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# Carbon nitride formation in gas-phase reactions of $\text{CH}_4$ , $\text{NH}_3$ and $\text{H}_2$ : an ab initio study

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Received 7 February 2000; in final form 21 February 2000

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## Abstract

Ab initio QCISD(T)/6-311 + (2d,2p) calculations have been carried out for an extensive study of gas-phase reactions among  $\text{CH}_4$ ,  $\text{NH}_3$  and their radicals. Our study shows that stable HCN molecules are readily formed by successive H abstraction reactions. Some of the reactions are strongly exothermic and have negligible energy barriers. In agreement with some recent experiments, our results indicate that H abstraction reactions, which make the chemical vapor deposition of diamond thin films successful, do not favor the formation of carbon nitride thin films. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Since Liu and Cohen [1,2] proposed that  $\beta\text{-C}_3\text{N}_4$  is stable and harder than the presently hardest material, diamond, considerable efforts in search for this material have been made using various experimental [3–8] and theoretical [1,2,9] approaches. However, the experimental evidence for the existence for polycrystalline carbon nitride films is limited [3,7,10,11]. Some of the experimental efforts made so far were directly analogous to the successful diamond growth using chemical vapor deposition (CVD) techniques [12–17]. Lee et al. [14] reported that the N to C concentration ratio in d.c. and r.f. plasma-assisted films is respectively about 0.36 and 0.16, which are very different from the stoichiometric values  $\text{N/C} =$

1.3–2.5 [9]. It has been found that the addition of  $\text{NH}_3$  to the reaction precursors,  $\text{CH}_4$  and  $\text{H}_2$ , of diamond CVD processes did not readily produce carbon nitride films [15–17]. Instead HCN was found to be the dominant species in the chamber. Chemical species such as  $\text{CH}_3\text{NH}_2$ , and  $\text{CH}_2\text{NH}$  were not observed by molecular beam mass spectrometry (MBMS) in the chamber. They attributed this phenomenon to the presumably fast H abstraction reactions from  $\text{CH}_3\text{—NH}_2$  or the dissociation of  $\text{CH}_3\text{—NH}_2$ . This study indicates that  $\text{C}_3\text{N}_4$  cannot readily self-assemble in a CVD process as diamond does from a mixture of hydrocarbons.

Among the extensive theoretical studies, attentions were concentrated mainly on the relative stability, structural and physical properties of different phases of carbon nitrides [18–20]. No effort has been made to analyze the chemical reactions involved in a CVD process for  $\text{C}_3\text{N}_4$  deposition.

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To realize the synthesis of carbon nitride materials by CVD methods, knowledge of the fundamental mechanisms of gas-phase reactions of carbon hydride species with nitrogen hydride species at the molecular level is very useful for improving the deposition of carbon nitride. In this Letter, we report an ab initio study of gas-phase reactions in CVD processes for carbon nitride formation. In particular, we have addressed the following two issues: (1) the energetics of different reaction channels involved in CVD when  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2$  are used as reactants and (2) the main factors which inhibit the formation of carbon nitride in CVD experiments.

## 2. Methodologies and computational details

$\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2$  were chosen as precursors since they are popular reaction sources used in CVD experiments [12–17]. The chosen reactants were limited to neutral species for simplification. This is usually the situation in CVD processes under thermal excitations, such as hot-filament CVD. The geometry of the reactants, transition states and products have been fully optimized with GAUSSIAN-98 [21]. The second-order Møller–Plesset perturbation (MP2) approach is used and a triple-zeta basis added two polarized and two diffuse functions are employed for the stationary points optimization, i.e. MP2/6-311++G\*\*. To obtain accurate electronic energies, single-point calculations were performed using high-level QCISD(T)/6-311++G(2d,2p)//MP2/6-311++G\*\* approach. In QCISD(T) [22] method, a quadratic CI calculation including single and double substitutions with a triples contribution to the energy were considered. For open-shell systems, the unrestricted Hartree–Fock method (UHF) and the  $n$ th order unrestricted Møller–Plesset perturbation theory are usually quite reliable and yield satisfactory energies and optimized structures. Though spin unrestricted wavefunctions are not eigenfunctions of the  $S^2$  operator, the spin contamination, after spin projection, is within acceptable values in this work. In all the present cases, the minimum equilibrium structures and transition states are confirmed by calculating the corresponding frequencies at the MP2/6-311++G(d,p) level. IRC calculations have

been performed to confirm that the transition states are really connected to the reactants and products.

## 3. Results and discussion

### 3.1. Hydrogen abstractions of $\text{NH}_3$ and $\text{CH}_4$

To form carbon nitride films, the C–N bond should be formed at the first step. This may involve the reactive radical species of  $\text{CH}_3$  and  $\text{NH}_2$  produced from the hydrogen abstraction reactions:



where the H atoms are produced from the thermal dissociation of  $\text{H}_2$ . The relative energies of the relevant reactions calculated at the QCISD(T)/6-311++G(2d,2p)//MP2/6-311++G\*\* level are presented in Table 1. The optimized structures of transition states are shown in Fig. 1. The corresponding transition states for reactions (1) and (2) are denoted as TS(1) and TS(2). In TS(1), the N–H bond being broken is elongated by 0.3156 Å, compared to the regular N–H bond in  $\text{NH}_3$ ; in TS(2), the C–H bond being broken is 0.3151 Å longer than that of  $\text{CH}_4$ , where the formed H–H bond length is 0.1209 and 0.1356 Å longer than that of  $\text{H}_2$ . The barrier heights including zero-point energy (ZPE) correction for reaction (1) and (2) are 14.0 and 13.75 kcal/mol, respectively. The reaction heats are 0.87 and –0.78 kcal/mol. For reaction (2), the barrier height obtained in this work agrees well with the experimental one, 11.9 kcal/mol [23], which is more satisfactory than other calculated values of 5.6 and 16.1 kcal/mol [24,25]. The activation barriers and reaction heats indicate that hydrogen abstraction from  $\text{CH}_4$  is relatively easier than that from  $\text{NH}_3$  since the interaction between N and H is normally stronger than that between C and H.

### 3.2. Formation of methylamine ( $\text{CH}_3\text{NH}_2$ )

For the experiments using hot-filament CVD [15,16], the channels of forming methylamine were suggested to be:

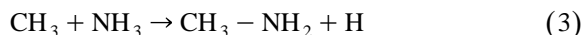


Table 1

Relative energies (kcal/mol, ZPE corrections are included) for different reactions at the QCISD(T)/6-311 + + G(2d, 2p)/MP2/6-311 + + G\* \* level

Reaction	$\Delta H$ (kcal/mol)	Barrier (kcal/mol)
(1) $\text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2$	0.87	14.07 TS(1)
(2) $\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2$	−0.78	13.75 TS(2)
(3) $\text{CH}_3 + \text{NH}_3 \rightarrow \text{CH}_3\text{—NH}_2 + \text{H}$	24.78	33.62 TS(3)
(4) $\text{CH}_4 + \text{NH}_2 \rightarrow \text{CH}_3\text{—NH}_2 + \text{H}$	23.13	74.43 TS(4)
(5) $\text{CH}_4 + \text{NH}_2 \rightarrow \text{CH}_3 + \text{NH}_3$	−1.64	15.37 TS(5)
(6) $\text{CH}_3 + \text{NH}_2 \rightarrow \text{CH}_3\text{—NH}_2$	−77.05	1.53 TS(6)
(7) $\text{CH}_3\text{NH}_2 \rightarrow \text{CH}_2\text{—NH} + \text{H}_2$	22.48	105.17 TS(7)
(8) $\text{CH}_3\text{NH}_2 \rightarrow \text{CH—NH}_2 + \text{H}_2$	58.14	79.86 TS(8)
(9) $\text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{—N} + \text{H}_2$	73.02	113.20 TS(9)
(10) $\text{CH}_3\text{NH}_2 + \text{H} \rightarrow \text{CH}_2\text{NH}_2 + \text{H}_2$	−11.65	8.79 TS(10)
(11) $\text{CH}_3\text{NH}_2 + \text{H} \rightarrow \text{CH}_3\text{NH} + \text{H}_2$	−6.19	10.083 TS(11)
(12) $\text{CH}_2\text{NH}_2 + \text{H} \rightarrow \text{NH}_2\text{CH} + \text{H}_2$	−31.18	−9.47 TS(12)
(13) $\text{CH}_2\text{NH}_2 + \text{H} \rightarrow \text{CH}_2\text{NH} + \text{H}_2$	−66.84	−1.99 TS(13)
(14) $\text{NH}_2\text{CH} + \text{H} \rightarrow \text{CHNH} + \text{H}_2$	−42.73	6.46 TS(14)
(15) $\text{CH}_2\text{NH} + \text{H} \rightarrow \text{CHNH} + \text{H}_2$	−7.47	13.89 TS(15)
(16) $\text{HN—CH} + \text{H} \rightarrow \text{HNC} + \text{H}_2$	−73.60	−7.15 TS(16)
(17) $\text{HN—CH} + \text{H} \rightarrow \text{HCN} + \text{H}_2$	−88.65	18.68 TS(17)

Reaction (4) is favored in methylamine formation since MBMS measurements at different filament temperatures found that the temperature for forming

$\text{NH}_2$  radicals was lower than that of  $\text{CH}_3$  radicals. In the present calculation, the barrier heights for reaction (3) and (4) are respectively 33.62 and 74.43

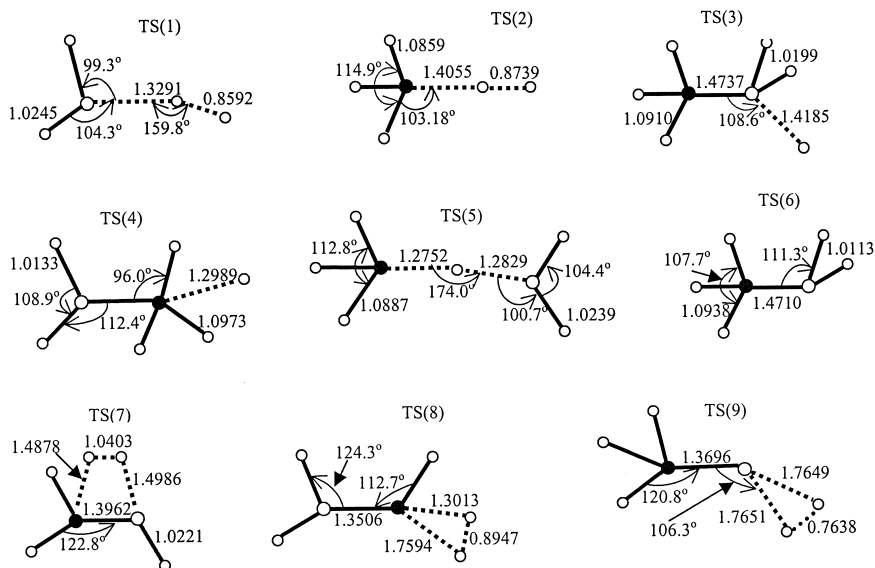


Fig. 1. Schematic transition states structures of TS(1)–TS(9). The geometrical data are calculated at the MP2/6-311 + + G(d,p) level. ●, ○ and ◦ represent C, N and H atoms, respectively. Bond length in Å and bond angle in degree.

kcal/mol; their reaction heats are 24.78 and 23.16 kcal/mol, respectively. The corresponding transition states are shown as TS(3) and TS(4) in Fig. 1. The larger barrier heights and endothermic values imply that the formation of C–N bond is not easy via reactions (3) and (4). Based on the consideration of the activation energy and reaction heat, the reaction (3) was found easier to occur than reaction (4) for methylamine formation, which does not agree with what is suggested by May et al. [15]. This difference may be ascribed to the high temperature factors in the experiment. Another possible reaction in the process of CVD using  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2$  as the reactants is,

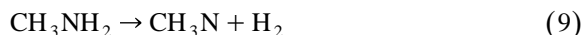
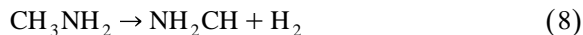


Its transition state TS(5) has a structure with a nearly linear N–H–C fragment; the N–H bond being formed and C–H bond being broken are 1.2829 and 1.2752 Å long, respectively. In reaction (5), our theoretical energy barrier height of 15.37 kcal/mol is close to the value of 15.4 kcal/mol calculated using G2M(RCC, MP2\*) method by Mebel et al. [26], which is much lower than those of reactions (3) and (4). Reaction (5) is an exothermic reaction and the difference between the calculated reaction heat and the experimental enthalpy of this reaction at 298 K [27] is only 0.96 kcal/mol. The combination of barrier height and enthalpy implies that the reaction (5) is much easier to occur than both reactions (3) and (4). In other words, the probability of C–N bond formation is largely reduced due to the presence of reaction (5). However, it has to be noted that the coupling of  $\text{CH}_3$  and  $\text{NH}_2$  radicals can produce  $\text{CH}_3\text{--NH}_2$  directly:



which has a reaction heat of  $\Delta H = -77.05$  kcal/mol. A transition state TS(6) was found for this reaction. However, by checking the imaginary frequency and IRC calculation, we found that TS(6) corresponds to the molecular internal rotation of  $\text{CH}_3$  in  $\text{CH}_3\text{--NH}_2$ . The corresponding barrier height is only 1.53 kcal/mol. The results agree with the fact that “radical coupling reactions are activationless and essentially diffusion controlled” [28]. Nevertheless, May et al. [15] did not observe  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_2\text{NH}$  directly by MBMS. It is very probable

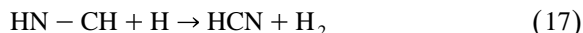
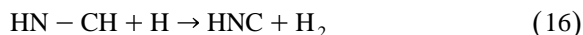
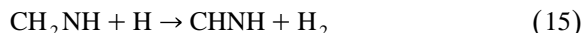
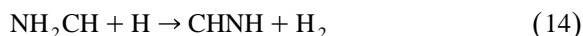
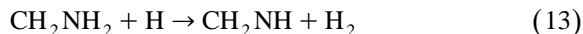
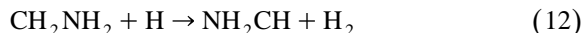
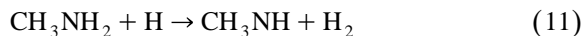
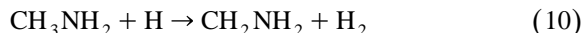
that the methylamine formed ( $\text{CH}_3\text{--NH}_2$ ) either undergoes successive H abstraction reactions (to be discussed in Section 3.3) or dehydrogenates as in the following reactions:



The corresponding barrier heights for these three channels of intra-molecular dehydrogenation are 105.17, 79.86 and 113.20 kcal/mol, while the reaction heats are 22.48, 58.14 and 73.02 kcal/mol, respectively. The respective transition states are TS(7)–TS(9) shown in Fig. 1. It seems from the barrier heights and reaction heats that  $\text{CH}_3\text{NH}_2$  is more difficult to dehydrogenate in an intra-molecular process. However, as we discuss in the following sections, it is relatively easy for the compound to undergo H abstraction reactions.

### 3.3. Successive H abstraction process

If  $\text{CH}_3\text{--NH}_2$  is formed via reactions (3), (4) or (6), in an environment of H atoms, the successive H abstraction processes are:



Reactions (10) and (11), respectively, correspond to the H atoms connected to C and N in  $\text{CH}_3\text{NH}_2$ , being abstracted by free H atoms in the chamber. TS(10) and (11) are their transition states shown in Fig. 2. Our calculated results show that reactions (10) and (11) are exothermic reactions and their respective activation barriers of 8.79 and 10.08 kcal/mol are much lower than those values in intra-molecular dehydrogenation. Similar to H abstraction from  $\text{NH}_3$  and  $\text{CH}_4$ , abstraction of an H atom

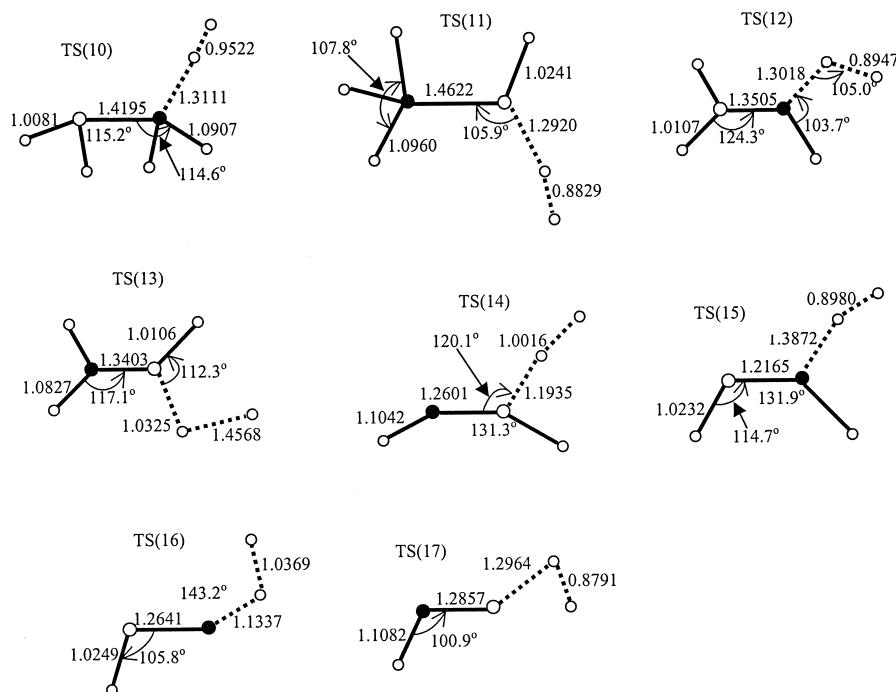


Fig. 2. Schematic transition states structures of TS(10)–TS(17). The geometrical data are calculated at the MP2/6-311 + + G(d,p) level. ●, ○ and ◦ represent C, N and H atoms, respectively. Bond length in Å and bond angle in degree.

connected to C atom of  $\text{CH}_3\text{NH}_2$  is relatively easier than that connected to N of  $\text{CH}_3\text{NH}_2$ . From the activation barriers and reaction heats, it can also be seen that H abstraction reactions (10) and (11) from  $\text{CH}_3\text{NH}_2$  are easier than the formation reactions of  $\text{CH}_3\text{NH}_2$  via reactions (3) and (4).

Reactions (12) and (13) correspond to further H abstractions from  $\text{CH}_2\text{NH}_2$  radicals. The respective transition states are TS(12) and TS(13) as shown in Fig. 2. For both cases of H abstraction from the  $\text{CH}_2$  group or the  $\text{NH}_2$  group, the barriers are negative at QCISD(T)/6-311 + + G(2d,2p)//MP2/6-311 + + G\*\* level, i.e.  $-9.47$  and  $-1.99$  kcal/mol. The reactions are largely exothermic. The negative activation barriers and exothermic reaction heats imply that these processes are easy and need no extra energies. Moreover, the abstraction products,  $\text{NH}_2\text{CH}$  and  $\text{CH}_2\text{NH}$ , are unstable. They will be readily abstracted by H via reactions (14) and (15). The respective transition states are TS(14) and TS(15). These two reactions have low activation barriers, which are  $6.46$  and  $13.89$  kcal/mol, respectively.

The main radical produced in these reactions is  $\text{CHNH}$  which further reacts with H to form HNC and HCN products via reactions (16) and (17). Reaction (16) also has a negative barrier height of  $-7.47$  kcal/mol and is exothermic. A higher activation barrier of  $13.89$  kcal/mol in reaction (17) than that of reaction (16) indicates that it is easier to form HNC than HCN via H abstraction reaction. Both of the reactions are strongly exothermic. The respective transition states TS(16) and TS(17) are shown in Fig. 2. However, HNC is a compound with lower stability and may convert to its isomer HCN which is more stable by  $15.04$  kcal/mol.

From the foregoing analysis, even if  $\text{CH}_3\text{NH}_2$  has been formed via reactions (3) and (4) or (6), it easily undergoes successive H abstractions through reactions (10)–(17) to produce the most stable compound HCN. The results explain and agree well with the experimental observation [15–17] that HCN is the main gas-phase product. It is worthwhile noting here that there were recent successful attempts to make carbon nitride films with plasma CVD using

CH<sub>4</sub>/N<sub>2</sub> gas mixtures instead of CH<sub>4</sub>/NH<sub>3</sub> [29]. In addition, intra-molecular dehydrogenation of CH<sub>3</sub>NH<sub>2</sub> is not favored in comparison with H abstraction reaction according to our calculation.

#### 4. Conclusions

Our calculations based on molecular orbital theory provide crucial information on the deposition of carbon nitride solid films using CH<sub>4</sub>, NH<sub>3</sub> and H<sub>2</sub> as reaction precursors under usual CVD conditions. The successive H abstractions from CH<sub>3</sub>–NH<sub>2</sub> are more favorable than its formation and its intra-dehydrogenation. Some of the H abstraction reactions are strongly exothermic and with negligible energy barriers indicating that it is easy to form stable HCN rather than deposition of carbon nitride due to successive H abstractions. As a result, HCN is the main product in a CVD reaction chamber and deposition of carbon nitride is inhibited.

#### Acknowledgements

The authors are thankful for the financial support from the Strategic Research Grant (No. 7000785) of the City University of Hong Kong.

#### References

- [1] A.Y. Liu, M.L. Cohen, *Science* 245 (1989) 841.
- [2] A.Y. Liu, M.L. Cohen, *Phys. Rev. B* 41 (1990) 10727.
- [3] C. Niu, Y.Z. Lu, C.M. Lieber, *Science* 261 (1993) 334.
- [4] L. Maya, D.R. Cole, E.W. Hagaman, *J. Am. Ceram. Soc.* 7 (1991) 1686.
- [5] J. Martin-Gil, F.J. Martin-Gil, M. Sarikaya, M. Qian, M.J. Yacamán, A. Rubio, *J. Appl. Phys.* 81 (1997) 2555.
- [6] L.P. Guo, Y. Chen, E.G. Wang, L. Li, Z.X. Zhao, *Chem. Phys. Lett.* 268 (1997) 26.
- [7] K.M. Yu, M.L. Cohen, E.E. Haller, W.L. Hansen, A.Y. Liu, I.C. Wu, *Phys. Rev. B* 49 (1994) 5034.
- [8] D. Marton, K.J. Boyd, A.H. Al-Bayati, S.S. Todorov, J.W. Rabalais, *Phys. Rev. Lett.* 73 (1994) 118.
- [9] A.Y. Liu, R.M. Wentzcovitch, *Phys. Rev. B* 50 (1994) 10362.
- [10] Z.M. Ren, Y.C. Du, Y. Qiu, J.D. Wu, Z.F. Ying, X.X. Xiong, F.M. Li, *Phys. Rev. B* 54 (1995) 5274.
- [11] O. Matsumoto, T. Kotaki, H. Shikano, K. Takemura, S. Tanaka, *J. Electrochem. Soc.* 41 (1994) 116.
- [12] X. Jiang, C.P. Klages, *Diamond. Rel. Mater.* 2 (1993) 1112.
- [13] Y.F. Zhang, Z.H. Zhou, H.L. Li, *Appl. Phys. Lett.* 68 (1996) 634.
- [14] S.T. Lee, H.K. Woo, Y.F. Zhang, C.S. Lee, Y.W. Lam, K.W. Wong, *Diamond Relat. Mater.* 6 (1997) 635.
- [15] P.W. May, P.R. Burridge, C.A. Rego, R.S. Tsang, M.N.R. Ashfold, K.N. Rosser, R.E. Tanner, D. Cherns, R. Vincent, *Diamond Relat. Mater.* 5 (1996) 354.
- [16] R.S. Tsang, P.W. May, M.N.R. Ashfold, K.N. Rosser, C.A. Rego, *Diamond Relat. Mater.* 6 (1997) 247.
- [17] S.M. Leeds, P.W. May, M.N.R. Ashfold, K.N. Rosser, *Diamond Relat. Mater.* 8 (1999) 226.
- [18] J. Ortega, O.F. Sankey, *Phys. Rev. B* 51 (1995) 2624.
- [19] D.M. Teter, R.J. Hemley, *Science* 271 (1996) 53.
- [20] J.E. Lowther, *Phys. Rev. B* 57 (1998) 5724.
- [21] M.J. Frisch et al., *GAUSSIAN 98*, Gaussian, Pittsburgh, PA, 1998.
- [22] J.A. Pople, M. Head-Gordon, K. Raghavachari, *J. Chem. Phys.* 87 (1987) 5968.
- [23] R.W. Shaw, *J. Phys. Chem. Ref. Data* 7 (1978) 1179, and numerous references therein.
- [24] P. Botschwina, W. Meyer, *Chem. Phys.* 20 (1977) 43.
- [25] K. Niblaeus, B.O. Roos, P.E.M. Siegbahn, *Chem. Phys.* 26 (1977) 59.
- [26] A.M. Mebel, M.C. Lin, *J. Phys. Chem. A* 103 (1999) 2088.
- [27] R.J. Kee, F.M. Rupley, J.A. Miller, Sandia Laboratories Report, SAND89-8009B, 1993.
- [28] N.L. Bauld, *Radicals, Ion Radicals, and Triplets: The Spin-Bearing Intermediates of Organic Chemistry*, Wiley–VCH, 1997.
- [29] Y.S. Gu, Y.P. Zhang, Z.J. Duan, X.R. Chang, Z.Z. Tian, N.X. Chen, C. Dong, D.X. Shi, X.F. Zhang, L. Yuan, *J. Mater. Sci.* 34 (1999) 3117.