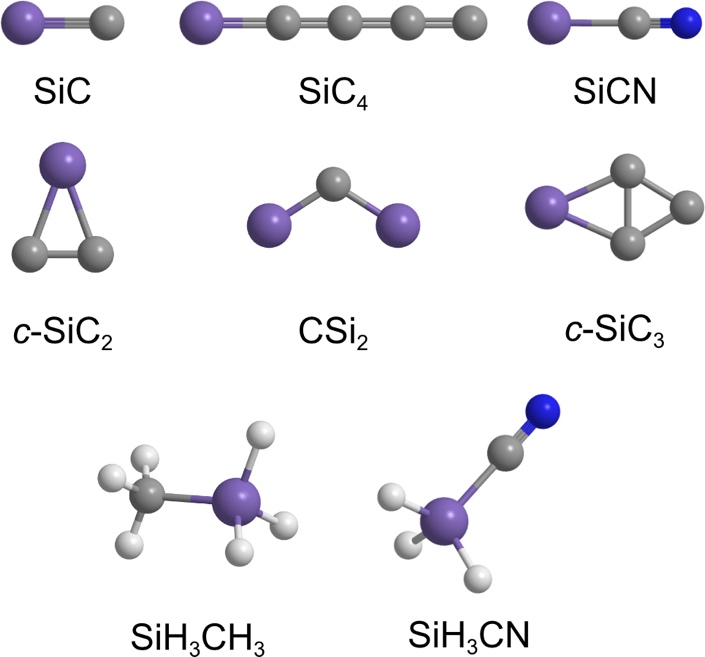
**Table 1**. Peak velocities (*v*p) and speed ratios (*S*) of the silicon (Si), 1,3-butadiene (CH2CHCHCH2) 1,2-butadiene (CH2CCHCH3), and 1-butyne (CH3CH2CCH) beams along with the corresponding collision energies (*E*C) and center-of-mass angles (ΘCM) for each reactive scattering experiment.

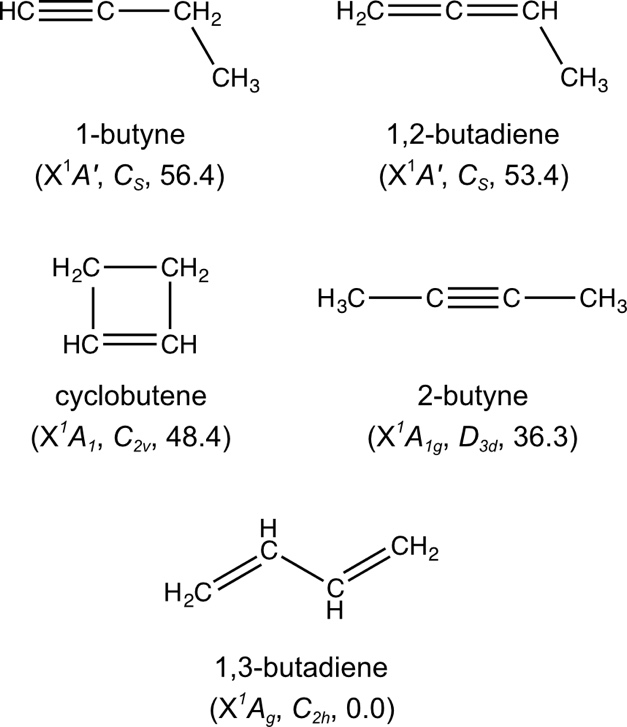
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Beam | *v*p  (m s−1) | *S* | *E*C  (kJ mol−1) | ΘCM  (degree) |
| Si(3P) | 970 ± 30 | 6.0 ± 0.5 | 14.5 ± 0.6 | 57.6 ± 0.9 |
| CH3CH2CCH (X1A′) | 793 ± 10 | 9.0 ± 0.3 |
|  |  |  |  |  |
| Si(3P) | 962 ± 17 | 5.9 ± 0.6 | 14.4 ± 0.3 | 57.9 ± 0.6 |
| CH2CCHCH3 ( X1A′) | 795 ± 10 | 8.9 ± 0.4 |
|  |  |  |  |  |
| Si(3P) | 1013 ± 7 | 4.9 ± 0.2 | 15.0 ± 0.2 | 55.9 ± 0.4 |
| CH2CHCHCH2 (X1Ag) | 777 ± 12 | 9.5 ± 0.3 |
|  |  |  |  |  |

**Table 2**. Experimental product branching ratios (%) derived from the reaction of ground state atomic silicon (Si(3P)) with 1,3-butadiene-2,3-d2 (CH2CDCDCH2) and 1,3-butadiene-1,1,4,4-d4 (CD2CHCHCD2) along with the computed branching ratios based on the RRKM rate constants.

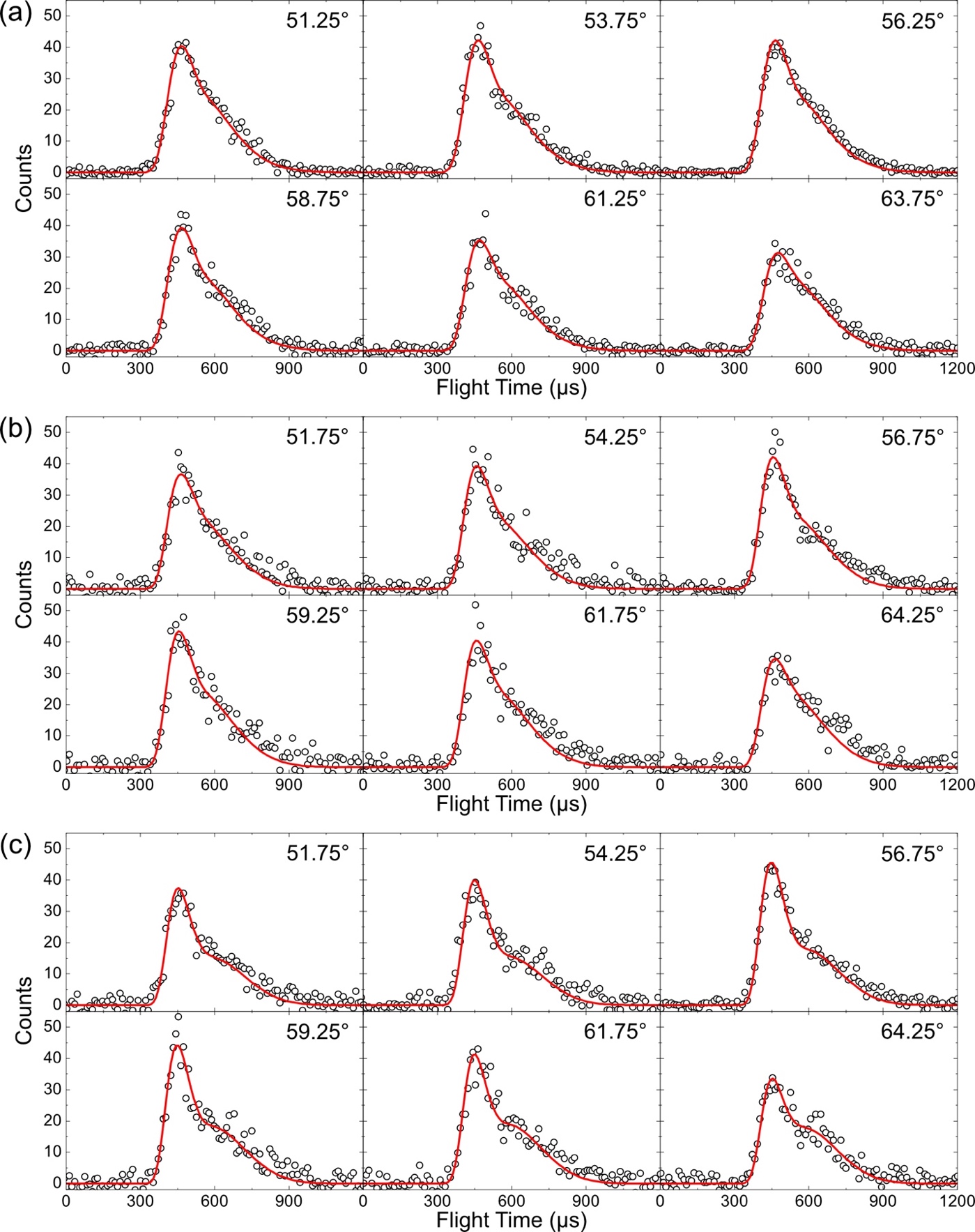
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Reaction Products | Experiment (%) | | Theory (%) | |
| Si(3P) + CH2CDCDCH2 | |  | |  | |
| SiC4H2D2 + H2 | 61 ± 9 | | 0.7 | |
| SiC4H3D + HD | 39 ± 9 | | 99.3 | |
| SiC4H4 + D2 | 0 | | 0 | |
| Si(3P) + CD2CHCHCD2 | |  | |  | |
| SiC4D4 + H2 |  | | 0 | |
| SiC4D3H + HD | 48 ± 9 | | 99.95 | |
| SiC4D2H2 + D2 | 48 ± 9 | | 0.05 | |



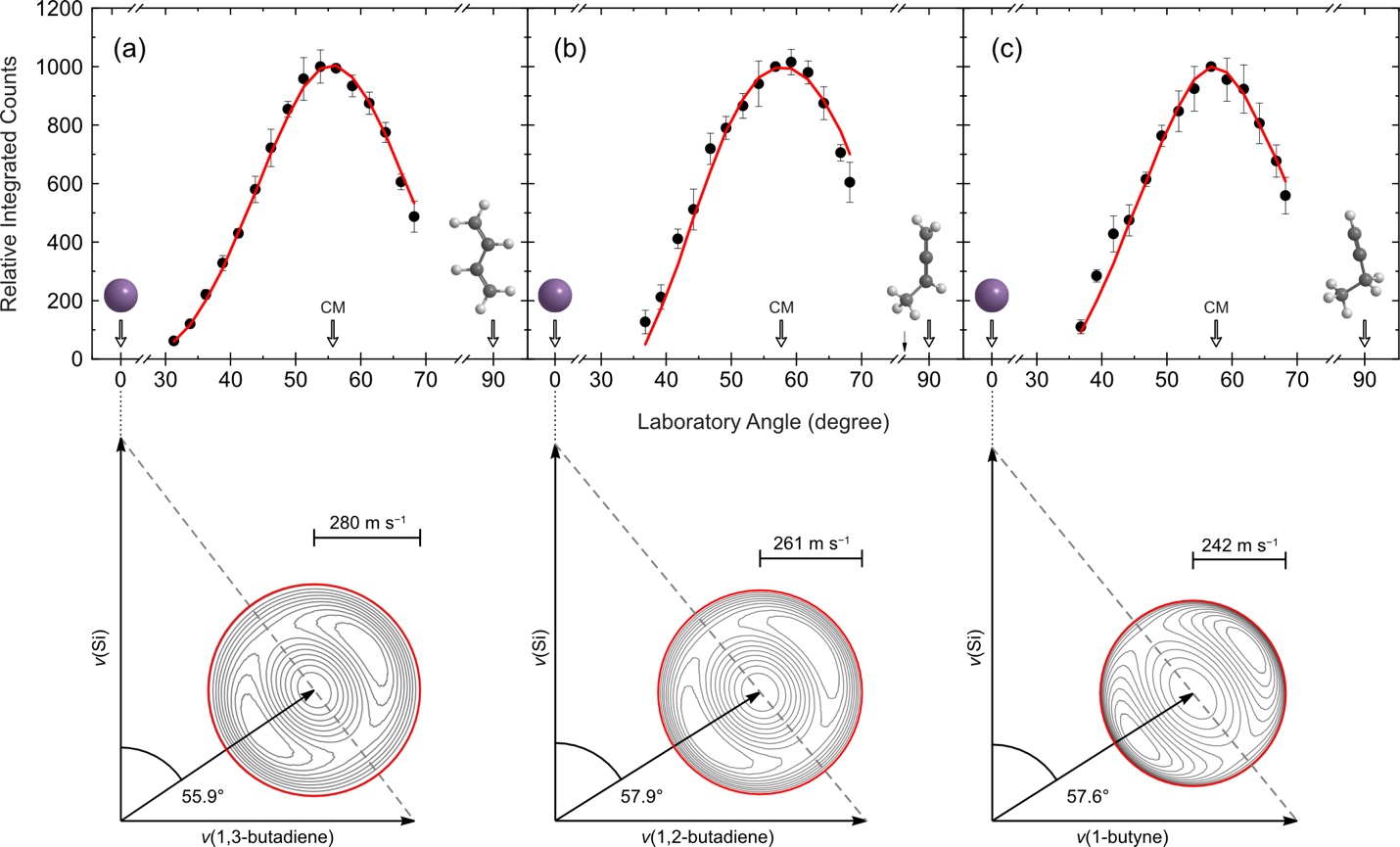
**Figure 1**. Molecules carrying silicon-carbon bonds detected in the circumstellar envelope of IRC+10216. Silicon, carbon, nitrogen, and hydrogen are indicated in purple, gray, blue, and white.



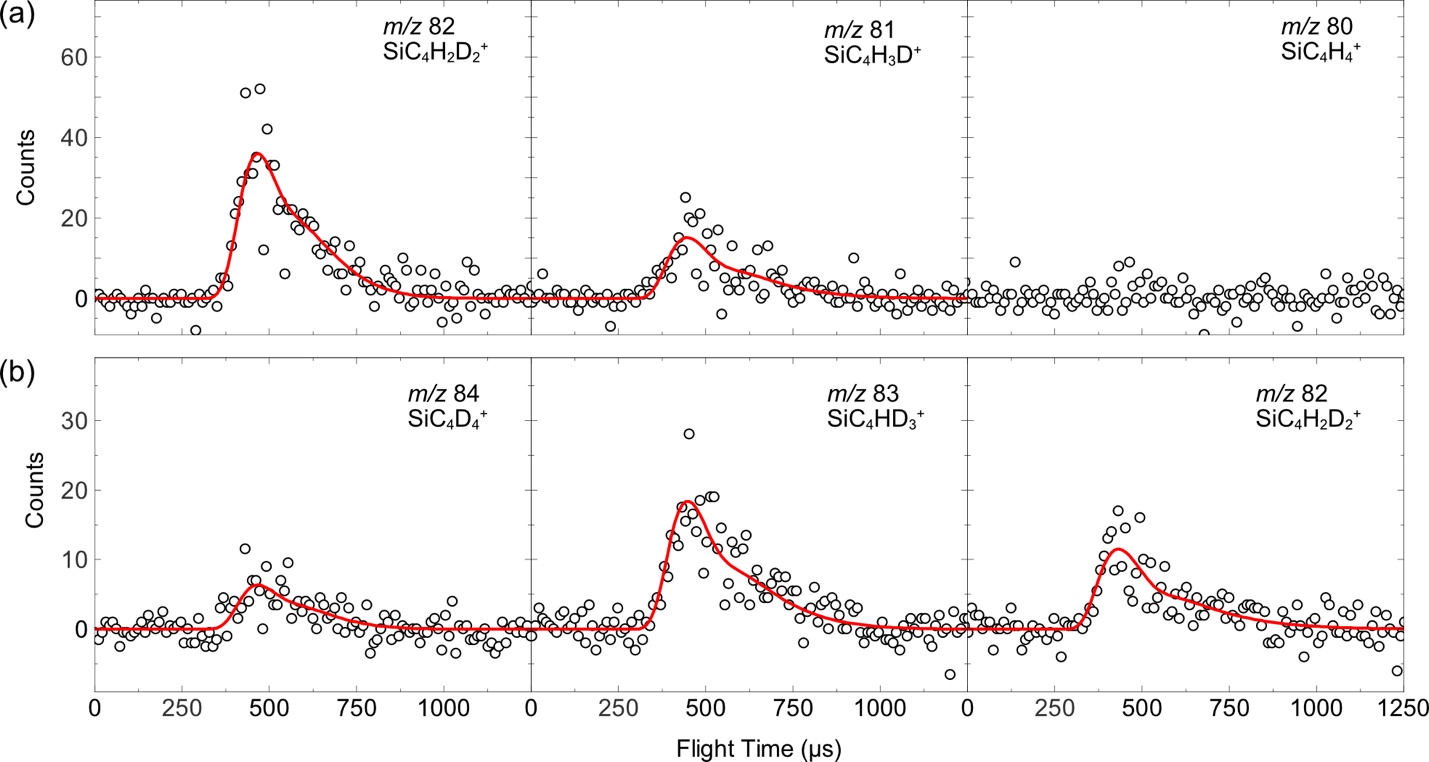
**Figure 2.** Energetically low-lying structural isomers of C4H6. Experimental enthalpies of formation (Δf*H*(298K) are taken from NIST and given relative to 1,3-butadiene in kJ mol−1.



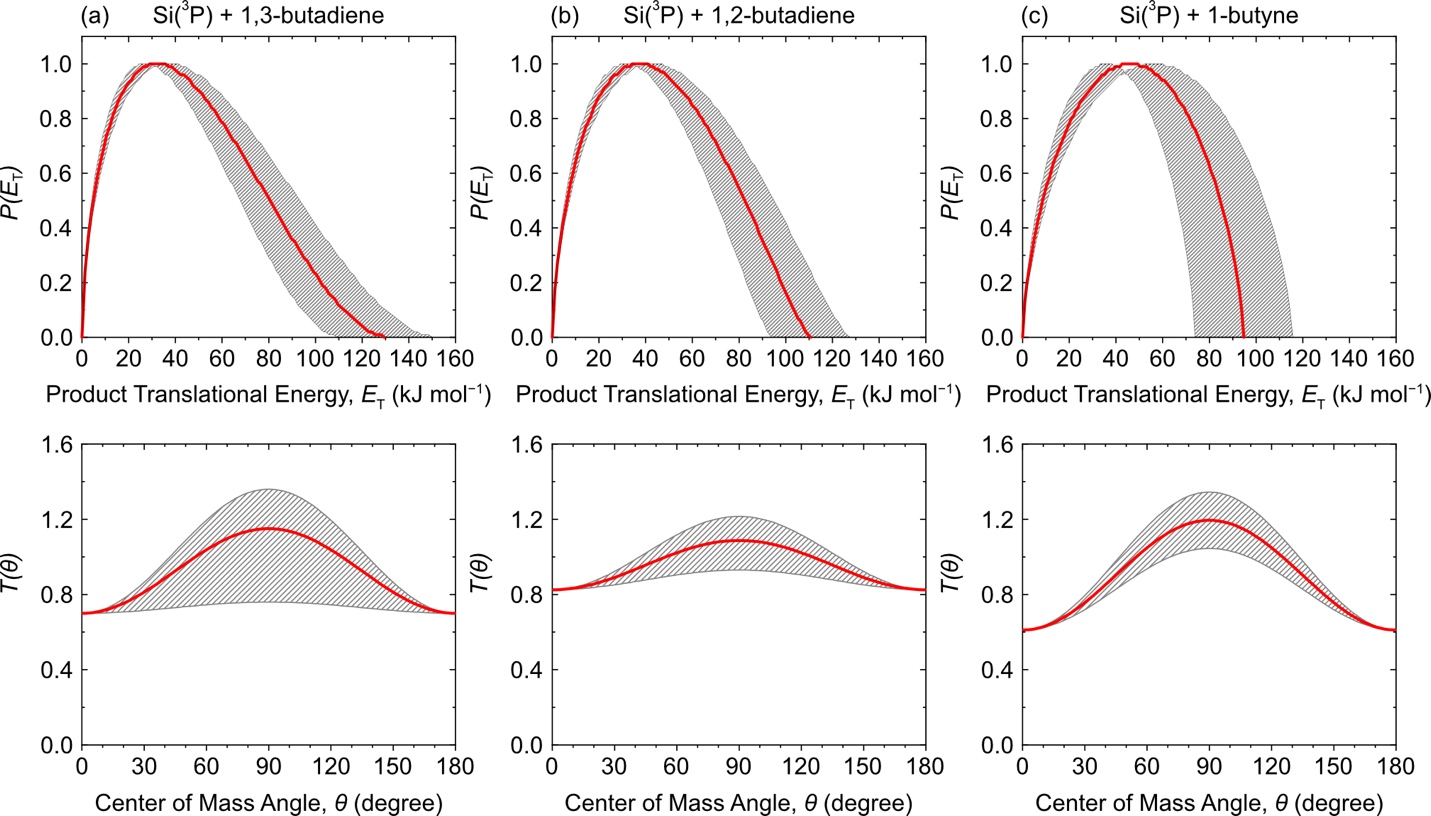
**Figure 3.** Time-of-flight (TOF) spectra recorded at mass-to-charge (*m/z*) 80 (SiC4H4+) from the reaction of ground state atomic silicon (Si(3P)) with (a) 1,3-butadiene (CH2CHCHCH2), (b) 1,2-butadiene (CH2CCHCH3), and (c) 1-butyne (CH3CH2CCH). The open circles are experimental data and the red lines the best fits.



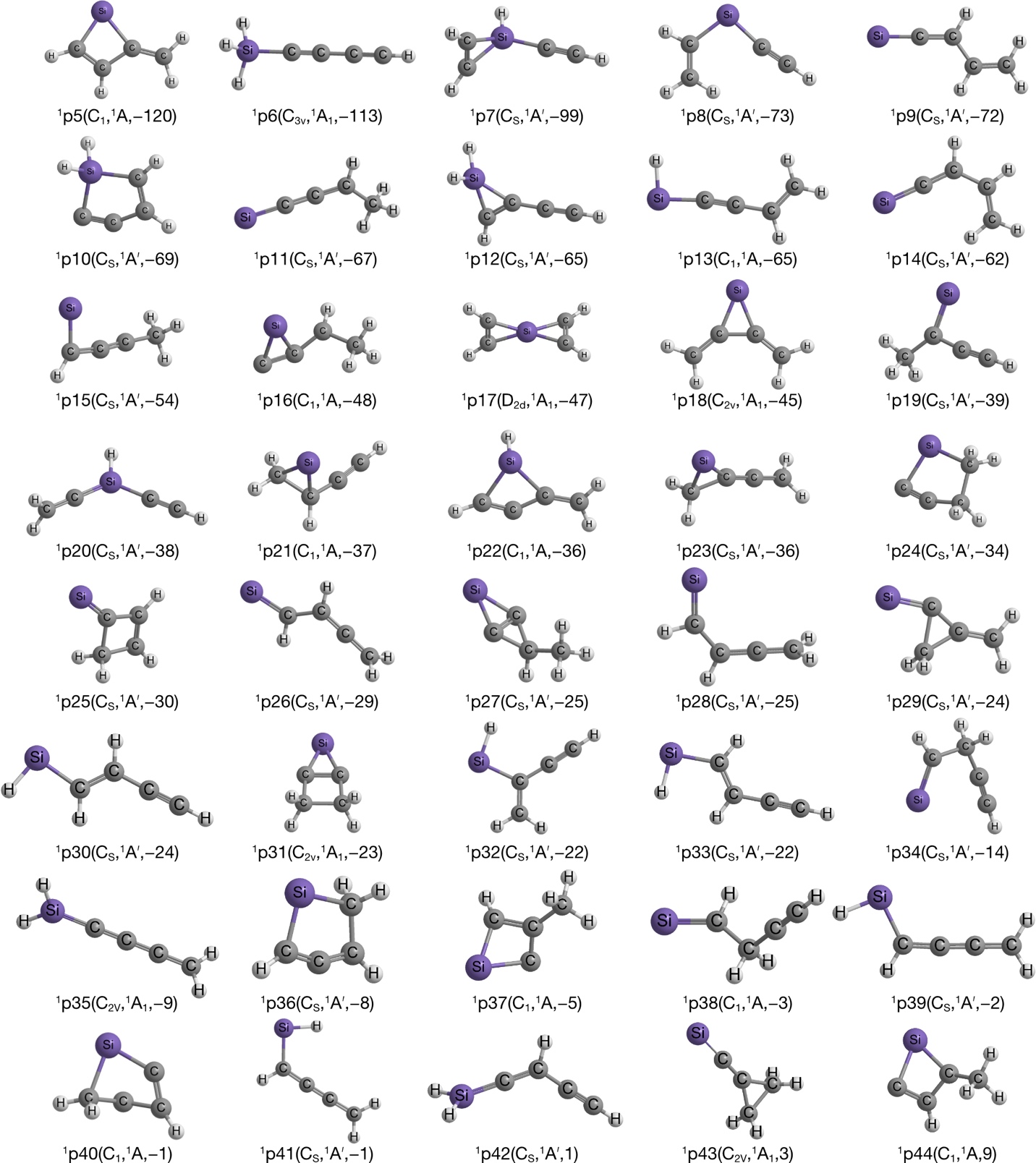
**Figure 4.** Laboratory angular distributions recorded at a mass-to-charge (*m/z*) ratio of 80 (SiC4H4+) in the reaction of ground state atomic silicon (Si(3P)) with (a) 1,3-butadiene (CH2CHCHCH2), (b) 1,2-butadiene (CH2CCHCH3), and (c) 1-butyne (CH3CH2CCH). The circles define the experimental data and the red lines represent the fitting based on the best-fit center-of-mass functions depicted in Figure 5. Error bars are ±1σ. The CM arrow indicates the center-of-mass angle. The corresponding Newton diagrams relating the laboratory reactant and CM frame product velocities are shown below each respective angular distribution. The SiC4H4 product flux is inlaid within the Newton circle (red), which has a radius equal to the maximum CM velocity of SiC4H4 as defined by the CM functions depicted in Figure 5.



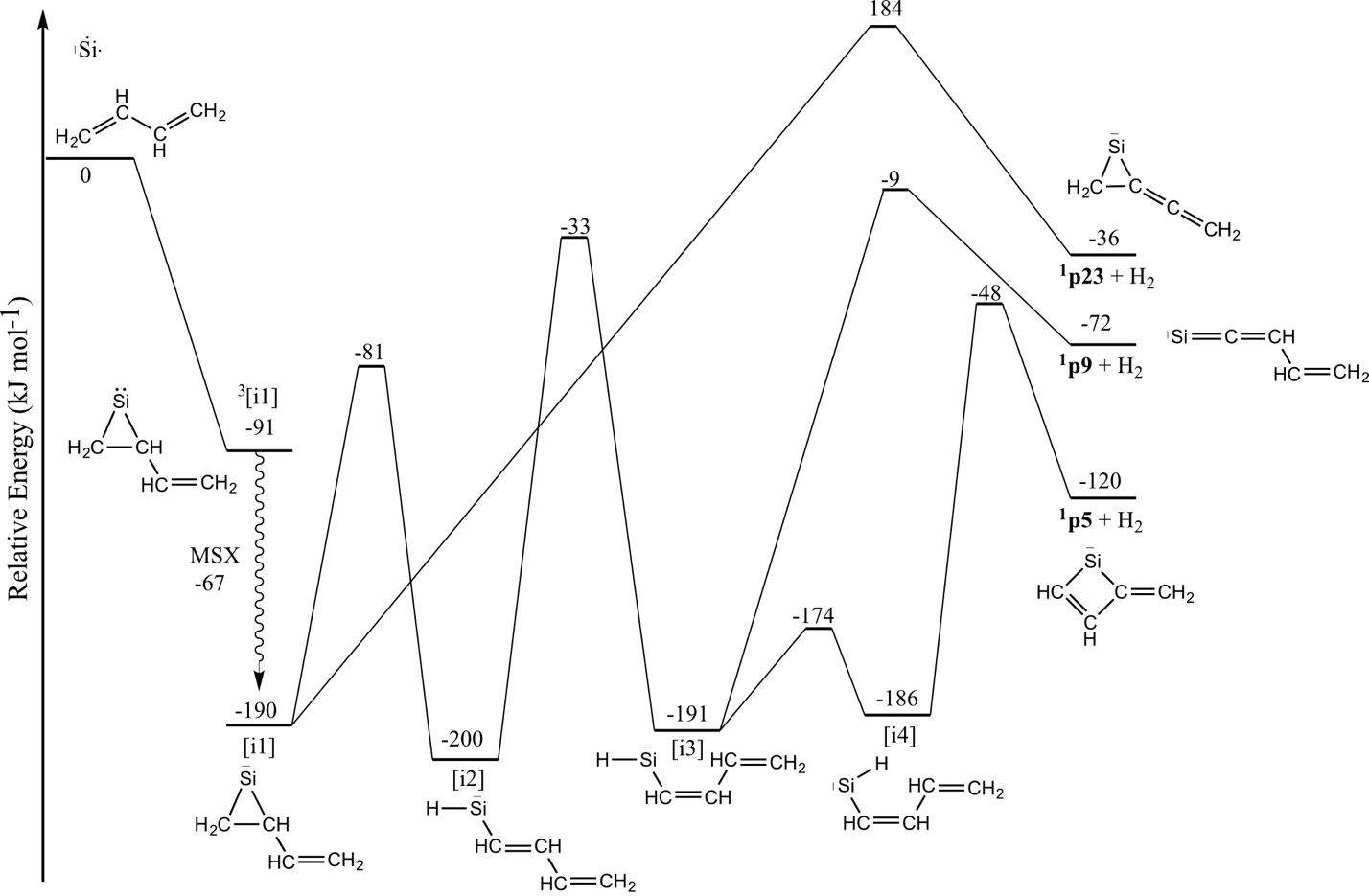
**Figure 5.** Time-of-flight (TOF) spectra for the reaction of the silicon atom (Si(3P)) with (a) 1,3-butadiene-2,3-d2 (CH2CDCDCH2) and (b) 1,3-butadiene-1,1,4,4-d4 (CD2CHCHCD2) leading to H2-, HD-, and D2-loss products. The open circles represent the experimental data, and the red line represents the fit obtained from the forward-convolution routine. Terminal/internal refers to the source(s) of the departing hydrogen and/or deuterium atoms with respect to the C4 backbone.



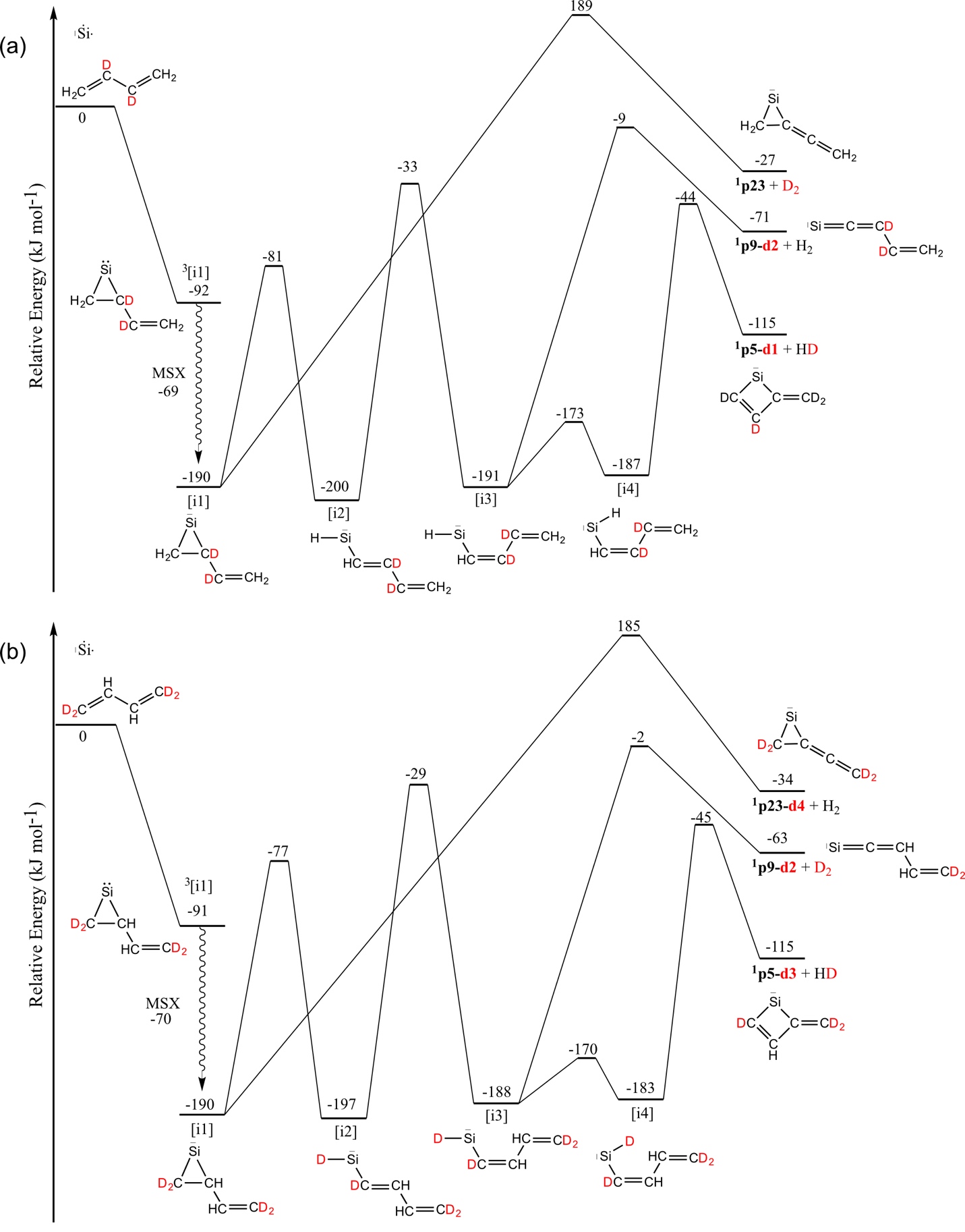
**Figure 6.** Center-of-mass (CM) functions for the formation of SiC4H4 via molecular hydrogen loss in the reactions of ground state atomic silicon (Si(3P)) with (a) 1,3-butadiene (CH2CHCHCH2), (b) 1,2-butadiene (CH2CCHCH3), and (c) 1-butyne (CH3CH2CCH). The translational energy flux distributions are on the top row, and the angular flux distributions on the bottom. The hatched areas define regions of acceptable fits.



**Figure 7.** Molecular structures of low-lying singlet SiC4H4 products 1p5−1p44, adopted from reference 37, along with their B3LYP//CCSD(T)/CBS relative energies in kJ mol−1 with respect to the separated Si(3P) and 1,3-butadiene (CH2CHCHCH2) reactants, point groups, and electronic wave functions.

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**Figure 8.** Pathways accounting for the formation of molecular hydrogen (H2) loss products in the reaction of the ground state silicon atom (Si(3P)) with 1,3-butadiene (CH2CHCHCH2). The energies are obtained at the B3LYP//CCSD(T)/CBS level.

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**Figure 9.** Pathways accounting for the formation of molecular hydrogen (H2), hydrogen deuteride (HD), and molecular deuterium (D2) loss products in the reaction of the ground state silicon atom (Si(3P)) with (a) 1,3-butadiene-2,3-d2 (CH2CDCDCH2) and (b) 1,3-butadiene-1,1,4,4-d4 (CD2CHCHCD2). The energies are obtained at the B3LYP//CCSD(T)/CBS level.