Electronic Supplementary Material for PCCP

Supplementary Material to

Dissociative Photoionization of Mono-, Di- and Trimethylamine Studied by a Combined Threshold Photoelectron Photoion Coincidence Spectroscopy and Computational Approach

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Table S1 Calculated frequencies, barriers, and rotational constants used in RRKM analysis

$NH_2(CH_3)$ frequencies / cm^{-1}	*316,* 851, 980, 1056, 1170, 1352, 1461, 1497, 1519, 1669, 2949, 3052, 3088, 3488, 3562
$NH_2(CH_3)$ rotational constants / GHz	103.44, 22.69, 21.82
$NH_2(CH_3)$ internal rotation	1 CH_3 rotor, V = 6 kJ/mol*, I = 3.12 amu·Å^2
$NH_2(CH_3)^+$ frequencies / cm^{-1}	*66,* 709, 912, 995, 1068, 1233, 1332, 1407, 1476, 1634, 2829, 3062, 3143, 3441, 3548
$NH_2(CH_3)^+$ rotational constants / GHz	106.11, 23.81, 22.08
$NH_2(CH_3)^+$ internal rotation	1 CH_3 free rotor, I = 3.22 amu·Å^2
$NH_2(CH_3)^+$ TS frequencies‡ / cm^{-1}	526, 556, 813, 932, 1085, 1201, 1324, 1422, 1572, 1738, 3108, 3228, 3466, 3578
$NH(CH_3)_2^+$ TS reverse barrier / kJ/mol ; critical freq. / cm^{-1}	1.8, 1000
$NH_2(CH_3)^+$ TS rotational constants / GHz	85.61, 24.50, 23.69
$NH(CH_3)_2$ frequencies / cm^{-1}	*250,* 383, 780, 942, 1036, 1098, 1168, 1185, 1268, 1444, 1471, 1476, 1488, 1494, 1519, 1520, 2912, 2918, 3041, 3042, 3088, 3089, 3518
$NH(CH_3)_2$ rotational constants / GHz	34.70, 9.26, 8.18
$NH(CH_3)_2$ internal rotation	2 CH_3 rotors, V = 14.2 kJ/mol, I = 3.03 amu·Å^2
$NH(CH_3)_2^+$ frequencies / cm^{-1}	*250,* 383, 780, 942, 1036, 1098, 1168, 1185, 1268, 1444, 1471, 1476, 1488, 1494, 1519, 1520, 2912, 2918, 3041, 3042, 3088, 3089, 3518
$NH(CH_3)_2^+$ rotational constants / GHz	40.48, 8.58, 7.76
$NH(CH_3)_2^+$ internal rotation	2 CH_3 free rotors, I = 3.09 amu·Å^2
$NH(CH_3)_2^+$ TS frequencies / cm^{-1}	*160,* 322, 459, 524, 706, 935, 1031, 1075, 1149, 1197, 1250, 1418, 1446, 1459, 1470, 1503, 1761, 3028, 3103, 3129, 3147, 3224, 3491
$NH(CH_3)_2^+$ TS rotational constants / GHz	36.87, 8.91, 8.16
$NH(CH_3)_2^+$ TS reverse barrier / kJ/mol ; critical freq. / cm^{-1}	4.0, 1190
$NH(CH_3)_2^+$ TS internal rotation	1 CH_3 rotor, V = 5.8 kJ/mol, I = 3.11 amu·Å^2
$N(CH_3)_3$ frequencies / cm^{-1}	*260,* 350, 421, 422, 831, 1058, 1059, 1071, 1119, 1119, 1204, 1305, 1306, 1443, 1444, 1482, 1482, 1484, 1491, 1501, 1513, 1513, 2888, 2890, 2906, 3049, 3049, 3054, 3089, 3094, 3094
$N(CH_3)_3$ rotational constants / GHz	8.68, 8.68, 4.91
$N(CH_3)_3$ internal rotation	3 CH_3 rotors, V = 18.2 kJ/mol , I = 3.13 amu·Å^2
$N(CH_3)_3^+$ frequencies / cm^{-1}	*85,* 334, 409, 411, 764, 1013, 1014, 1017, 1018, 1088, 1132, 1293, 1293, 1417, 1420, 1422, 1452, 1452, 1455, 1486, 1486, 1503, 3005, 3005, 3016, 3062, 3064, 3064, 3165, 3168, 3168
$N(CH_3)_3^+$ rotational constants / GHz	8.42, 8.42, 4.57
$N(CH_3)_3^+$ internal rotation	3 CH_3 free rotors, I = 3.22 amu·Å^2
$N(CH_3)_3^+$ TS frequencies / cm^{-1}	*146,* 316, 345, 402, 491, 549, 832, 868, 1012, 1075, 1123, 1165, 1174, 1186, 1328, 1429, 1445, 1448, 1452, 1469, 1474, 1502, 1763, 3022, 3025, 3105, 3118, 3120, 3145, 3147, 3225
$N(CH_3)_3^+$ TS rotational constants / GHz	8.73, 8.37, 4.76
$N(CH_3)_3^+$ TS reverse barrier / kJ/mol ; critical freq. / cm^{-1}	7.4, 1200
$N(CH_3)_3^+$ TS internal rotation	2 CH_3 rotors, V = 6.9 kJ/mol, I = 3.19 amu·Å^2

Frequencies corresponding to (degenerate) internal rotations are in italics. Optimized transition state (TS) frequencies are underlined. *The methylamine internal rotation barrier was decreased to better reproduce the shape of the thermal energy distribution based on the breakdown diagram. ‡Ab initio frequencies. Fit frequencies are discussed in the text.

Figure S1. Potential energy curve of H-loss from monomethylamine at different levels of theory.

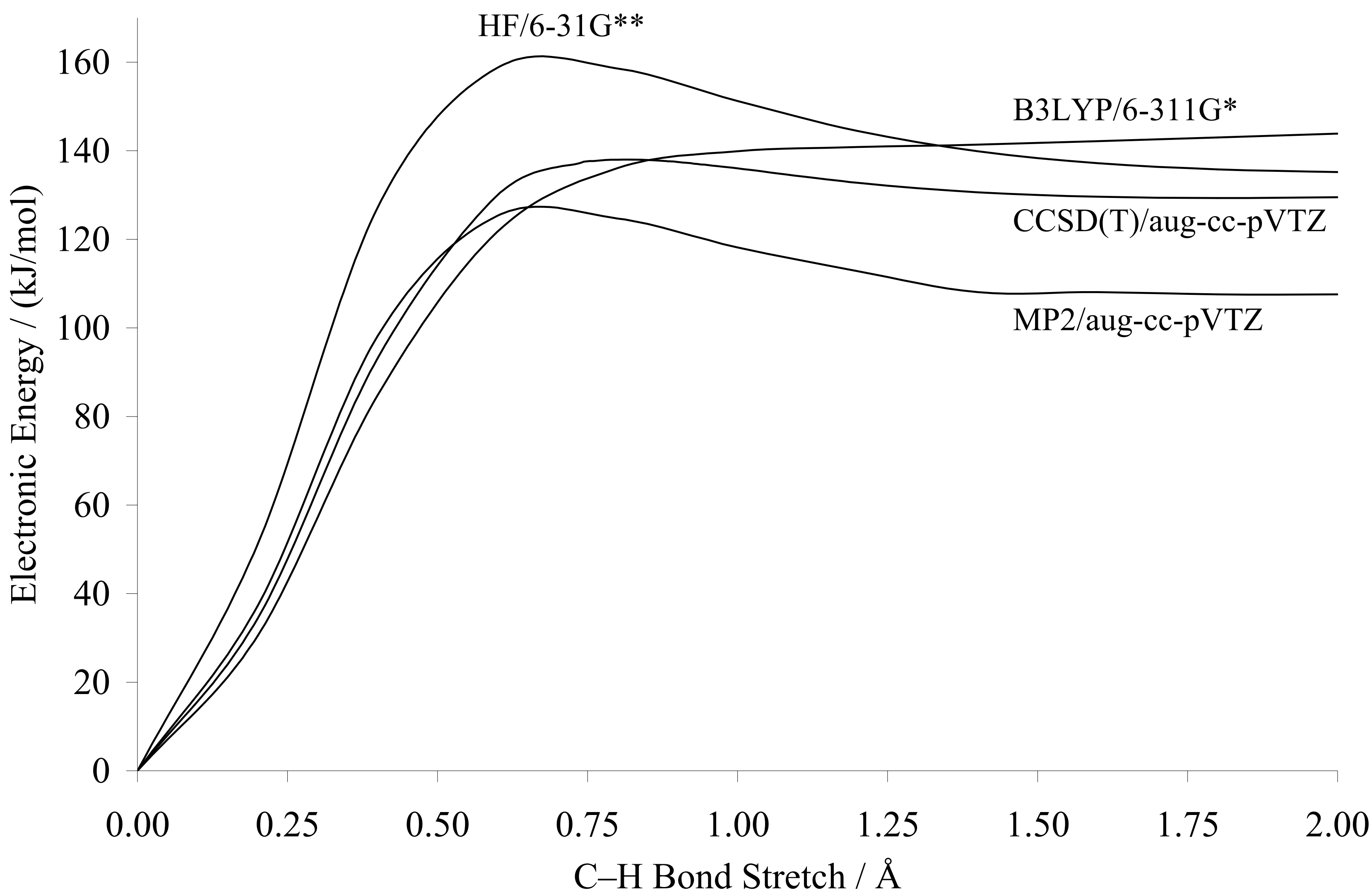

Figure S2. Error analysis obtained by plotting the error in fitting data as a function of the assumed reaction enthalpy. Transition state frequencies were varied to obtain a best fit to the data. The steepness of the goodness of fit curve indicates how sensitive the fit is to the onset.