

Thermochemistry of N–N Containing Ions: a TPEPICO Study of Ionized Methyl- and Tetramethylhydrazine

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TABLE S1: Calculated Vibrational Frequencies and Rotational Constants for the Methylhydrazine Ion, its Transition States and Dissociation Products

TABLE S2: Calculated Vibrational Frequencies and Rotational Constants for the Tetramethylhydrazine Ion, its Transition States and Dissociation Products

TABLE S1: Calculated Vibrational Frequencies and Rotational Constants for the Methylhydrazine Ion, its Transition States and Dissociation Products

	harmonic frequencies (cm ⁻¹) ^a and rotational constants (GHz)
CH ₃ NHNH ₂ ⁺⁺	121, 332, 423, 479, 574, 899, 1061, 1080, 1246, 1356, 1414, 1433, 1443, 1511, 1619, 2943, 3025, 3068, 3376, 3415, 3502, 44.7 GHz, 9.5 GHz, 8.3 GHz
CH ₂ NHNH ₂ ⁺	280, 496, 644, 683, 950, 976, 1021, 1129, 1328, 1411, 1471, 1636, 1684, 3071, 3188, 3367, 3372, 3482, 58.0 GHz, 10.5 GHz, 9.0 GHz
NHNH ₂ ⁺	1036, 1160, 1212, 1434, 1582, 1714, 3185, 3221, 3315, 210.1 GHz, 35.4 GHz, 30.3 GHz
N ₂ H ₂ ⁺ (cis)	835, 880, 940, 2027, 3002, 3059, 458.1 GHz, 39.8 GHz, 36.6 GHz
N ₂ H ₂ ⁺ (iso)	948, 1056, 1489, 1693, 3036, 3129, 311.2 GHz, 39.9 GHz, 35.4 GHz
N ₂ H ₂ ⁺ (trans)	887, 971, 1188, 1932, 3102, 3112, 449.2 GHz, 39.8 GHz, 36.5 GHz
CH ₃ [•]	500, 1370, 1370, 3011, 3178, 3178, 142.2 GHz, 284.5 GHz, 284.5 GHz
CH ₄	1314, 1314, 1314, 1522, 1522, 2926, 3028, 3028, 3028, 157.0 GHz, 157.0 GHz, 157.0 GHz
transition states for hydrogen loss	
TS(45) ₁ (<i>R</i> * = 2.297 Å)	214, 242, 324, 496, 666, 689, 926, 958, 1017, 1125, 1327, 1399, 1464, 1637, 1651, 3075, 3193, 3368, 3380, 3480, 36.8 GHz, 9.1 GHz, 8.4 GHz
TS(45) ₂ (<i>R</i> * = 2.197 Å)	241, 277, 367, 496, 675, 683, 921, 956, 1018, 1124, 1326, 1393, 1461, 1634, 1639, 3075, 3193, 3369, 3382, 3481, 37.8 GHz, 9.2 GHz, 8.4 GHz
TS(45) ₃ (<i>R</i> * = 2.097 Å)	257, 334, 431, 495, 670, 688, 912, 956, 1019, 1121, 1326, 1383, 1456, 1617, 1636, 3073, 3192, 3370, 3385, 3484, 38.8 GHz, 9.2 GHz, 8.4 GHz
TS(45) ₄ (<i>R</i> * = 1.997 Å)	274, 400, 488, 525, 648, 706, 899, 962, 1023, 1116, 1325, 1367, 1449, 1595, 1633, 3072, 3191, 3373, 3389, 3489, 39.7 GHz, 9.3 GHz, 8.4 GHz
transition states for methyl loss	
TS(31) ₁ (<i>R</i> * = 4.661 Å)	20, 64, 91, 101, 109, 834, 840, 1073, 1145, 1377, 1378, 1407, 1486, 1668, 3019, 3199, 3199, 3258, 3262, 3403, 43.2 GHz, 1.8 GHz, 1.7 GHz
TS(31) ₂ (<i>R</i> * = 4.461 Å)	21, 71, 99, 113, 122, 835, 843, 1075, 1146, 1377, 1378, 1407, 1486, 1668, 3019, 3199, 3199, 3258, 3262, 3402, 41.6 GHz, 1.9 GHz, 1.9 GHz
TS(31) ₃ (<i>R</i> * = 4.361 Å)	22, 75, 103, 120, 129, 835, 844, 1076, 1146, 1378, 1378, 1407, 1486, 1668, 3019, 3198, 3199, 3257, 3261, 3401, 41.0 GHz, 2.0 GHz, 2.0 GHz
TS(31) ₄ (<i>R</i> * = 4.061 Å)	28, 87, 121, 147, 154, 838, 849, 1079, 1146, 1377, 1378, 1407, 1487, 1669, 3019, 3197, 3199, 3256, 3261, 3400, 39.3 GHz, 2.3 GHz, 2.2 GHz
TS(31) ₅ (<i>R</i> * = 3.761 Å)	29, 102, 140, 176, 184, 844, 852, 1080, 1146, 1377, 1378, 1406, 1487, 1668, 3018, 3196, 3199, 3256, 3261, 3399, 38.2 GHz, 2.6 GHz, 2.6 GHz
TS(31) ₆ (<i>R</i> * = 3.661 Å)	30, 107, 147, 187, 194, 846, 853, 1079, 1146, 1377, 1378, 1406, 1486, 1668, 3018, 3196, 3199, 3256, 3261, 3400, 37.9 GHz, 2.8 GHz, 2.7 GHz
TS(31) ₇ (<i>R</i> * = 3.561 Å)	30, 113, 154, 198, 206, 847, 854, 1078, 1145, 1377, 1378, 1405, 1486, 1668, 3018, 3196, 3199, 3257, 3262, 3400, 37.6 GHz, 2.9 GHz, 2.8 GHz
TS(31) ₈ (<i>R</i> * = 3.061 Å)	28, 151, 211, 274, 279, 829, 887, 1066, 1144, 1376, 1380, 1399, 1478, 1665, 3016, 3193, 3201, 3265, 3267, 3407, 36.6 GHz, 3.8 GHz, 3.6 GHz
TS(31) ₉ (<i>R</i> * = 2.661 Å)	35, 193, 281, 387, 400, 769, 949, 1037, 1143, 1373, 1379, 1383, 1459, 1657, 3016, 3193, 3201, 3278, 3284, 3426, 36.4 GHz, 4.7 GHz, 4.5 GHz
TS(31) ₁₀ (<i>R</i> * = 2.561 Å)	41, 206, 302, 430, 449, 740, 974, 1022, 1142, 1369, 1374, 1384, 1451, 1654, 3016, 3193, 3202, 3284, 3292, 3433, 36.4 GHz, 5.0 GHz, 4.7 GHz
TS(31) ₁₁ (<i>R</i> * = 2.461 Å)	51, 221, 322, 484, 507, 700, 1000, 1004, 1140, 1356, 1374, 1385, 1442, 1649, 3016, 3193, 3202, 3291, 3302, 3443, 36.5 GHz, 5.3 GHz, 5.0 GHz
estimated transition states for methane loss ^{b,c}	
TS(30) ₁ (fit 1)	45, 123, 157, 177, 212, 39.3 GHz, 2.3 GHz, 2.2 GHz
TS(30) ₂ (fit 2)	42, 116, 148, 168, 201, 39.3 GHz, 2.3 GHz, 2.2 GHz
TS(30) ₃ (fit 3)	40, 109, 140, 158, 189, 39.3 GHz, 2.3 GHz, 2.2 GHz

^a Vibrational frequencies calculated at the B3-LYP/6-31+G(d) level of theory, scaled by 0.9614. ^b Only the five lowest vibrational frequencies were scaled to get a good fit of the breakdown curves. The transition states were estimated using the methylhydrazine ion vibrational frequencies, see text for details. ^c Rotational constants estimated from TS(31)₄ (*R** = 4.061 Å).

TABLE S2: Calculated Vibrational Frequencies and Rotational Constants for the Tetramethylhydrazine Ion, its Transition States and Dissociation Products

	harmonic frequencies (cm ⁻¹) ^a and rotational constants (GHz)
(CH ₃) ₂ NN(CH ₃) ₂ ⁺⁺	76, 85, 112, 151, 151, 156, 179, 322, 404, 443, 484, 678, 855, 1018, 1028, 1057, 1068, 1077, 1084, 1102, 1163, 1204, 1313, 1397, 1402, 1417, 1420, 1438, 1442, 1442, 1442, 1460, 1460, 1465, 1466, 1504, 2940, 2941, 2943, 2944, 3025, 3026, 3030, 3030, 3059, 3062, 3064, 3066, 4.4GHz, 3.3GHz, 2.0 GHz
(CH ₃) ₂ NNCH ₃ ⁺	85, 135, 188, 274, 327, 409, 468, 556, 721, 950, 967, 1002, 1075, 1118, 1133, 1151, 1233, 1356, 1386, 1395, 1406, 1424, 1432, 1436, 1453, 1464, 1641, 2936, 2962, 2972, 2990, 3039, 3055, 3060, 3090, 3097, 8.4 GHz, 4.0 GHz, 2.9 GHz
C ₃ H ₈ N ₂ ⁺⁺ isomer I (C ₁)	78, 120, 166, 330, 447, 454, 534, 548, 802, 858, 918, 953, 1041, 1068, 1115, 1135, 1238, 1341, 1362, 1409, 1430, 1435, 1439, 1453, 1496, 2892, 2950, 2987, 3067, 3078, 3085, 3094, 3203, 9.7 GHz, 4.0 GHz, 3.0 GHz
C ₃ H ₈ N ₂ ⁺⁺ isomer I (C _s)	81, 109, 163, 328, 445, 453, 534, 547, 801, 858, 918, 952, 1040, 1067, 1115, 1133, 1237, 1341, 1361, 1409, 1430, 1434, 1438, 1453, 1495, 2891, 2949, 2987, 3067, 3079, 3084, 3094, 3203, 9.7GHz, 4.0 GHz, 3.0 GHz
C ₃ H ₈ N ₂ ⁺⁺ isomer II	18, 174, 208, 323, 463, 469, 544, 588, 753, 864, 939, 958, 1037, 1097, 1100, 1128, 1229, 1348, 1367, 1400, 1425, 1432, 1449, 1461, 1494, 2895, 2950, 2981, 3065, 3067, 3075, 3091, 3205, 8.8 GHz, 4.4 GHz, 3.0 GHz
C ₃ H ₈ N ₂ ⁺⁺ isomer III	77, 109, 120, 248, 338, 385, 468, 662, 739, 992, 999, 1016, 1030, 1094, 1115, 1215, 1271, 1390, 1392, 1418, 1422, 1433, 1441, 1452, 1535, 2929, 2939, 3008, 3012, 3024, 3071, 3082, 3140, 8.4 GHz, 4.3 GHz, 3.0 GHz
C ₃ H ₈ N ₂ ⁺⁺ isomer IV	77, 151, 156, 183, 270, 324, 567, 736, 750, 867, 921, 1045, 1057, 1108, 1109, 1237, 1296, 1367, 1375, 1398, 1411, 1425, 1439, 1453, 1889, 2954, 2955, 2962, 2998, 3029, 3039, 3048, 3063, 15.5 GHz, 2.6 GHz, 2.3 GHz
C ₃ H ₈ N ₂ ⁺⁺ isomer V	34, 126, 167, 186, 297, 433, 488, 607, 845, 866, 937, 1054, 1069, 1114, 1129, 1184, 1334, 1368, 1401, 1417, 1419, 1427, 1432, 1468, 1678, 2933, 2942, 2983, 3000, 3030, 3057, 3070, 3349, 21.3 GHz, 2.3 GHz, 2.2 GHz
C ₃ H ₈ N ₂ ⁺⁺ isomer VI	123, 144, 190, 269, 314, 430, 645, 774, 922, 983, 1051, 1059, 1096, 1117, 1126, 1174, 1174, 1382, 1387, 1417, 1420, 1435, 1438, 1449, 1515, 2927, 2927, 3016, 3030, 3031, 3074, 3075, 3142, 7.8 GHz, 4.9 GHz, 3.4 GHz
C ₃ H ₈ N ₂ ⁺⁺ isomer VII	144, 195, 340, 351, 404, 407, 555, 690, 771, 801, 926, 963, 967, 1043, 1071, 1194, 1208, 1287, 1345, 1384, 1393, 1423, 1434, 1448, 1463, 2942, 2957, 3006, 3025, 3025, 3053, 3302, 3321, 6.6 GHz, 5.5 GHz, 3.8 GHz
C ₃ H ₈ N ₂ ⁺⁺ isomer VIII	157, 208, 312, 458, 616, 751, 822, 858, 885, 887, 932, 1013, 1084, 1160, 1195, 1204, 1240, 1293, 1296, 1313, 1441, 1451, 1457, 1468, 1484, 2950, 2956, 2990, 3024, 3035, 3051, 3422, 3447, 7.2 GHz, 7.2 GHz, 3.9 GHz
C ₃ H ₈ N ₂ ⁺⁺ isomer IX	106, 230, 329, 371, 582, 633, 750, 778, 847, 910, 942, 948, 1074, 1088, 1168, 1182, 1222, 1250, 1288, 1345, 1407, 1435, 1442, 1471, 1601, 2957, 2961, 3015, 3016, 3017, 3074, 3362, 3482, 10.7 GHz, 4.5 GHz, 3.4 GHz
CH ₃ [•]	500, 1370, 1370, 3011, 3178, 3178, 142.2 GHz, 284.5 GHz, 284.5 GHz
CH ₄	1314, 1314, 1314, 1522, 1522, 2926, 3028, 3028, 3028, 157.0 GHz, 157.0 GHz
transition states for methyl loss	
TS(73) ₁ (R* = 2.366 Å)	63, 80, 112, 141, 177, 205, 267, 321, 402, 420, 485, 512, 550, 743, 916, 955, 991, 1014, 1064, 1089, 1119, 1155, 1236, 1368, 1376, 1385, 1386, 1396, 1423, 1433, 1437, 1444, 1452, 1458, 1500, 2928, 2953, 2957, 2992, 3016, 3025, 3030, 3072, 3078, 3087, 3182, 3193, 3.8GHz, 2.7 GHz, 1.9 GHz
TS(73) ₂ (R* = 2.466 Å)	54, 81, 101, 129, 171, 191, 268, 321, 400, 406, 422, 465, 551, 743, 866, 953, 988, 1008, 1065, 1089, 1121, 1157, 1235, 1370, 1375, 1383, 1386, 1394, 1422, 1432, 1436, 1443, 1452, 1458, 1516, 2926, 2954, 2958, 2992, 3015, 3027, 3033, 3075, 3080, 3089, 3181, 3193, 3.8 GHz, 2.6 GHz, 1.8 GHz

TS(73) ₃ ($R^* = 2.566 \text{ \AA}$)	45, 85, 92, 113, 167, 181, 267, 321, 349, 368, 409, 456, 553, 743, 824, 953, 985, 1005, 1066, 1090, 1124, 1159, 1234, 1370, 1374, 1381, 1388, 1393, 1421, 1431, 1435, 1442, 1452, 1459, 1533, 2924, 2955, 2959, 2993, 3014, 3029, 3035, 3077, 3081, 3090, 3180, 3191, 3.7 GHz, 2.5 GHz, 1.8 GHz
TS(73) ₄ ($R^* = 2.666 \text{ \AA}$)	54, 82, 95, 101, 165, 174, 266, 305, 318, 326, 408, 458, 555, 742, 789, 952, 983, 1003, 1067, 1091, 1125, 1160, 1234, 1370, 1373, 1380, 1389, 1392, 1420, 1431, 1435, 1440, 1453, 1460, 1549, 2923, 2956, 2960, 2995, 3013, 3031, 3038, 3078, 3082, 3092, 3179, 3190, 3.7 GHz, 2.4 GHz, 1.8 GHz
TS(73) ₅ ($R^* = 2.766 \text{ \AA}$)	62, 74, 92, 98, 163, 172, 261, 276, 287, 325, 408, 460, 556, 741, 760, 951, 981, 1001, 1067, 1092, 1127, 1161, 1233, 1369, 1373, 1379, 1389, 1392, 1419, 1430, 1434, 1440, 1453, 1462, 1562, 2921, 2957, 2961, 2997, 3012, 3032, 3040, 3078, 3083, 3093, 3178, 3189, 3.6 GHz, 2.4 GHz, 1.7 GHz
estimated transition states for methane loss ^{b,c}	
TS(72) ₁ (fit 1)	15, 17, 22, 30, 30, 3.6 GHz, 2.4 GHz, 1.7 GHz
TS(72) ₂ (fit 1)	57, 64, 84, 113, 113, 3.6 GHz, 2.4 GHz, 1.7 GHz
TS(72) ₃ (fit 2)	17, 19, 25, 33, 33, 3.6 GHz, 2.4 GHz, 1.7 GHz
TS(72) ₄ (fit 2)	72, 81, 106, 143, 144, 3.6 GHz, 2.4 GHz, 1.7 GHz
TS(72) ₅ (fit 3)	16, 18, 23, 32, 32, 3.6 GHz, 2.4 GHz, 1.7 GHz
TS(72) ₆ (fit 3)	68, 77, 101, 136, 136, 3.6 GHz, 2.4 GHz, 1.7 GHz
TS(72) ₇ (fit 4)	17, 19, 25, 33, 33, 3.6 GHz, 2.4 GHz, 1.7 GHz
TS(72) ₈ (fit 4)	75, 84, 110, 148, 148, 3.6 GHz, 2.4 GHz, 1.7 GHz

^a Vibrational frequencies calculated at the B3-LYP/6-31+G(d) level of theory, scaled by 0.9614. ^b Only the five lowest vibrational frequencies were scaled to get a good fit of the breakdown curves. The transition states were estimated using the tetramethylhydrazine ion vibrational frequencies, see text for details. ^c Rotational constants estimated from TS(73)₅ ($R^* = 2.766 \text{ \AA}$).