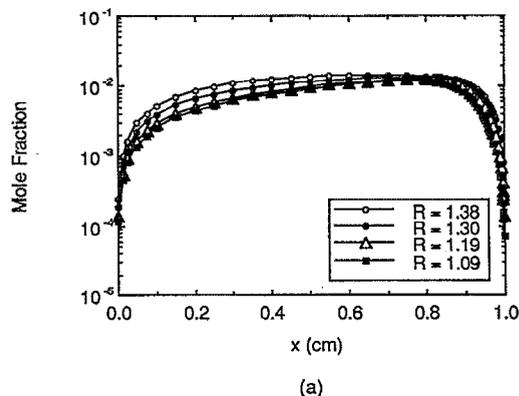
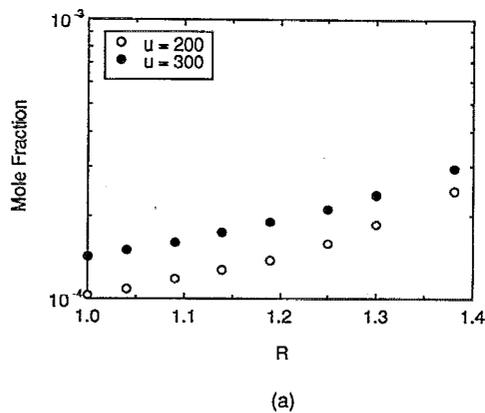


FIG. 4. Spatial variation of (a) H-atom mole fraction and (b) CH_3 radical mole fraction.

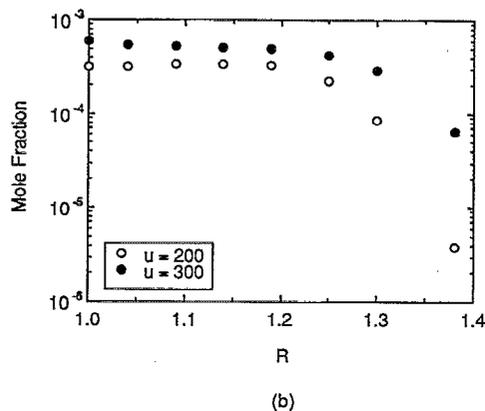
$R < 1.2$). We interpret this as the onset of larger (C_3 and C_4) hydrocarbons, which will be followed by the formation of benzene. This value of R corresponds to an equivalence ratio of approximately 2.1, and it is interesting to note that this is close to the observed sooting point of approximately 2.0 in oxygen-acetylene flames.³⁰ It is also noteworthy that the rapid fall in H mole fraction near the substrate surface is caused primarily by heterogeneous activity (catalytic recombination) and not by volume recombination at these pressures.

Figure 5 shows the variations of both H and CH_3 mole fractions at the surface with respect to R at two different flow velocities. We find that the H-atom surface mole fraction is less sensitive to flow velocity than the methyl radical surface concentration, especially for $R > 1.3$. This suggests that the atomic hydrogen concentration at the surface is reaction rate limited. In contrast, we find that the CH_3 concentration at the surface is influenced by volume reactivity (depletion of CH_3 associated with soot formation) and flow velocity in addition to surface reactivity.

Figure 6 compares the computed diamond growth rates for the nonsooting and near-sooting mechanisms. We first note that for the nonsooting mechanism, the predicted growth rate continues to increase with increasing fuel to oxidizer ratios (decreasing R). This trend is not observed experimentally.^{16,17} In comparison, the computational results with the near-sooting mechanism predicts optimum



(a)



(b)

FIG. 5. Variation of (a) H-atom and (b) CH_3 radical with R for inlet flow velocity of 200 and 300 cm/s.

growth for $R=1.2$. This value is slightly lower than the value of $R=1.3$ observed experimentally. This discrepancy can be accounted for in part by the fact that the computational study includes a significant argon component to the flow. Argon (as well as other inert diluents) is known to reduce the sooting tendencies of fuels. The addition of argon to the flow tends to shift the peak in the growth rate towards the lower values of R . It is interesting to note that the predicted maximum growth rates of $0.2 \mu\text{m/h}$ are com-

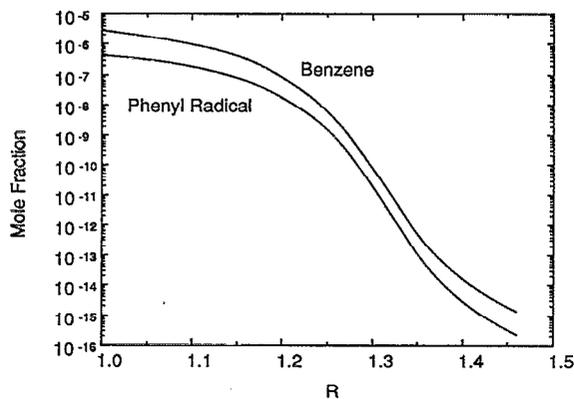


FIG. 6. Variation in the computed diamond growth rates with R for both the nonsooting and near-sooting mechanism.

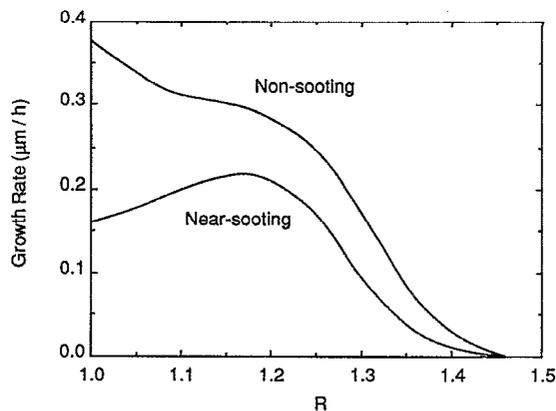


FIG. 7. Variation of benzene (C_6H_6) and phenyl radical (C_6H_5) gas-phase concentrations near the substrate with R for an inlet flow velocity of 200 cm/s.

parable to those measured experimentally.¹⁷ Furthermore, we find that the leveling off (and subsequent drop) in growth rate for $R < 1.3$ is consistent with the production of benzene (C_6H_6) and phenyl radicals (C_6H_5) near the surface (Fig. 7). Both mechanisms predict a substantial drop in growth rate for $R > 1.2$, due mainly to the oxidative pyrolysis of acetylene and smaller hydrocarbons.

The spatial variations of other major carbon-carrying species mole fractions for $R=1.2$ and flow velocity of 200 cm/s are shown in Fig. 8. Species other than C_2H_2 , CH_4 , and CH_3 are not present in sufficient quantity at the substrate to account for observed growth rates. It is evident from Fig. 8 that C_2H_2 is the dominant hydrocarbon specie in the flow and to not include it as a potential precursor is somewhat precarious. We note however that recent growth experiments performed in a microbalance reactor³⁷ strongly support CH_3 as opposed to C_2H_2 as the growth precursor. Whether CH_3 or C_2H_2 is the dominant precursor is the subject of ongoing debate.

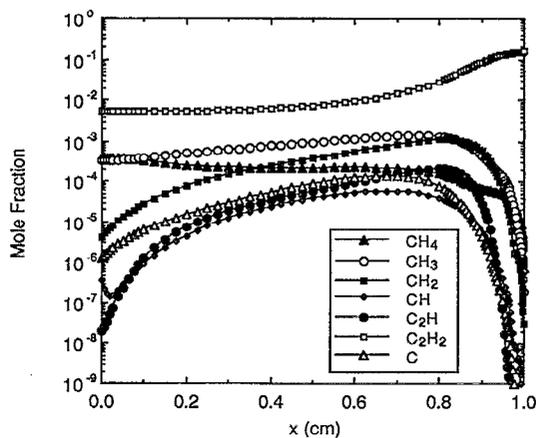


FIG. 8. Spatial variation of major and minor carbon-carrying species with $R=1.2$ and an inlet flow velocity of 200 cm/s.

IV. CONCLUSIONS

In the present investigation we have demonstrated, through numerical simulation, that the level of methyl radicals present in the post primary flame region of fuel rich oxygen acetylene flames is established as a balance between oxidation and cyclization. Under conditions for diamond growth described here, we have found that optimum growth rates are predicted for $R=1.2$, and predicted only if one accounts for the formation of cyclic aromatics. We have also demonstrated that the surface flux of the suspected precursor to diamond growth (CH_3) is significantly increased by increasing the inlet mixture velocity. We therefore conclude that increasing the flow velocity (or volumetric flow rate), to the extent that we are able to stabilize the flame on the substrate surface, is expected to result in significant increases in diamond growth rates (even at these low pressures). Simulation of diamond synthesis in low pressure flames at higher flow velocities (greater flame stretch) and for alternate growth mechanisms are presently underway.

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- ¹K. A. Spear, *J. Am. Ceram. Soc.* **72**, 171 (1980).
- ²J. C. Angus and C. C. Hayman, *Science* **241**, 913 (1988).
- ³W. A. Yarbrough and R. Messier, *Science* **247**, 688 (1988).
- ⁴M. A. Cappelli and P. H. Paul, *J. Appl. Phys.* **67**, 2602 (1989).
- ⁵F. Akatsuka, Y. Hirose, and K. Komaki, *Jpn. J. Appl. Phys.* **27**, L1600 (1988).
- ⁶Y. Hirose and M. Mitsuzumi, *N. Diamond* **4**, 34 (1988).
- ⁷L. M. Hanssen, W. A. Carrington, J. E. Butler, and K. A. Snail, *Matt. Lett.* **7**, 289 (1988).
- ⁸P. G. Kosky and D. S. McAtee, *Matt. Lett.* **8**, 369 (1989).
- ⁹Y. Tzeng, C. Cutshaw, R. Phillips, T. Srivinyunon, A. Ibrahim, and B. H. Loo, *Appl. Phys. Lett.* **56**, 134 (1990).
- ¹⁰L. M. Hanssen, K. A. Snail, W. A. Carrington, J. E. Butler, S. Kellog, and D. B. Oakes, *Thin Solid Films* **196**, 271 (1991).
- ¹¹R. Komanduri, K. A. Snail, and L. L. Fehrenbacher, *Philos. Mag. Lett.* **62**, 283 (1990).
- ¹²K. A. Snail, J. A. Freitas, C. L. Vold, and L. M. Hanssen, *Proceedings of the 2nd International Symposium on Diamond Materials*, Washington, D.C., May 6-10, 1991.
- ¹³K. A. Snail and C. Craigie, *Appl. Phys. Lett.* **58**, 1875 (1991).
- ¹⁴M. Murayama, S. Kojima, and K. Uchida, *J. Appl. Phys.* **69**, 7924 (1991).
- ¹⁵Y. Tzeng, R. Phillips, C. Cutshaw, T. Srivinyunon, B. H. Loo, and P. Wang, *Appl. Phys. Lett.* **58**, 2645 (1991).
- ¹⁶J. A. Cooper Jr. and W. A. Yarbrough, *SPIE Vol.* **1325**, 41 (1990).
- ¹⁷N. G. Glumac and D. G. Goodwin, *Thin Solid Films* **212**, 122 (1992).
- ¹⁸H. Schlichting, *Boundary Layer Theory*, 6th ed. (McGraw-Hill, New York, 1968).
- ¹⁹R. J. Kee, J. A. Miller, G. H. Evans, and G. Dixon-Lewis, 22nd Symposium (International) on Combustion/The Combustion Institute, Pittsburgh, PA, 1988, p. 1479.
- ²⁰M. E. Coltrin, R. J. Kee, and G. H. Evans, *J. Electrochem. Soc.* **136**, 819 (1989).
- ²¹D. G. Goodwin and G. G. Gavillet, *J. Appl. Phys.* **68**, 6393 (1990).
- ²²R. J. Kee, J. F. Grcar, M. D. Smooke, and J. A. Miller, Sandia Report No. SAND 85-8240, 1985.
- ²³R. J. Kee, F. M. Rupley, and J. A. Miller, Sandia Report No. SAND 89-8009, 1989.
- ²⁴M. E. Coltrin, R. J. Kee, and F. M. Rupley, Sandia Report No. SAND 90-8003, 1990.
- ²⁵R. J. Kee, F. M. Rupley, and J. A. Miller, Sandia Report No. SAND 87-8215B, 1987.
- ²⁶J. A. Miller and C. T. Bowman, *Prog. Energy Combust. Sci.* **15**, 287 (1989).
- ²⁷J. A. Miller, J. V. Volponi, J. L. Durant Jr., J. E. M. Goldsmith, G. A. Fisk, and R. J. Kee, 23rd Symposium (International) on Combustion/The Combustion Institute, Pittsburgh, PA, 1990, P. 187.
- ²⁸J. A. Miller and C. F. Melius, *Combustion and Flame* (to be published, 1992).
- ²⁹M. Frenklach, D. W. Clary, W. C. Gardiner Jr., and S. E. Stein, 20th Symposium (International) on Combustion/The Combustion Institute, Pittsburgh, PA, 1984, p. 887.
- ³⁰K. Brezinsky, H. S. Hura, and I. Glassman, presented at the Symposium on Advances in Soot Chemistry, 194th National Meeting of the American Chemical Society, New Orleans, LA, August 30-September 4, 1987.
- ³¹E. Bastin, J.-L. Delfau, M. Reuillon, C. Vovelle, and J. Warnatz, 22nd Symposium (International) on Combustion/The Combustion Institute, Pittsburgh, PA, 1988, p. 313.
- ³²J. Troe, 15th Symposium (International) on Combustion/The Combustion Institute, Pittsburgh, PA, 1975, p. 667.
- ³³S. J. Harris, *Appl. Phys. Lett.* **56**, 2298 (1990).
- ³⁴B. J. Harrison, E. J. Dawnkaski, D. Srivastava, and D. W. Brenner, *Science* **255**, 835 (1992).
- ³⁵D. G. Goodwin, *Appl. Phys. Lett.* **59**, 277 (1991).
- ³⁶T. G. Owano, D. G. Goodwin, C. H. Kruger, and M. A. Cappelli, *Proceedings of the 2nd International Conference on the New Diamond Science and Technology*, Washington, D.C., September 23-27, 1990, p. 487.
- ³⁷S. J. Harris and A. M. Weiner, *Thin Solid Films* **212**, 201 (1992).