Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplement 2: Reaction energy profiles

All energy profiles are calculated with MP2/aug–cc–pVTZ, unless stated otherwise. Zero point energy and basis set superposition error corrections are not included in shown results.

1 $\mathbf{SiH_4 + NH_3 \longrightarrow SiH_3NH_2 + H_2}$

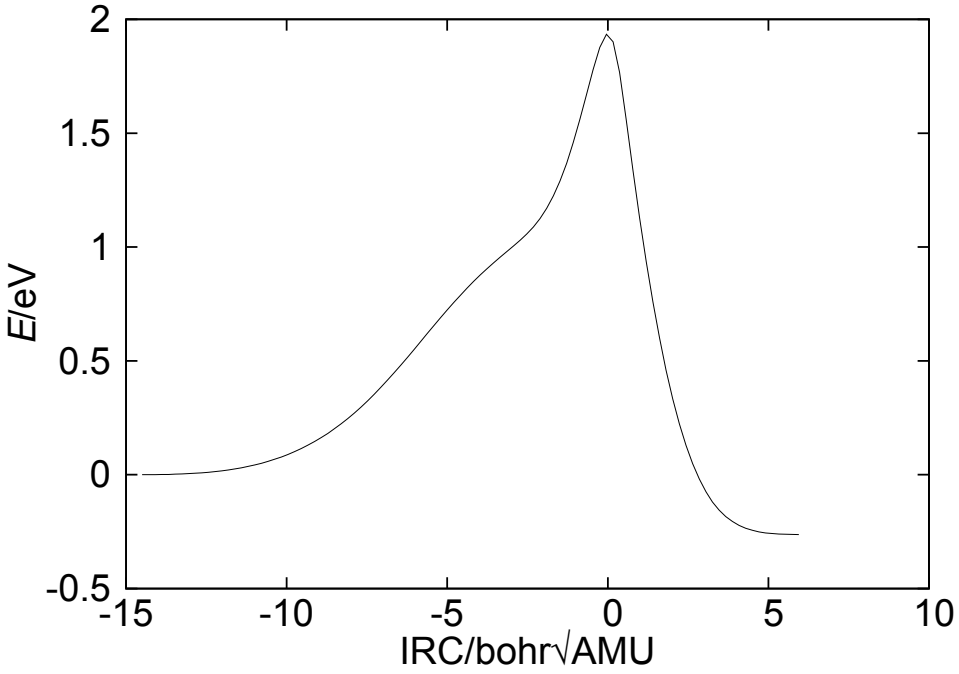

Figure 1

2 $\mathbf{NH_3 + SiH_3NH_2 \longrightarrow (NH_2)_2SiH_2 + H_2}$

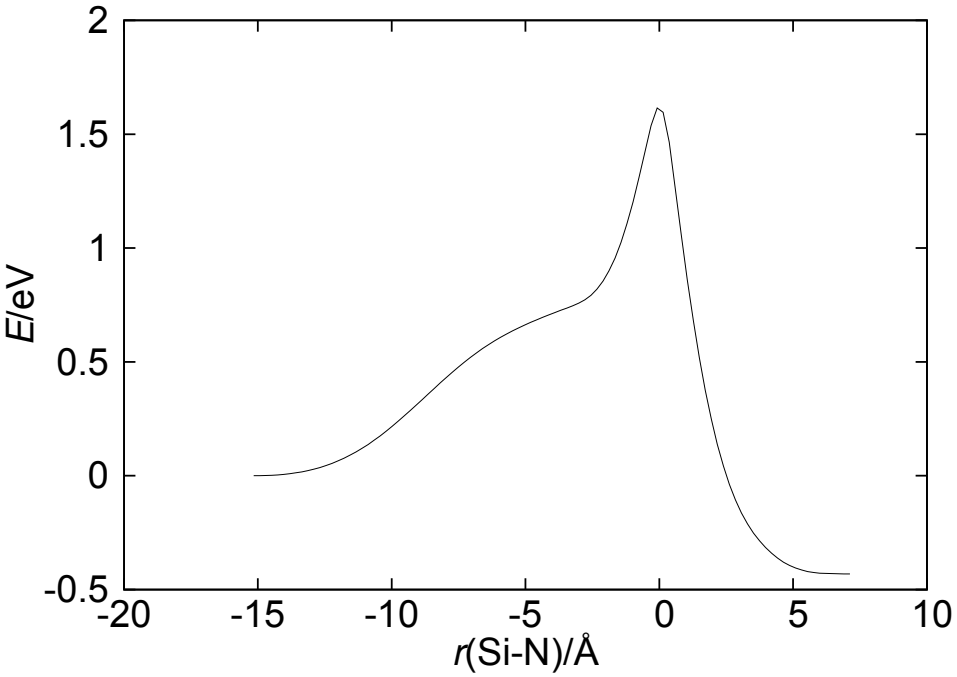

Figure 2

3 $\mathbf{NH_3 + (NH_2)_2SiH_2 \longrightarrow (NH_2)_3SiH + H_2}$

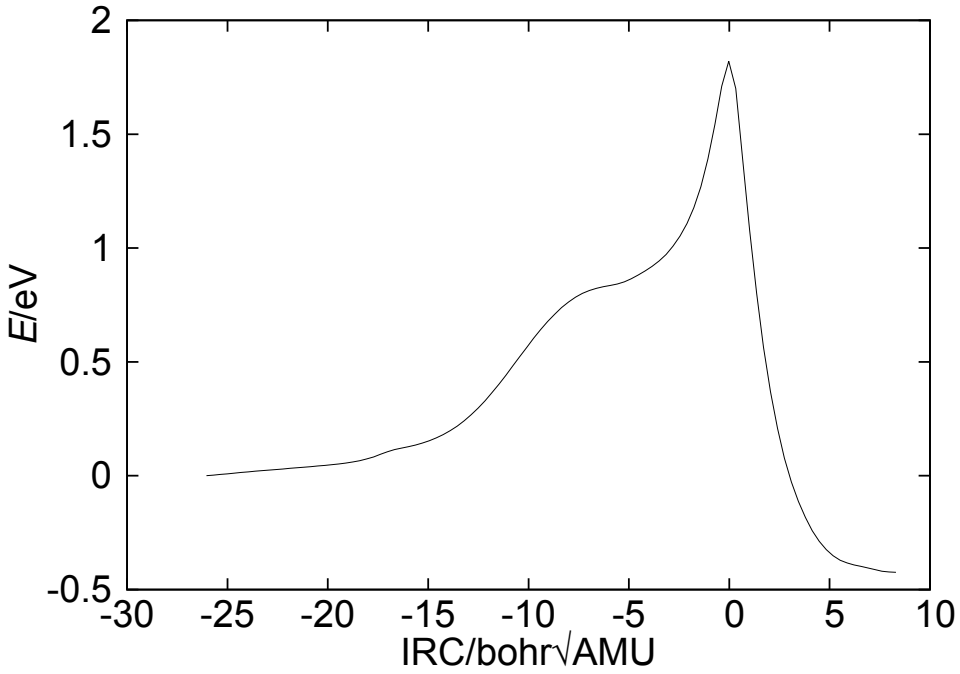

Figure 3

4 $\mathbf{NH_3 + (NH_2)_3SiH \longrightarrow Si(NH_2)_4 + H_2}$

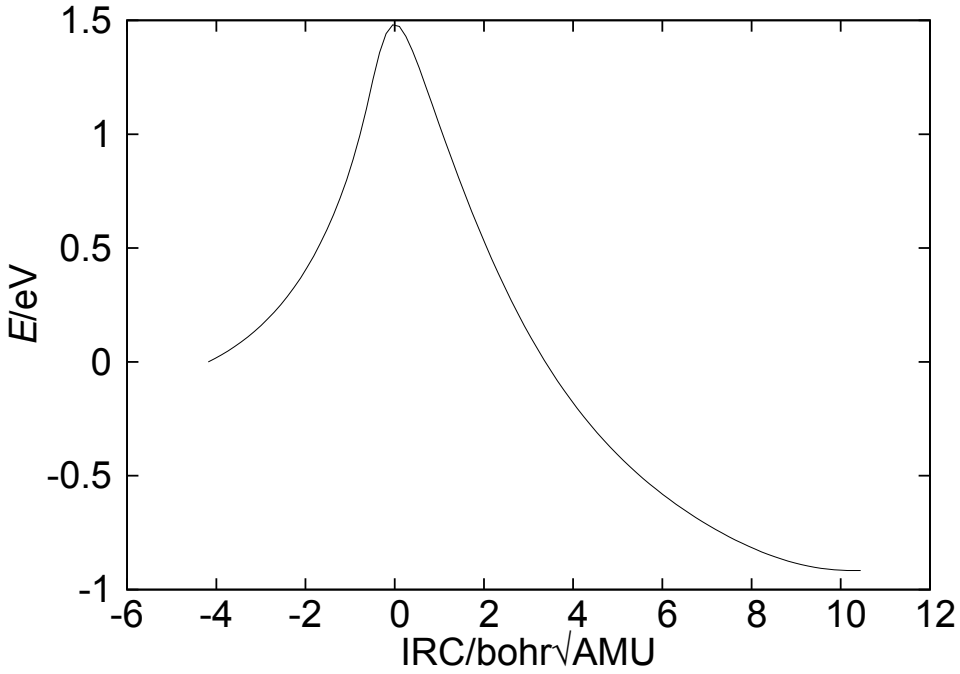

Figure 4

5 $\mathbf{SiH_3NH_2 + SiH_4 \longrightarrow (SiH_3)_2NH + H_2}$

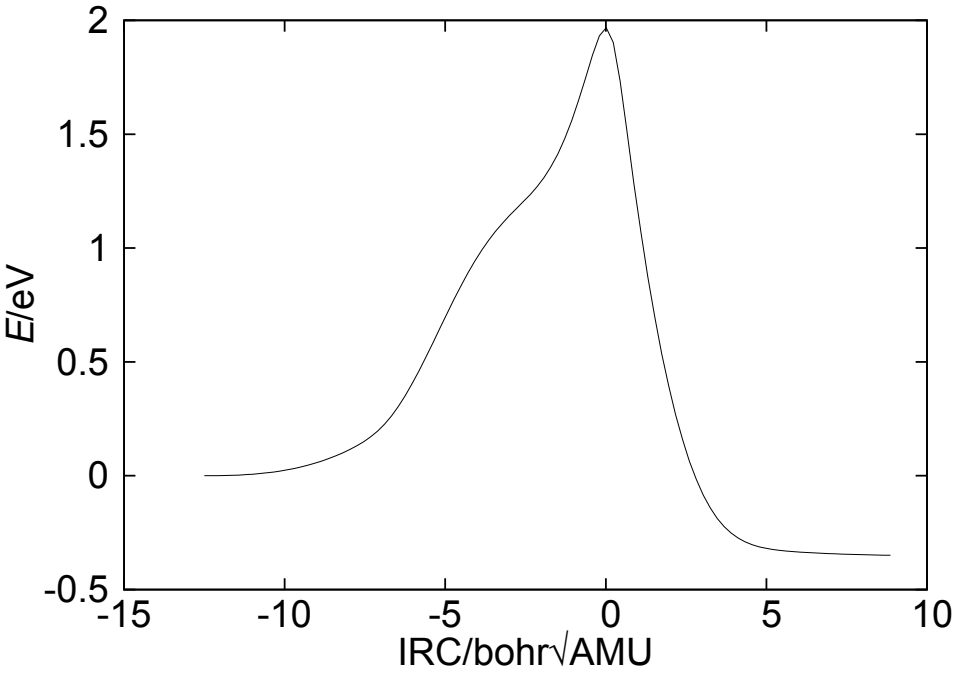

Figure 5

6 $(SiH_3)_2NH + SiH_4 \longrightarrow (SiH_3)_3N + H_2$

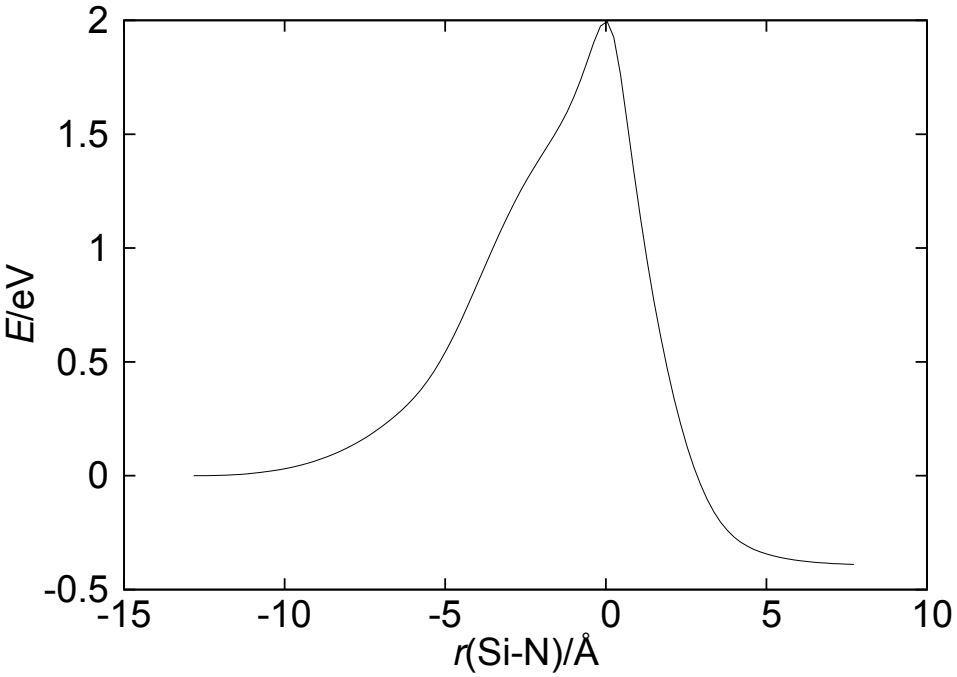

Figure 6

7 $\mathbf{SiH_3NH_2 + (NH_2)_3SiH \longrightarrow SiH_3NHSi(NH_2)_3 + H_2}$

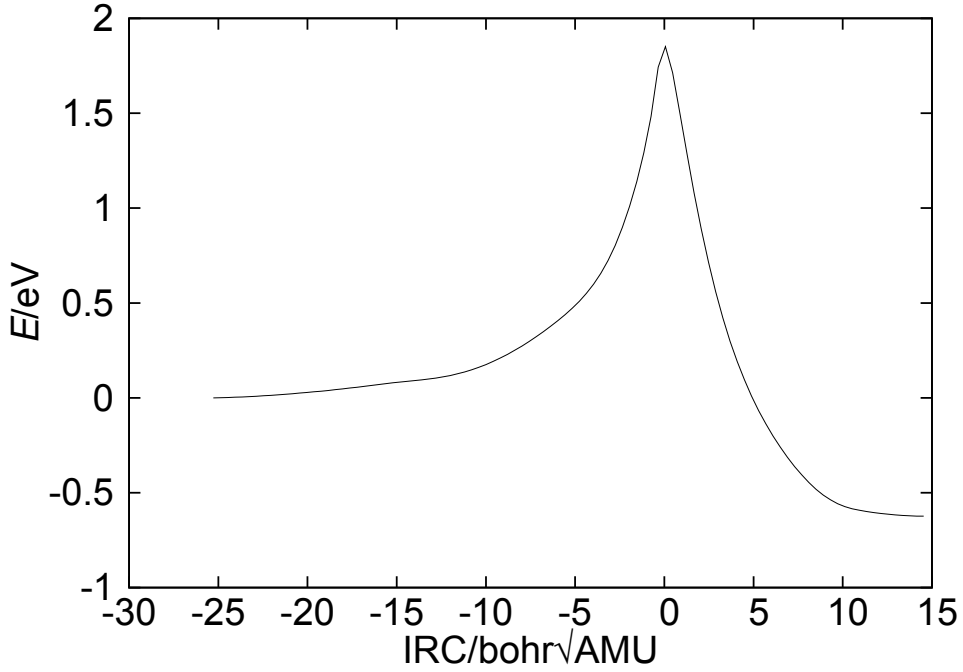

Figure 7

8 $\mathbf{SiH_3NH_2 \longrightarrow SiHNH_2 + H_2}$

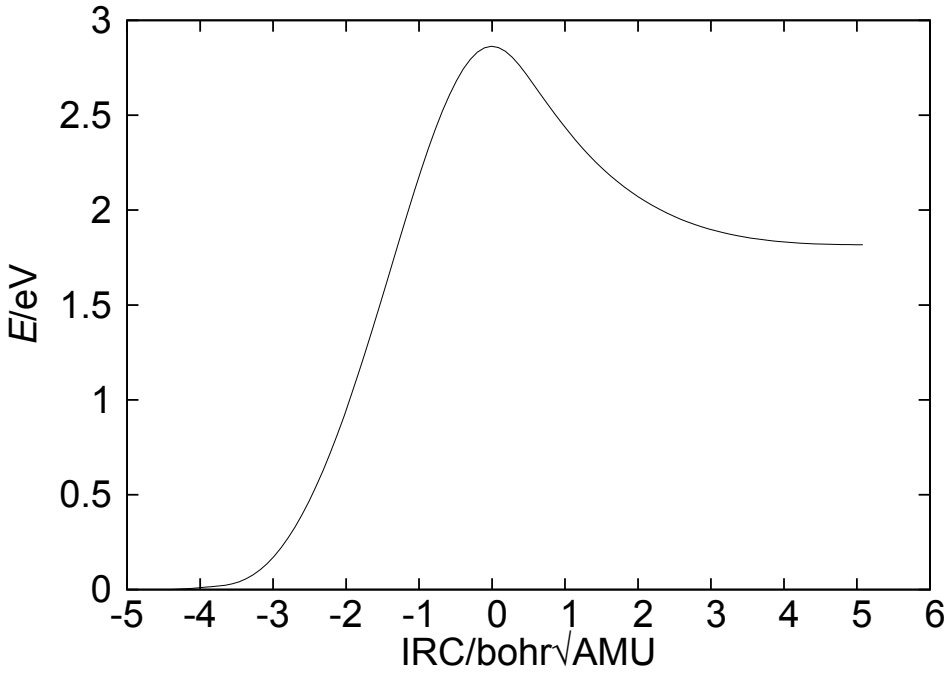

Figure 8

9 $(NH_2)_2SiH_2 \longrightarrow (NH_2)_2Si + H_2$

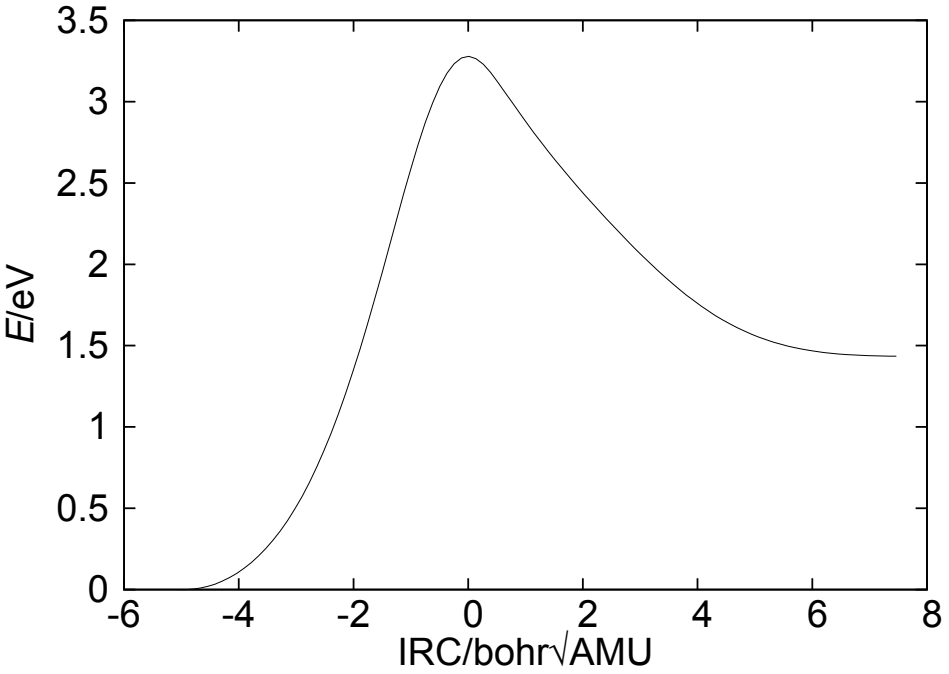

Figure 9

10 $\mathbf{NH_2SiH_3 \longrightarrow SiH_3^{\cdot} + NH_2^{\cdot}}$

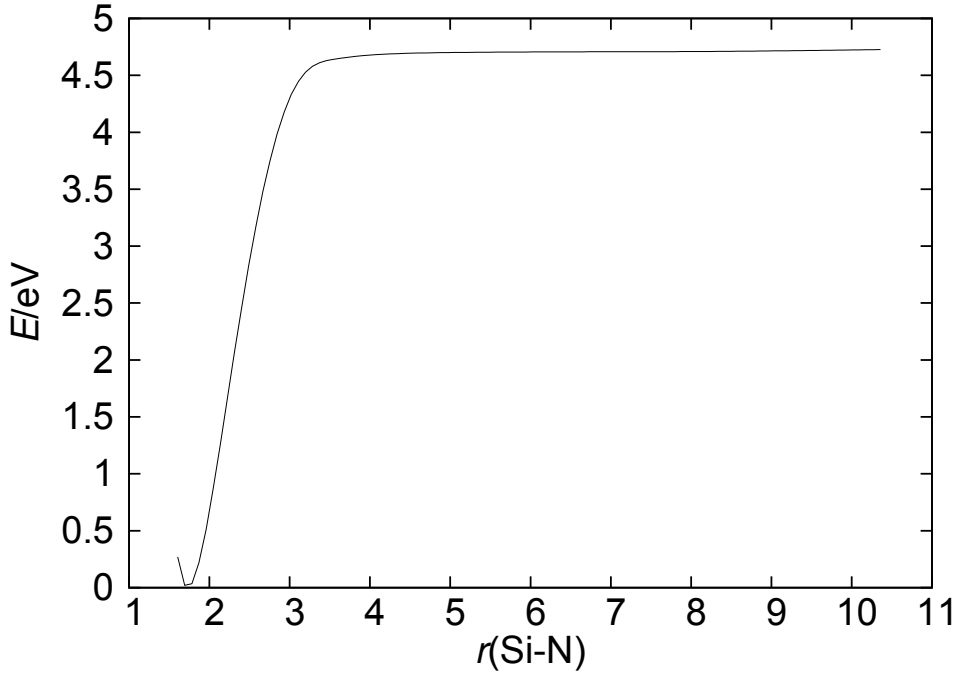

Figure 10: Energies are calculated with CASPT2/aug–cc–PVTZ with the active space: (10,10).

11 $(NH_2)_2SiH_2 \longrightarrow NH_2SiH_2^{\cdot} + NH_2^{\cdot}$

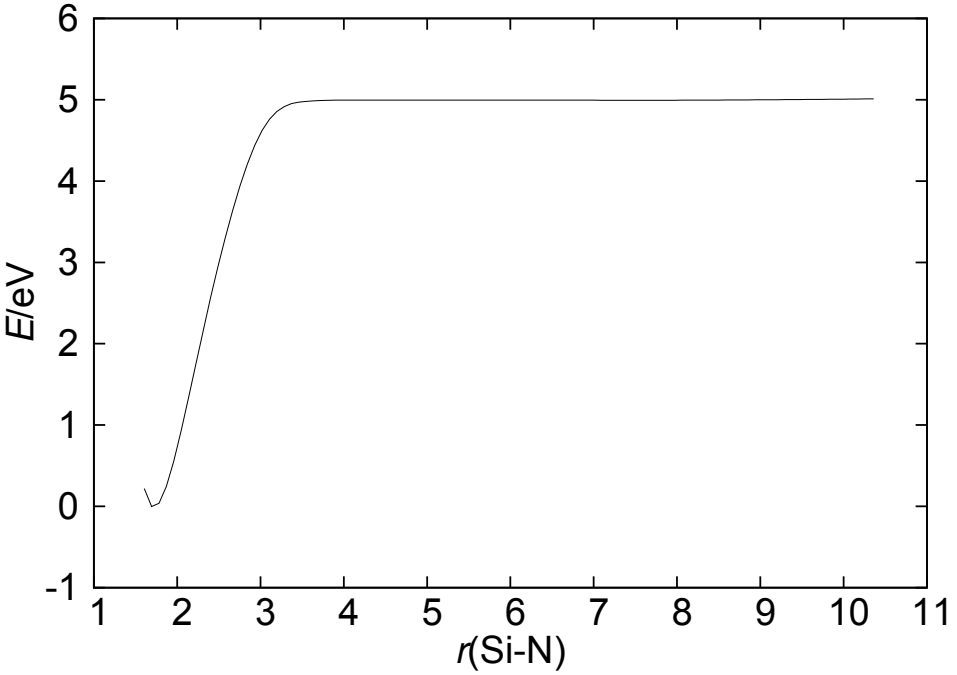

Figure 11: Energies are calculated with CASPT2/aug–cc–PVTZ with the active space: (10,10).

12 $(NH_2)_3SiH \rightarrow (NH_2)_2SiH^{\cdot} + NH_2^{\cdot}$

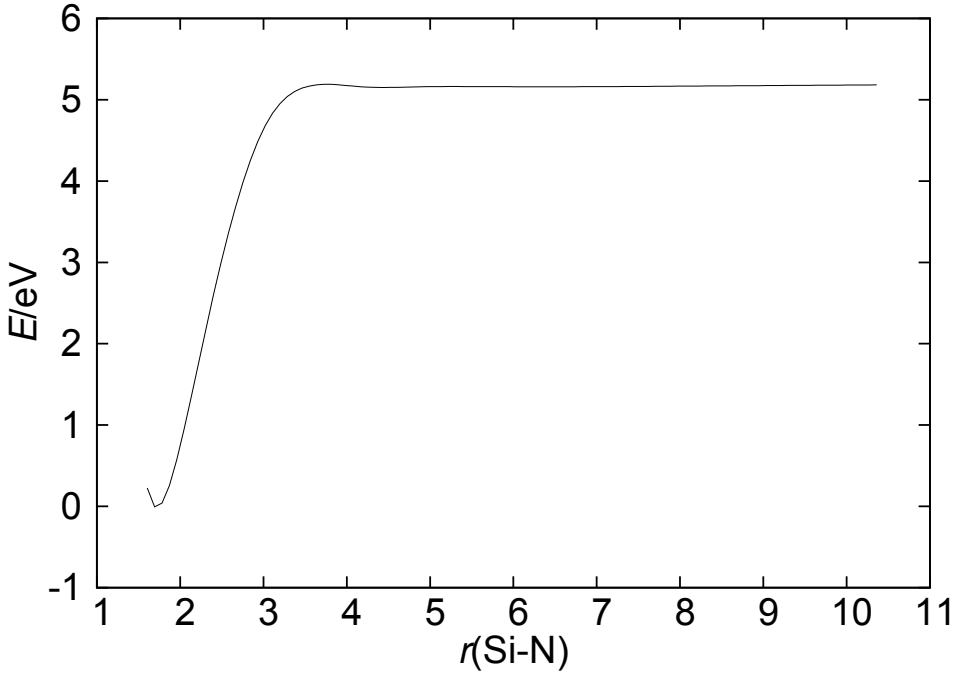

Figure 12: Energies are calculated with CASPT2/aug–cc–PVTZ with the active space: (10,10).

13 $(NH_2)_4Si \longrightarrow (NH_2)_3Si^{\cdot} + NH_2^{\cdot}$

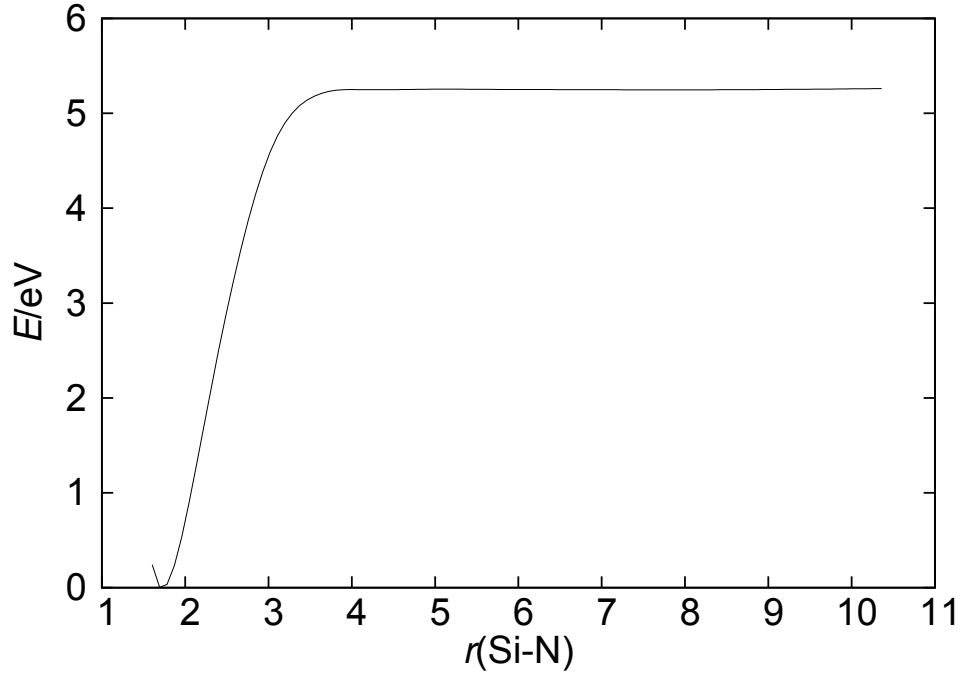

Figure 13: Energies are calculated with CASPT2/aug–cc–PVTZ with the active space: (10,10).

14 $(SiH_3)_2NH \longrightarrow SiH_3NH^{\cdot} + SiH_3^{\cdot}$

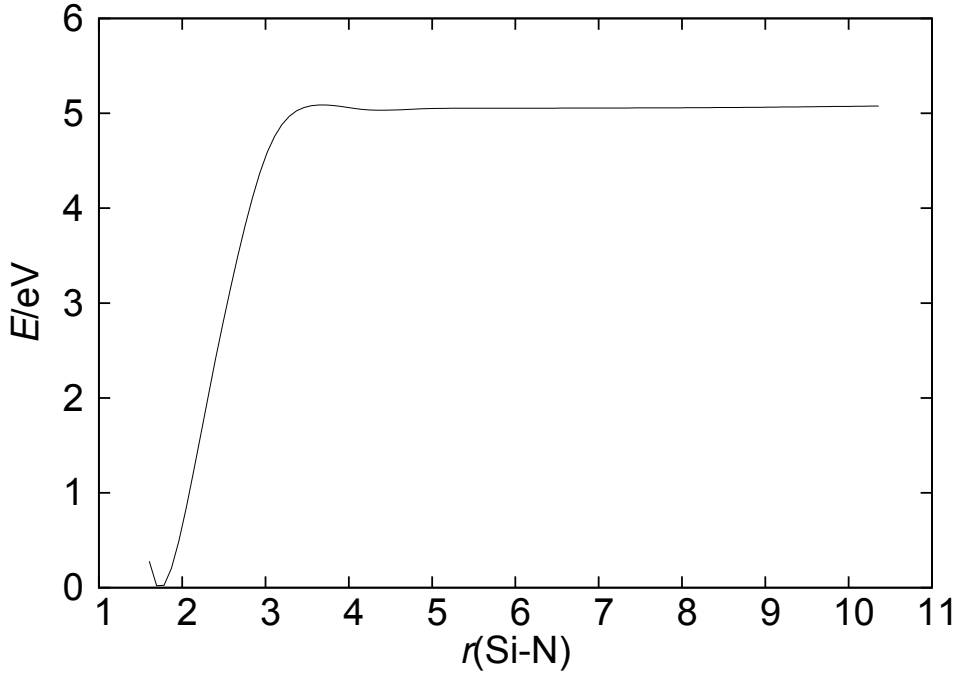

Figure 14: Energies are calculated with CASPT2/aug–cc–PVTZ with the active space: (10,10).

15 $(SiH_3)_3N \longrightarrow (SiH_3)_2N^{\cdot} + SiH_3^{\cdot}$

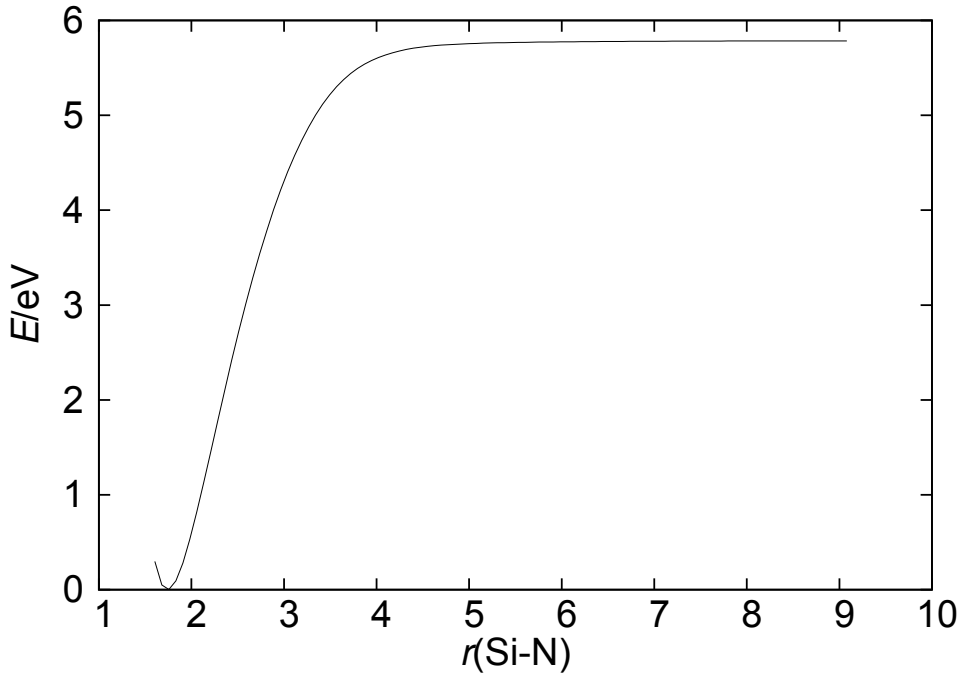

Figure 15: Energies are calculated with CASPT2/aug–cc–PVTZ with the active space: (10,10).

16 $\mathbf{NH_3 + SiH_3^{\cdot} \longrightarrow NH_3SiH_3^{\cdot}}$

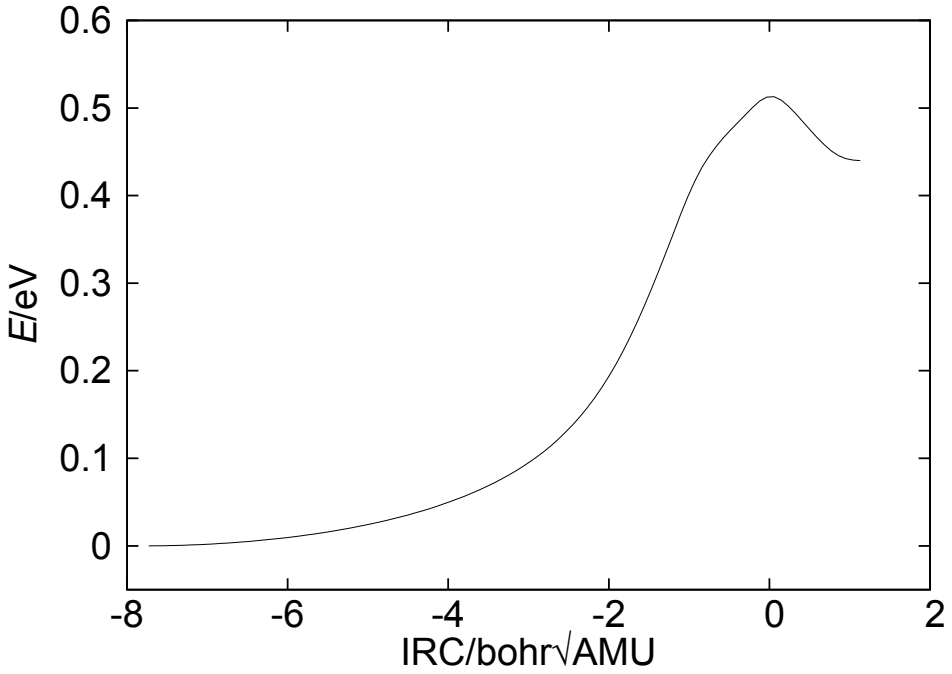

Figure 16

17 $\mathbf{NH_2SiH_2^{\cdot} + NH_3 \longrightarrow NH_2SiH_2NH_3^{\cdot}}$

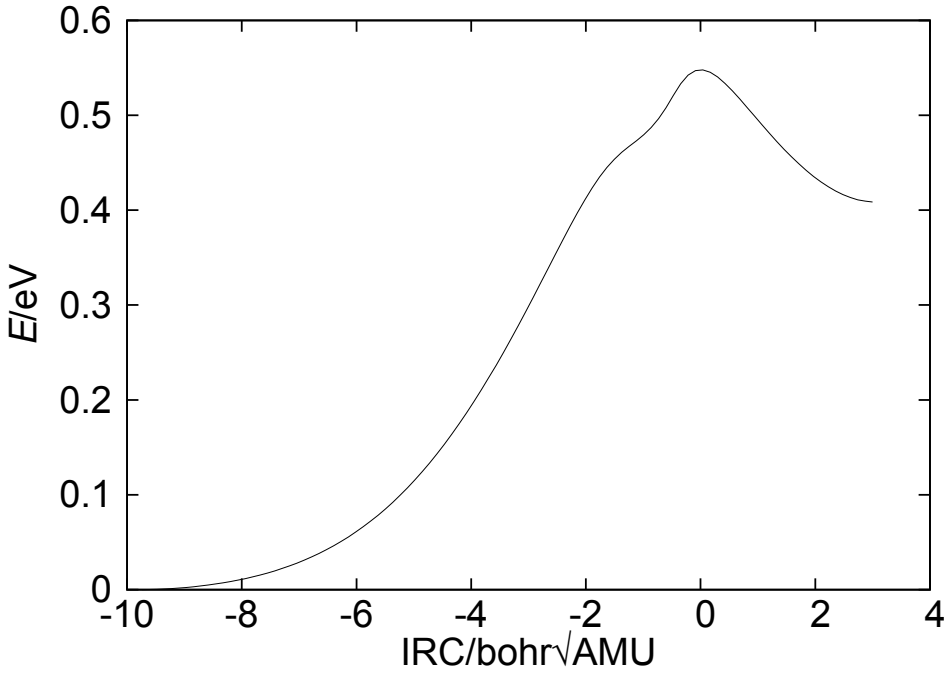

Figure 17

18 $(NH_2)_2SiH^{\cdot} + NH_3 \longrightarrow (NH_2)_2SiHNH_3^{\cdot}$

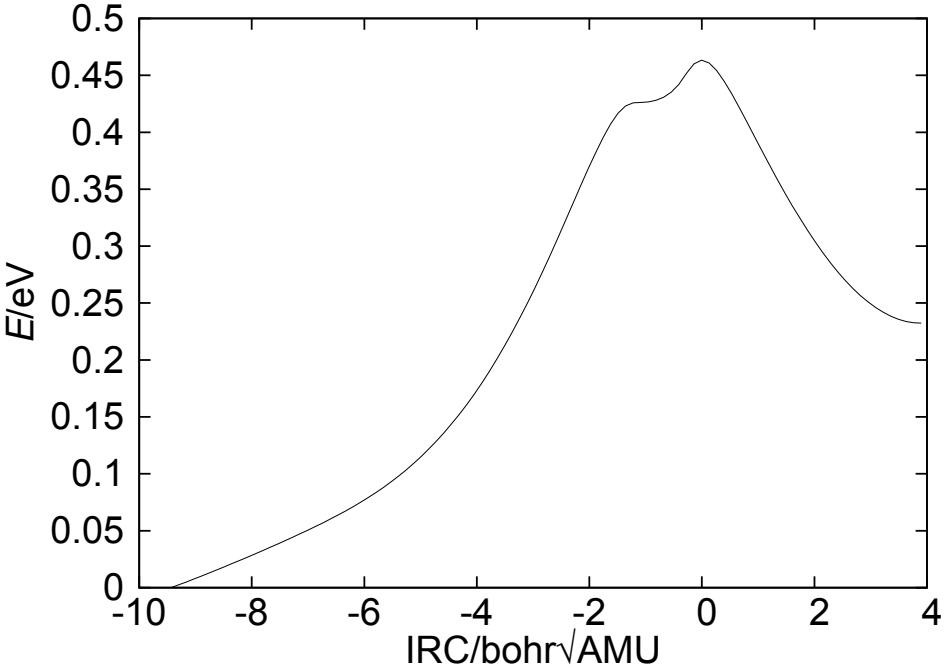

Figure 18

19 $\mathbf{NH_3SiH_3^{\cdot} \longrightarrow NH_2SiH_3 + H^{\cdot}}$

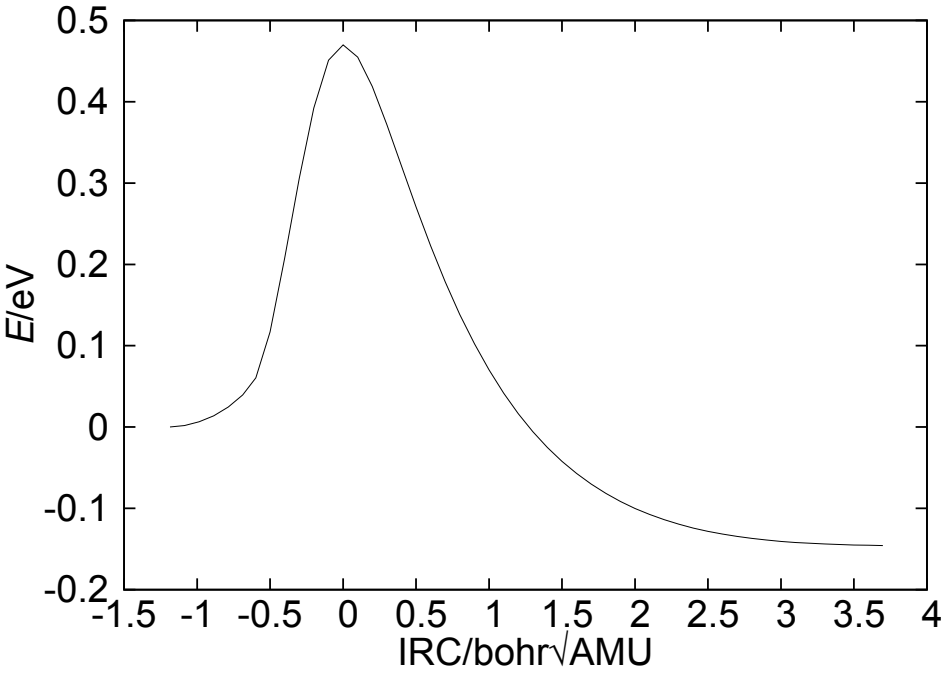

Figure 19

20 $\mathbf{NH_2SiH_2NH_3^{\cdot} \longrightarrow (NH_2)_2SiH_2 + H^{\cdot}}$

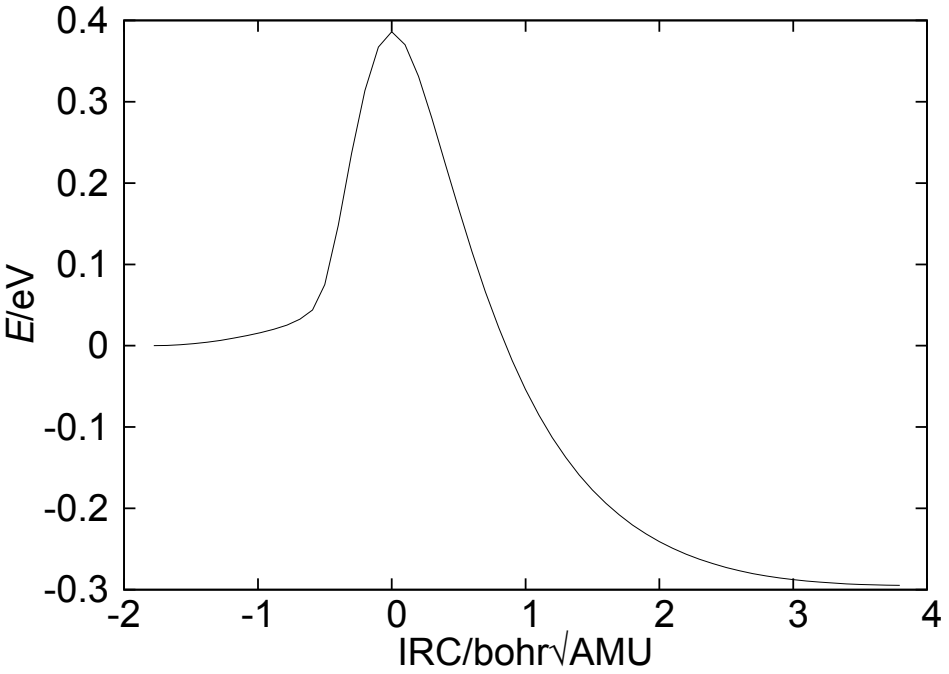

Figure 20

21 $(NH_2)_2SiHNH_3^{\cdot} \longrightarrow (NH_2)_3SiH + H^{\cdot}$

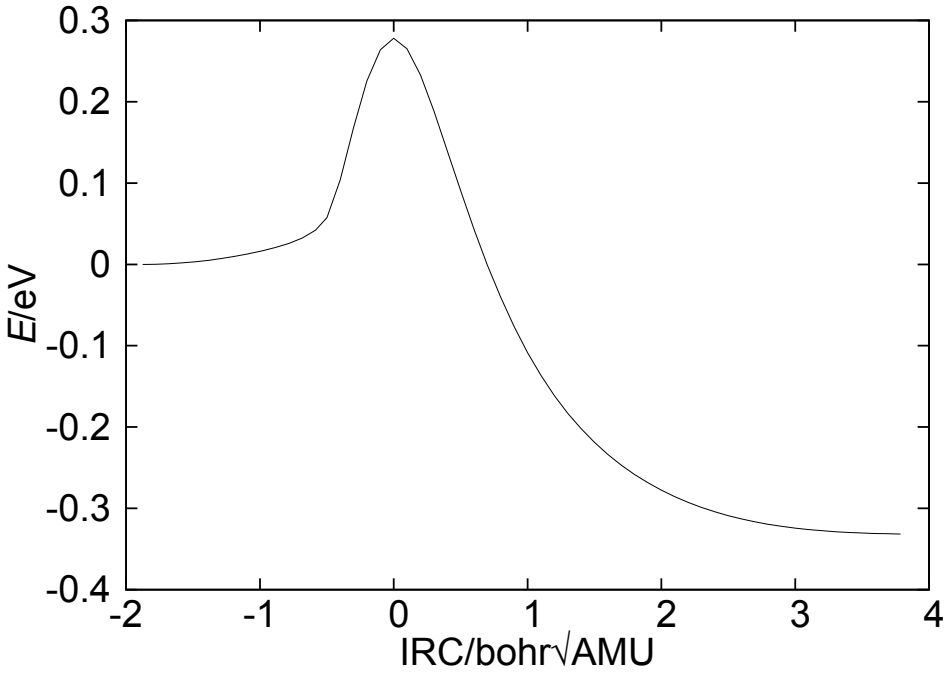

Figure 21

22 $(NH_2)_3SiNH_3^{\cdot} \longrightarrow (NH_2)_4SiH + H^{\cdot}$

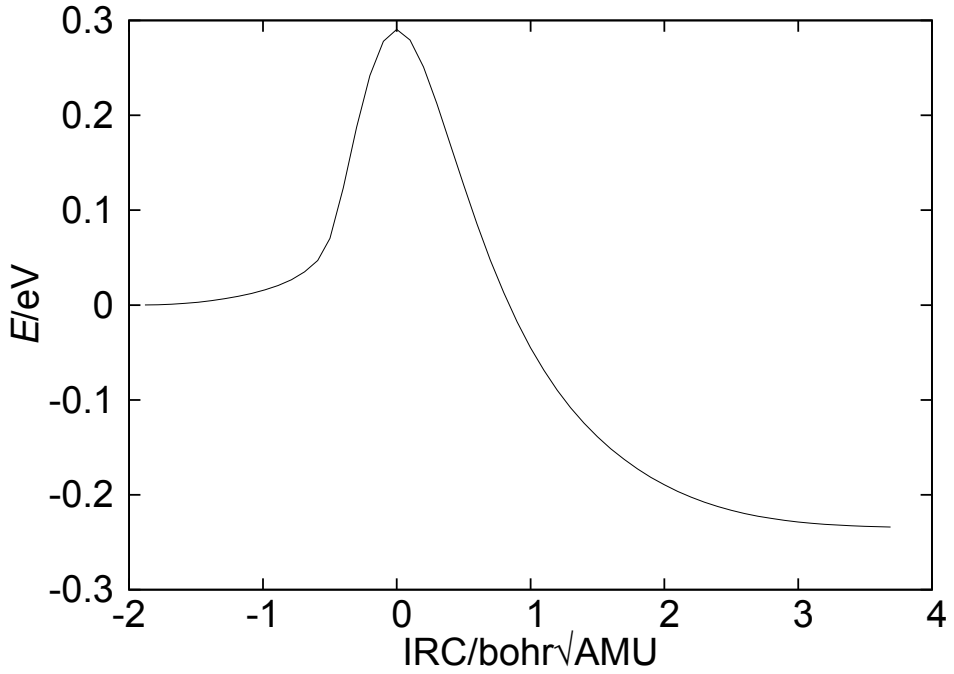

Figure 22

23 $\mathbf{SiH_2{-}NH_3 \longrightarrow SiH_2 + NH_3}$

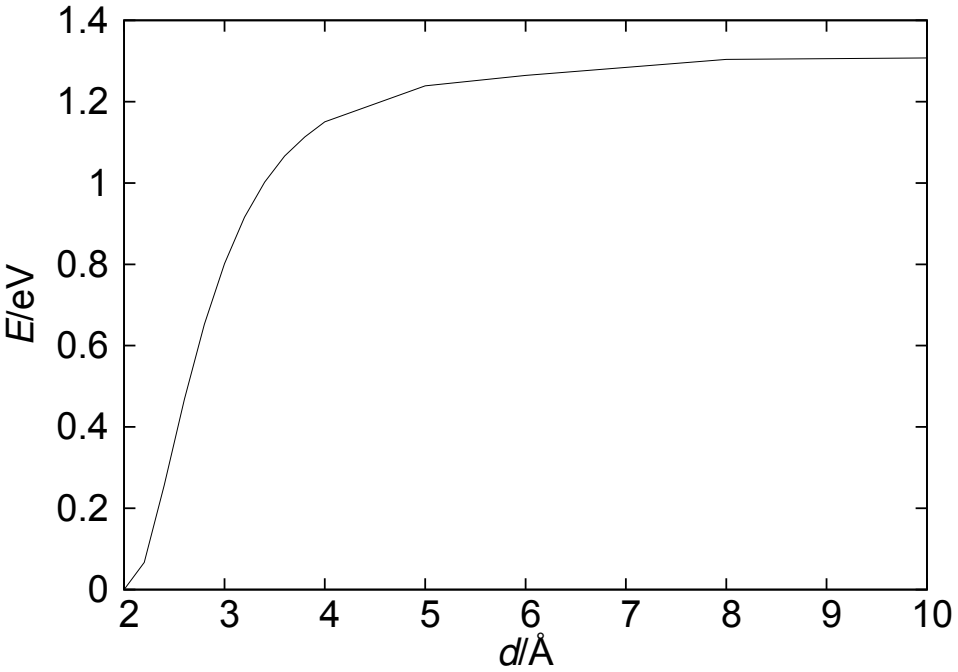

Figure 23: Energies are calculated with CASPT2/aug–cc–PVTZ with the active space: (10,10).

24 $SiH_2{-}NH_2SiH_3 \longrightarrow SiH_2 + NH_2SiH_3$

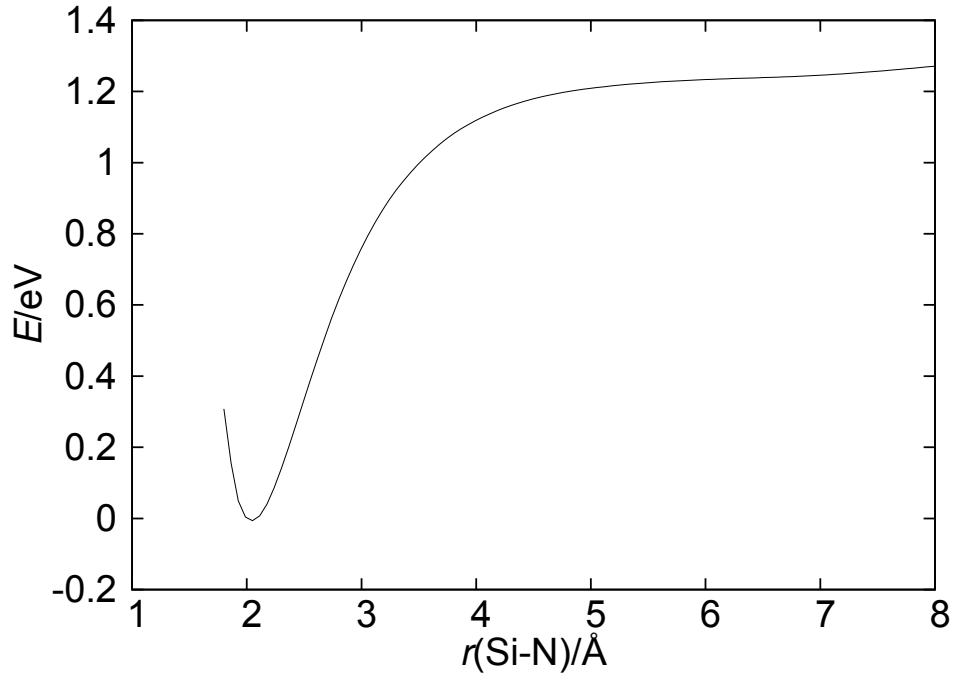

Figure 24: Energies are calculated with CASPT2/aug–cc–PVTZ with the active space: (10,10).

25 $\mathbf{SiH_2{-}NH(SiH_3)_2 \longrightarrow SiH_2 + NH(SiH_3)_2}$

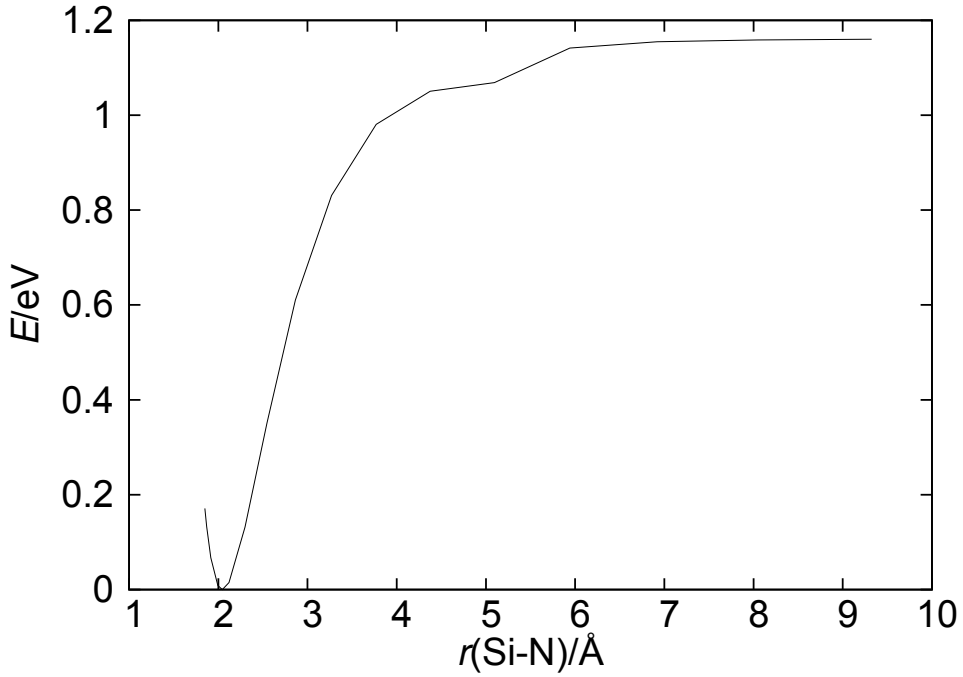

Figure 25: Energies are calculated with CASPT2/aug–cc–PVTZ with the active space: (10,10).

26 $NH_3 - SiH_2 \rightarrow NH_2SiH_3$

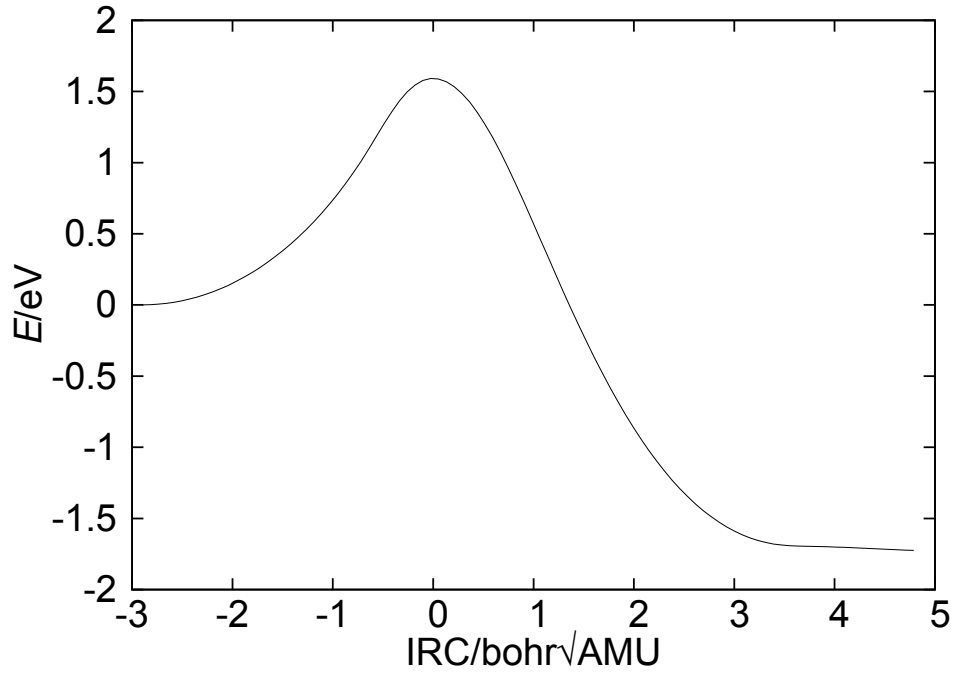

Figure 26

27 $SiH_2 - NH_2SiH_3 \longrightarrow NH(SiH_3)_2$

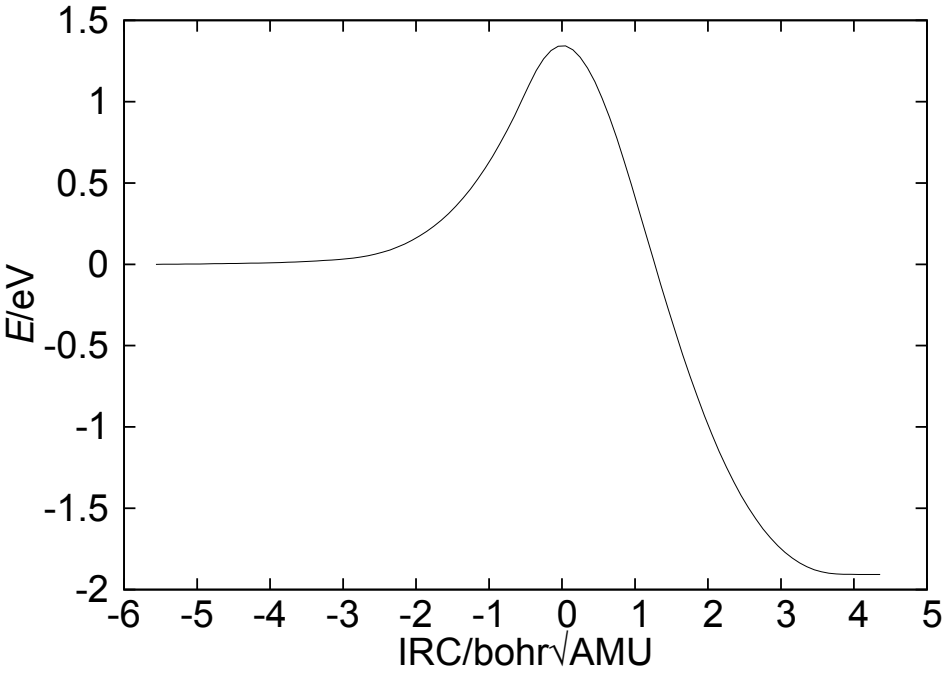

Figure 27

28 $\mathbf{SiH_2{-}NH(SiH_3)_2 \longrightarrow N(SiH_3)_3}$

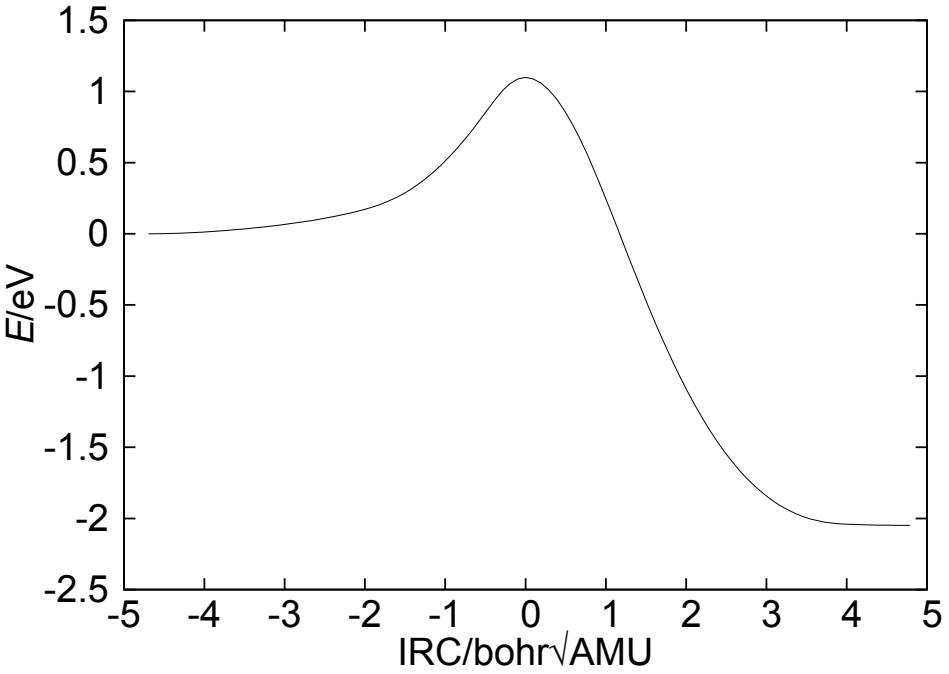

Figure 28

29 $\mathbf{NH_2^{\cdot} + SiH_4 \longrightarrow NH_2SiH_3 + H^{\cdot}}$

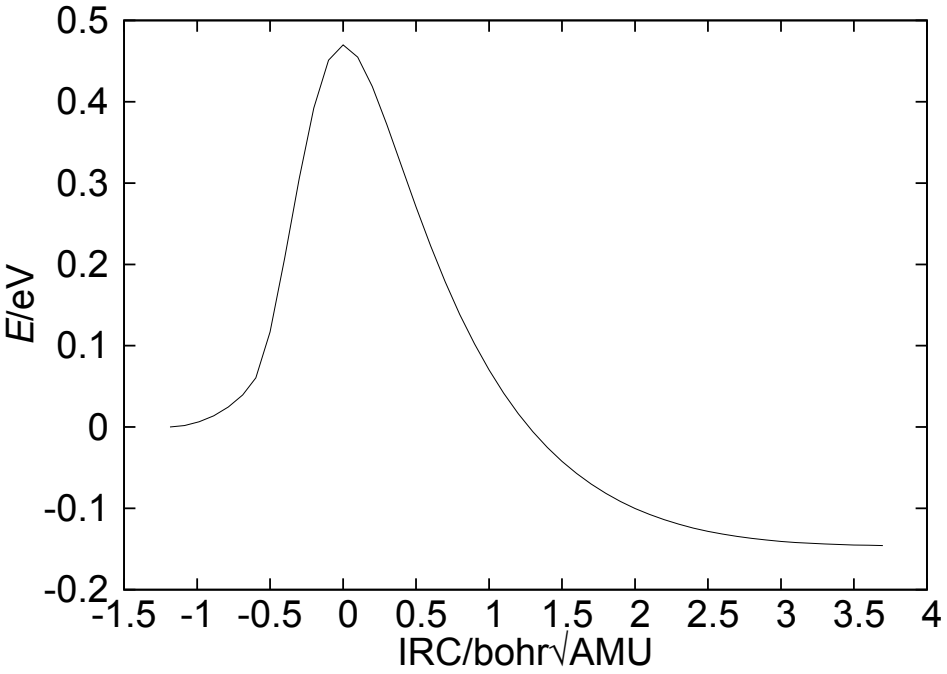

Figure 29

30 $\mathbf{NH_2^{\cdot} + NH_2SiH_3 \longrightarrow (NH_2)_2SiH_2 + H^{\cdot}}$

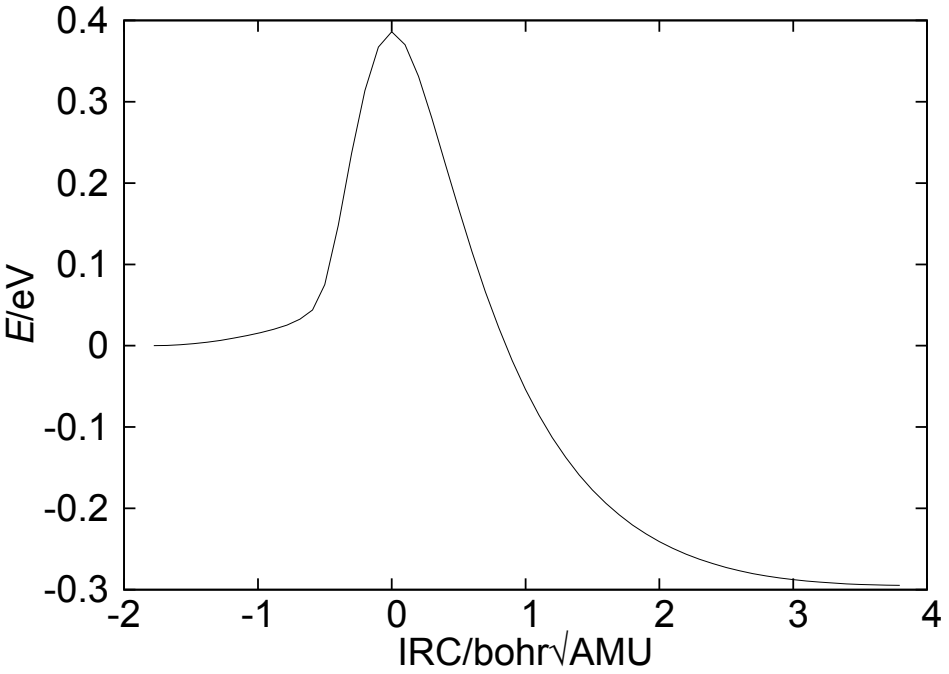

Figure 30

31 $\mathbf{NH_2^{\cdot} + (NH_2)_2SiH_2 \longrightarrow (NH_2)_3SiH + H^{\cdot}}$

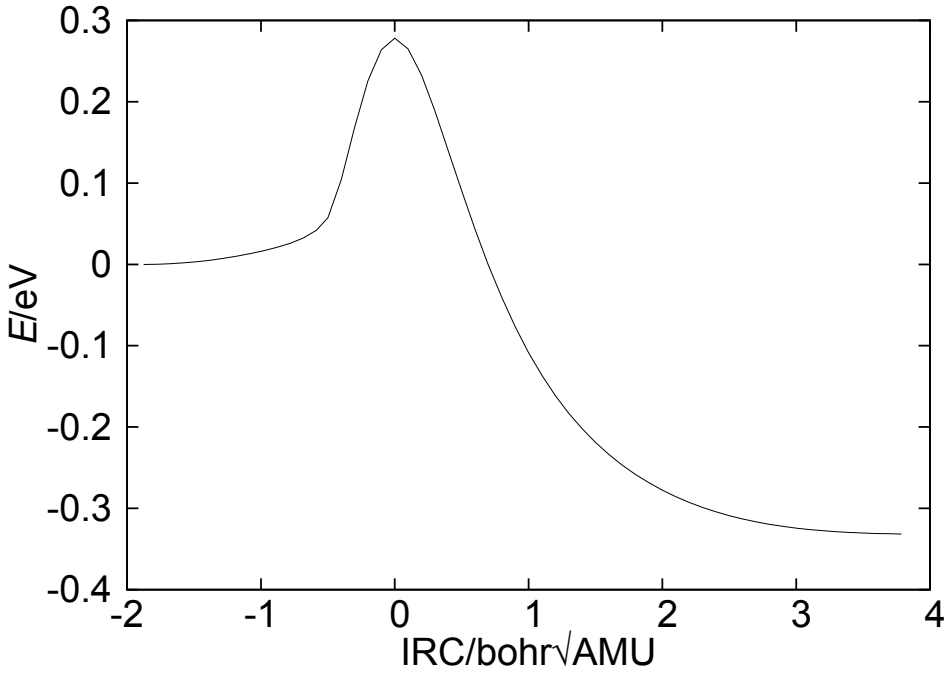

Figure 31

32 $\mathbf{NH_2^{\cdot} + (NH_2)_3SiH \longrightarrow (NH_2)_4Si + H^{\cdot}}$

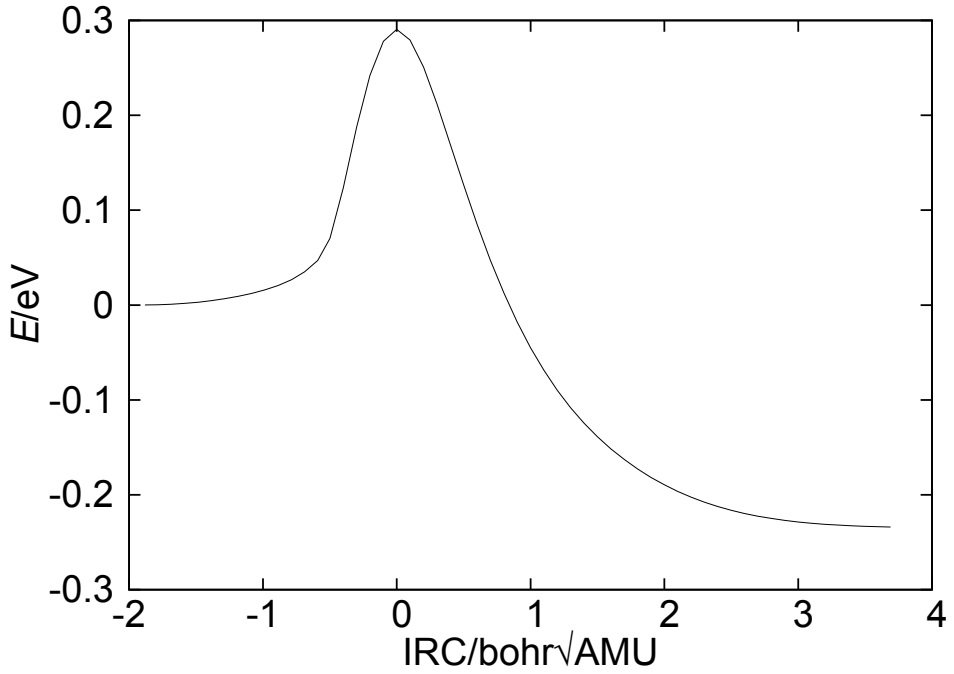

Figure 32

33 $\mathbf{SiH_3^{\cdot} + SiH_4 \longrightarrow SiH_4 + SiH_3^{\cdot}}$

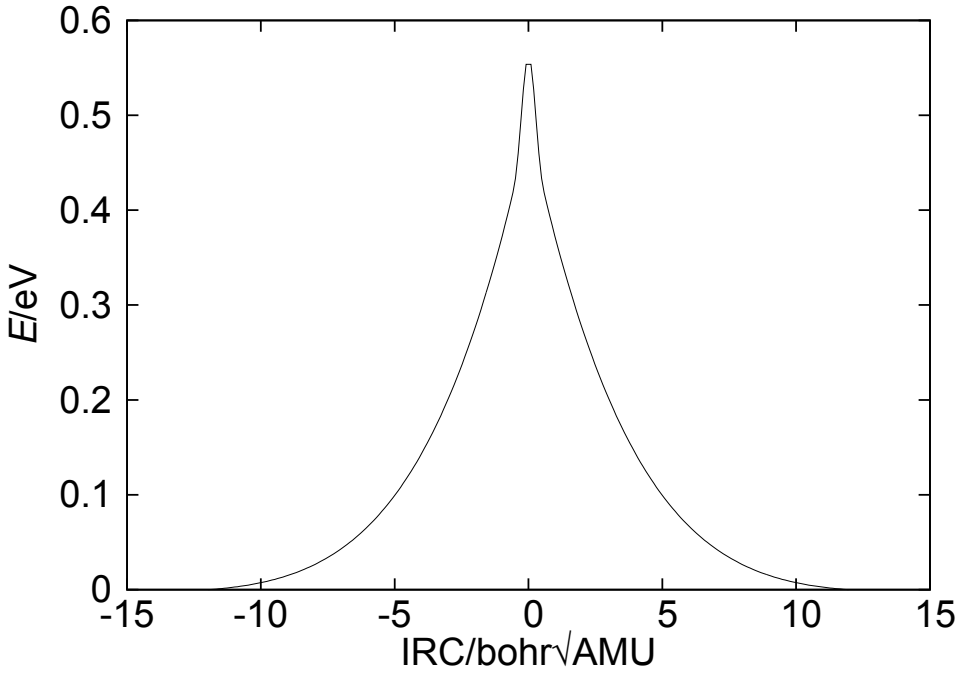

Figure 33

34 $\mathbf{SiH_3^{\cdot} + NH_2SiH_3 \longrightarrow NH_2SiH_2^{\cdot} + SiH_4}$

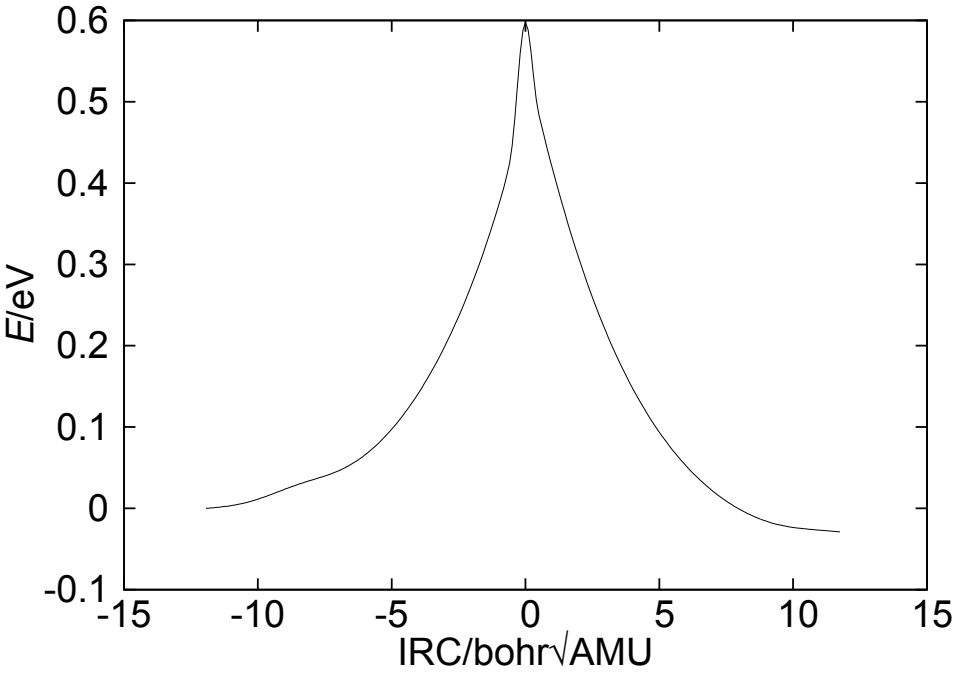

Figure 34

35 $\mathbf{SiH_3^{\cdot} + (NH_2)_2SiH_2 \longrightarrow (NH_2)_2SiH^{\cdot} + SiH_4}$

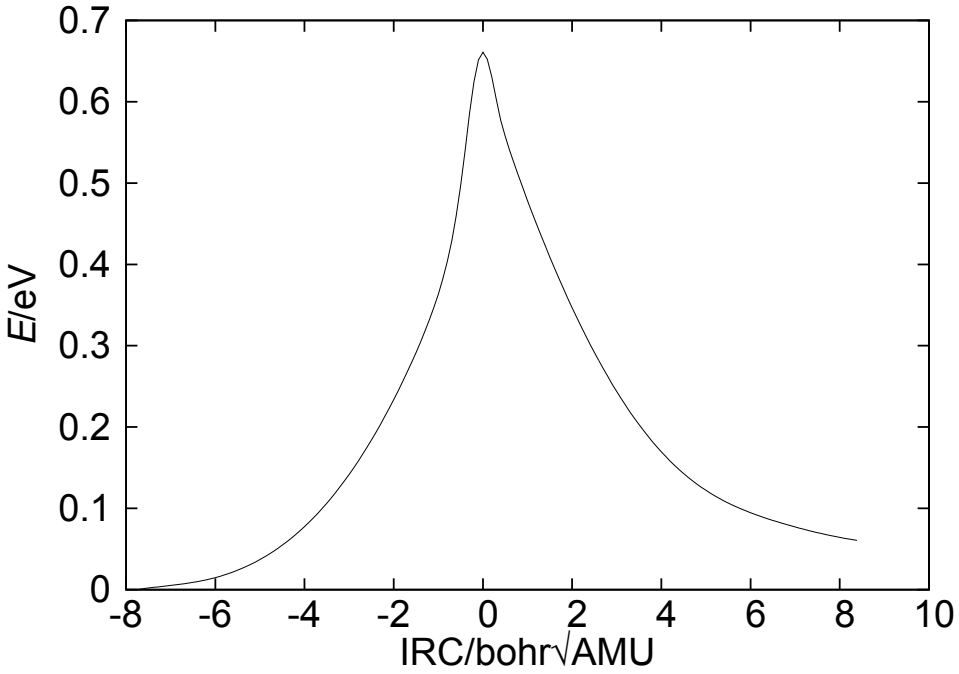

Figure 35

36 $\mathbf{SiH_3^{\cdot} + (NH_2)_3SiH \longrightarrow (NH_2)_3Si^{\cdot} + SiH_4}$

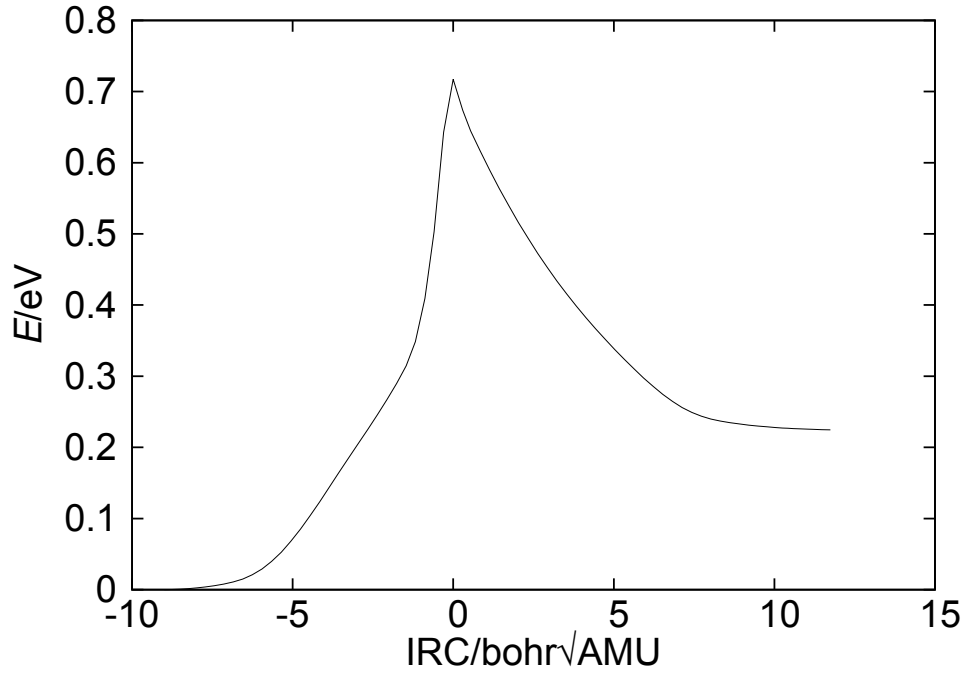

Figure 36

37 $\mathbf{NH_2^{\cdot} + SiH_4 \longrightarrow NH_3 + SiH_3^{\cdot}}$

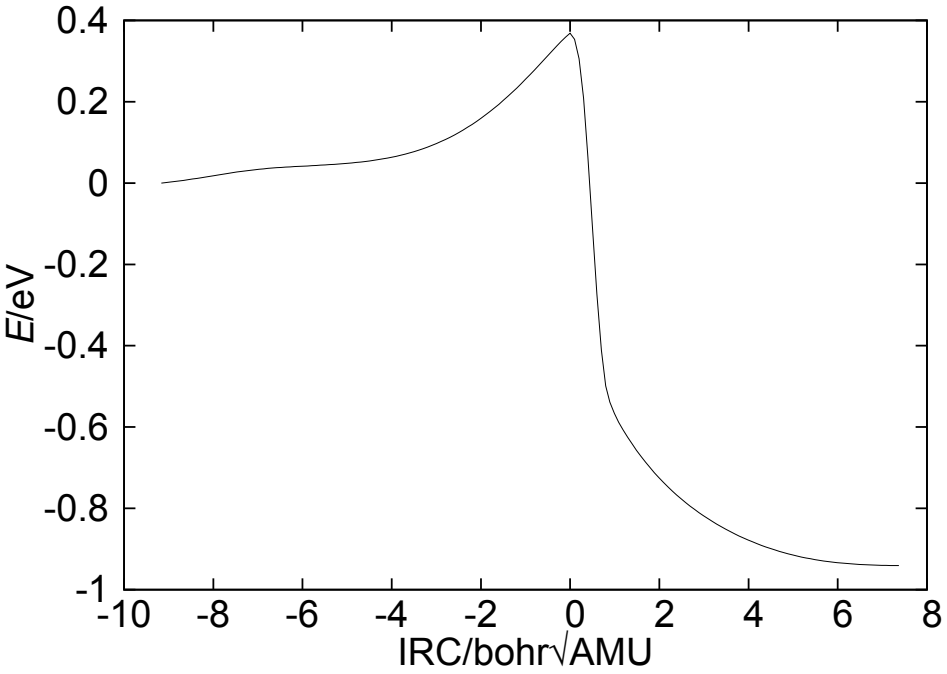

Figure 37

38 $\mathbf{NH_2^{\cdot} + NH_2SiH_3 \longrightarrow NH_2SiH_2^{\cdot} + NH_3}$

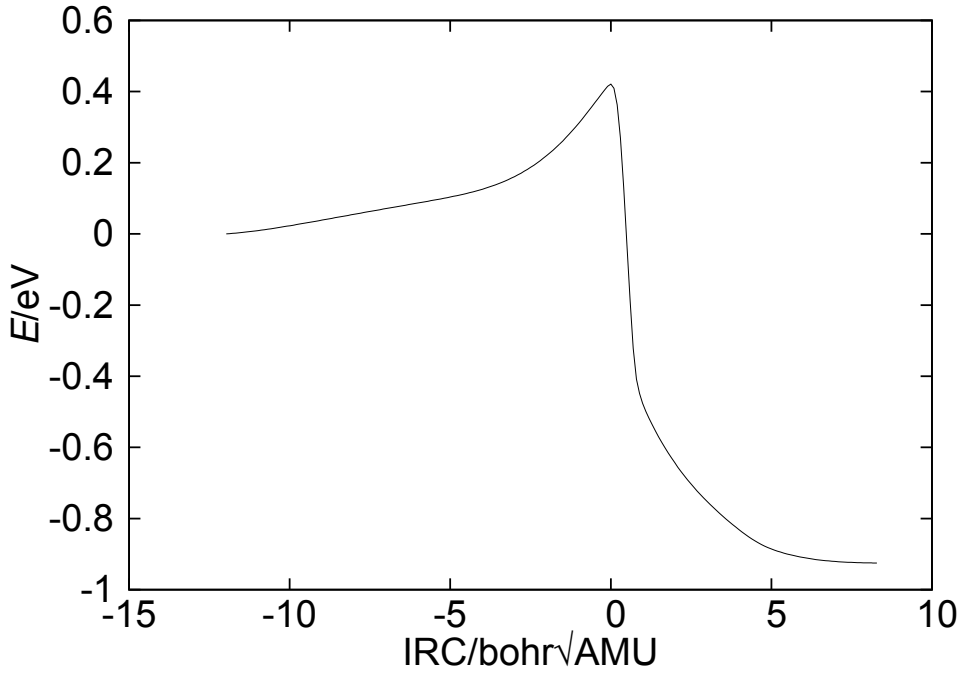

Figure 38

39 $\mathbf{NH_2^{\cdot} + (NH_2)_2SiH_2 \longrightarrow (NH_2)_2SiH^{\cdot} + NH_3}$

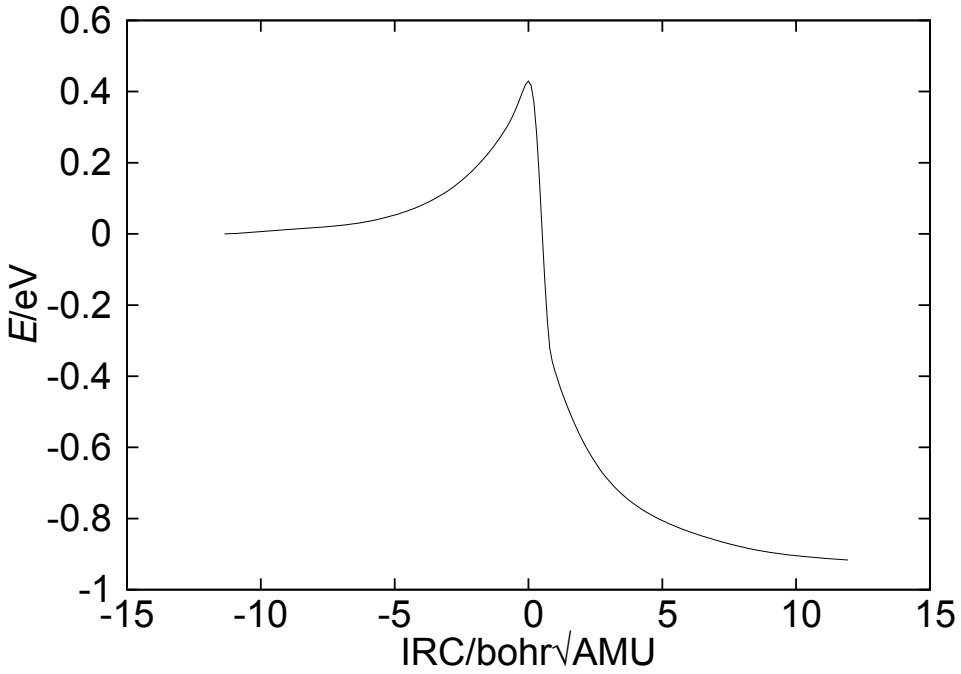

Figure 39

40 $\mathbf{NH_2^{\cdot} + (NH_2)_3SiH \longrightarrow (NH_2)_3Si^{\cdot} + NH_3}$

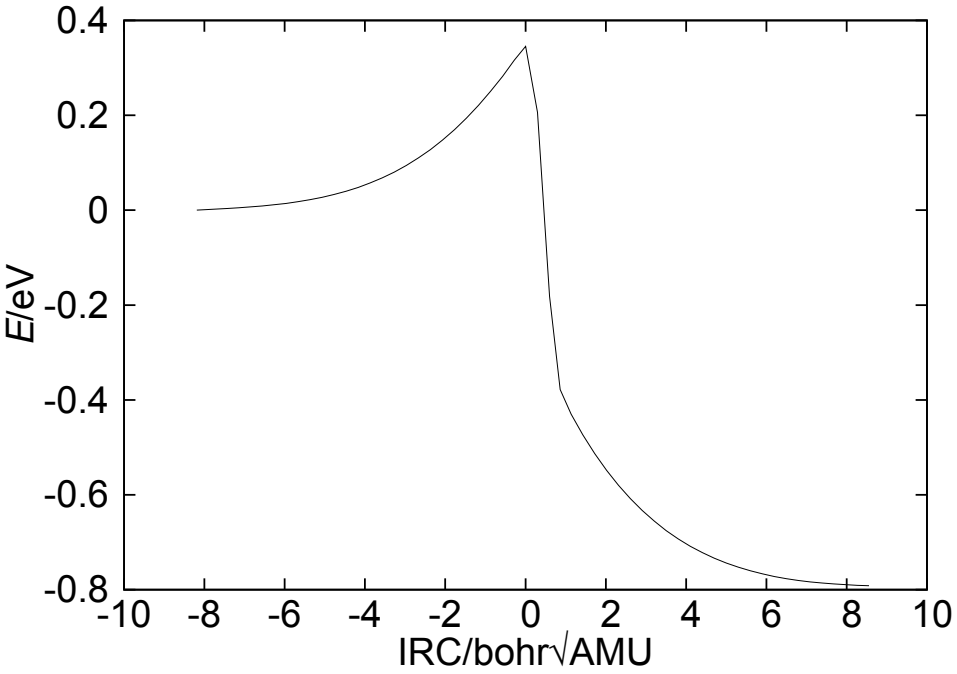

Figure 40

41 $\mathbf{H^{\cdot} + SiH_4 \longrightarrow H_2 + SiH_3^{\cdot}}$

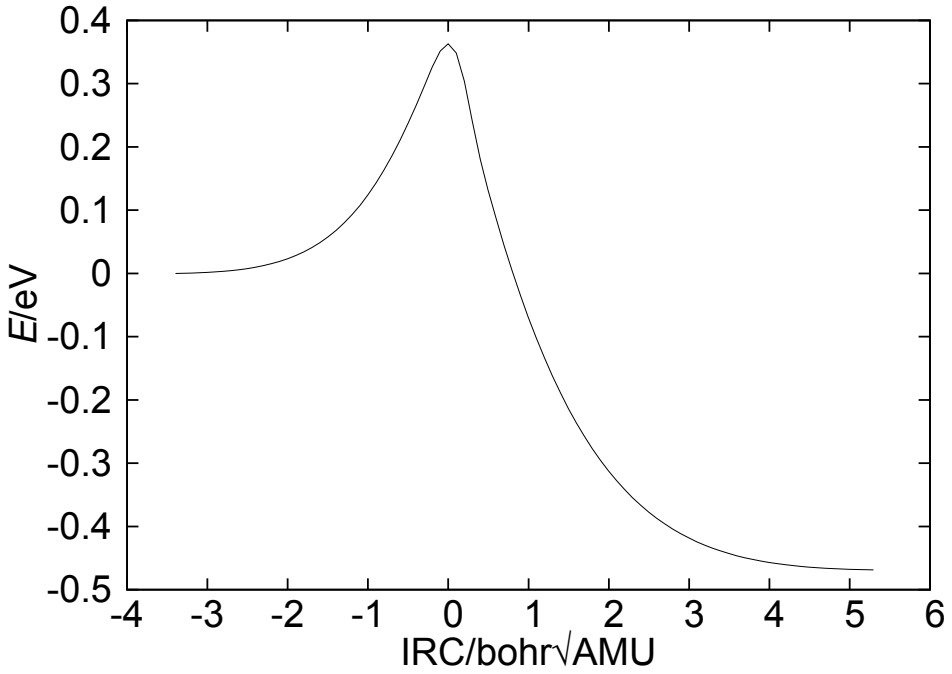

Figure 41

42 $\mathbf{H^{\cdot} + NH_2SiH_3 \longrightarrow NH_2SiH_2^{\cdot} + H_2}$

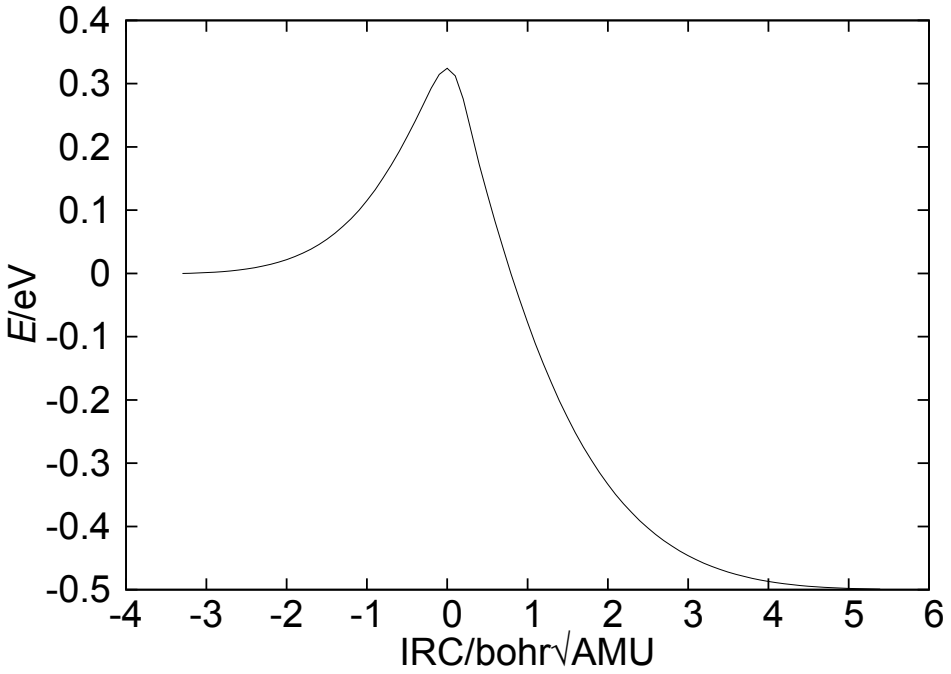

Figure 42

43 $\mathbf{H^{\cdot} + (NH_2)_2SiH_2 \longrightarrow (NH_2)_2SiH^{\cdot} + H_2}$

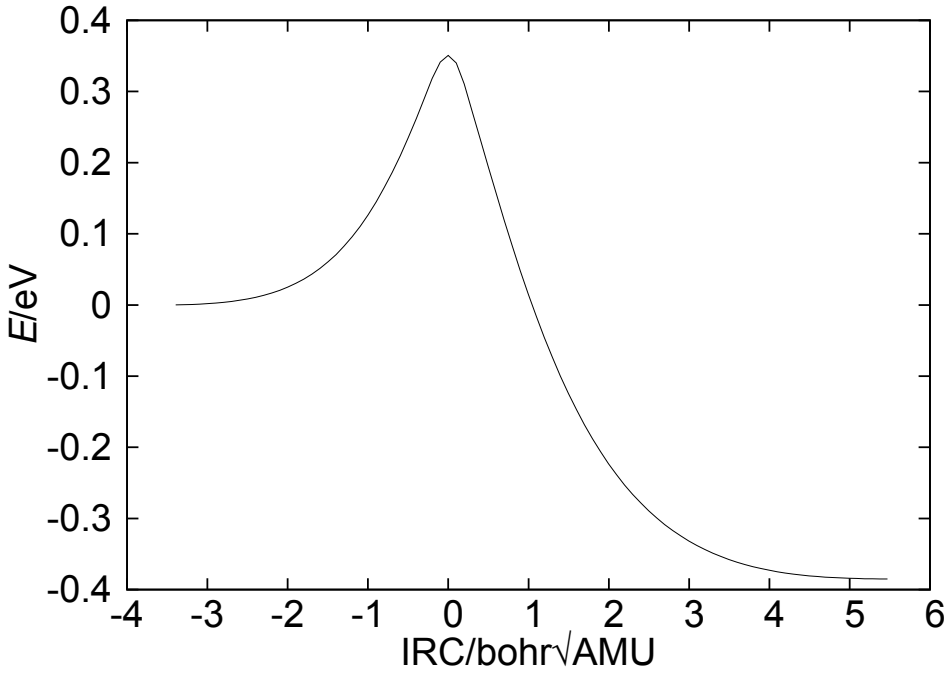

Figure 43

44 $\mathbf{H^{\cdot} + (NH_2)_3SiH \longrightarrow (NH_2)_3Si^{\cdot} + H_2}$

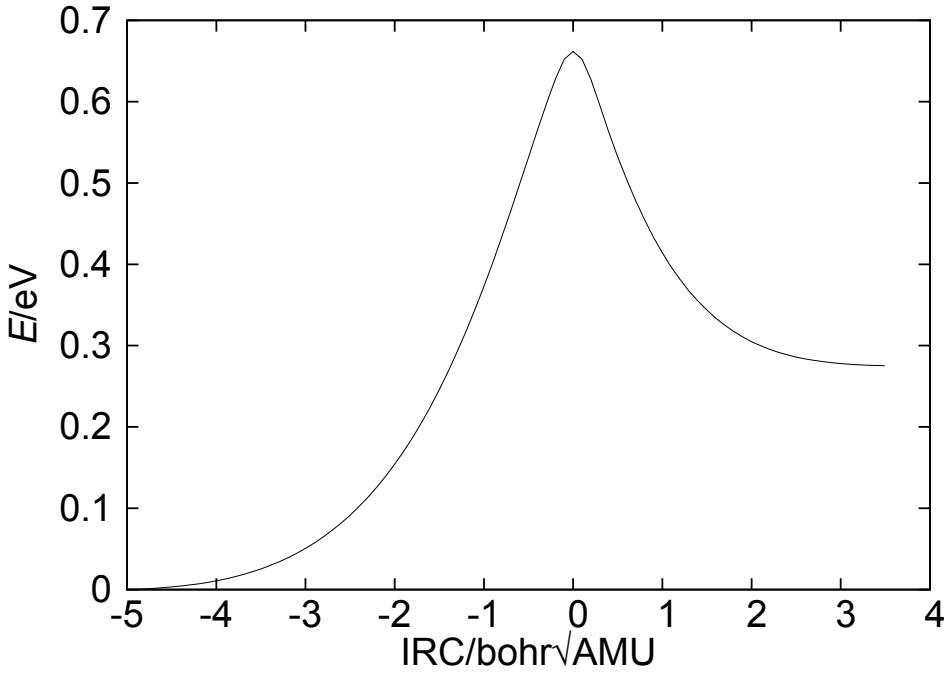

Figure 44