Electronic Supplementary Material

Controlling tunnelling in methane loss from acetone ions by deuteration

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Harmonic vibrational frequencies

Harmonic vibrational frequencies play a role in the RRKM model when calculating densities and numbers of states, as well as in the zero-point-energy isotope effect calculations to convert the acetone-d6 methyl-loss appearance energy to acetone-h6 methyl-loss appearance energy. The densities and numbers of states close to the dissociation threshold, i.e. at large internal energies, will be affected by anharmonic effects significantly, and, combined with the inherent assumptions of RRKM theory, we expect the ab initio results only to be a rough estimate, and the transitional modes, corresponding to bending and rotational motions in the transition state, can be scaled significantly. The methane-loss transition state geometry has been located using MP2 theory; all other geometries have been optimized using DFT with the B3LYP functional. The methyl-loss transition state geometry was optimized at an arbitrarily chosen R(C–C) = 3.25 Å bond length, at which the leaving methyl radical is almost planar already. The frequency analysis at this non-stationary geometry yielded one imaginary frequency corresponding to the reaction coordinate, ca. $40i$ cm^{-1} in both acetone-h6 and -d6.

On the other hand, even though zero point energy scaling factors are not available for the exact methods used, they are typically on the order of 0.97 for similar levels of theory, i.e. very close to unity. Furthermore, ZPE scaling factors are typically evaluated for neutrals, and are hardly benchmarked for ions. In the ZPE isotope effect calculation, not scaling the frequencies adds a small, max. 1.5 meV uncertainty to the ZPE shift, and we feel that a marginal improvement in the accuracy does not justify adding a further step to the data analysis. Thus, the harmonic frequencies are not scaled in ZPE calculations.

Table S1. *Ab initio* harmonic frequencies in cm^{-1} used in the statistical model to calculate the thermal energy distribution of the neutral and the density of states of the parent ion.

CH$_3$COCH$_3$	CD$_3$COCD$_3$	CH$_3$COCH$_3^+$	CD$_3$COCD$_3^+$
66	47	73	52
132	97	133	99
380	319	335	289
490	407	367	348
536	483	475	400
782	670	688	644
884	695	893	679
889	715	900	729
1083	895	1001	846
1116	981	1061	897
1232	1021	1073	923
1386	1052	1299	987
1387	1054	1343	1011
1461	1059	1419	1033
1465	1071	1423	1046
1472	1103	1440	1051
1488	1240	1459	1060
1786	1778	1624	1590
3024	2174	3025	2168
3031	2178	3031	2173
3079	2277	3104	2298
3086	2283	3111	2302
3139	2326	3178	2357
3140	2329	3178	2361

Table S2. Vibrational frequencies in cm^{-1} used in the RRKM rate equation to calculate the number of states of the methyl and methane loss transition states. The lowest five frequencies, i.e. the transitional modes, have been scaled by the factor given in the last row. The same scaling factor has been applied to methyl loss from both actone-h6 and acetone-d6, which leads to no kinetic shift in these channels, in accordance with the experiment. The large amplitude motions in the parent ion are considered low frequency harmonic vibrations, which leads to an overestimated density of states of the parent ion at the dissociation threshold, tightening the transition state. To compensate for this, the transition state transitional frequencies have to be scaled with a rather low factor. The methane loss scaling factor is then determined based on the observed dissociation rates and ketene cation abundances, in the context of the tunneling parameters.

$[CH_3COCH_3-CH_3]^{+\ddagger}$	$[CD_3COCD_3-CD_3]^{+\ddagger}$	$[CH_3COCH_3-CH_4]^{+\ddagger}$
14	*10*	*14*
39	*34*	*39*
48	*36*	*48*
98	*70*	*98*
101	*73*	*101*
358	326	358
405	360	405
803	620	803
894	810	894
1008	827	1008
1037	868	1037
1365	1005	1365
1399	1007	1399
1403	1033	1403
1405	1034	1405
1407	1086	1407
2340	2152	2340
3003	2185	3003
3085	2285	3085
3087	2298	3087
3103	2341	3103
3266	2433	3266
3267	2434	3267
$f = 0.402$		$f = 0.235$

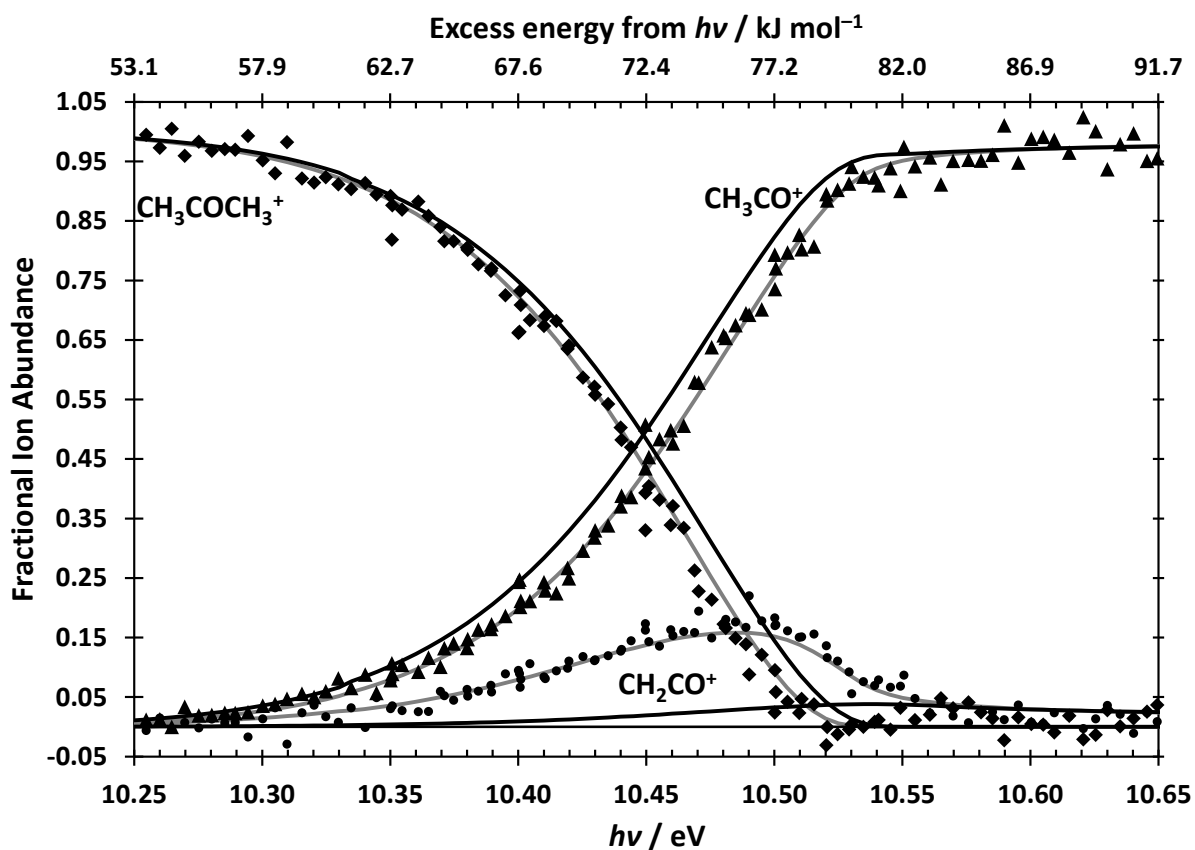# The contribution of tunneling

Figure S1. Simulated breakdown diagram for acetone-h6 without tunneling effects. The light continuous lines correspond to the tunnelling model also shown in the main text. The dark continuous lines are a result of the same model but without tunnelling contributions. While the methyl loss breakdown curve is only slightly outside the experimental scatter, the CH_2CO^+ signal is only reproduced in the model, as constrained by the known thermochemical data, if tunnelling is included. The methane-loss channel is predominantly but not exclusively a result of quantum tunnelling in light acetone.