Isotopic Studies of the Ammonia Decomposition Reaction Mediated by Sodium Amide: Supplementary Information

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EXPERIMENTAL DETAILS

Raman Microscopy

$NaNH_2$ and $NaND_2$ starting materials were characterised by Raman microscopy (Bruker Senterra system with OPUS 7.0 software) using an incident beam of 532 nm. Spectra were collected over 4500–100 cm^{-1}. The spectra are shown in Figure S1. Peaks for $NaNH_2$ can be assigned to NH_2 asymmetric stretch (3265 cm^{-1}), NH_2 symmetric stretch (3213 cm^{-1}), NH_2 bend (1535 cm^{-1}) and lattice modes (532 cm^{-1}, 469 cm^{-1}, 246 cm^{-1}, 177 cm^{-1} and 110 cm^{-1}).[1] There is also a small peak at 3633 cm^{-1} caused by some oxidation (to NaOH) upon transferral to the Raman microscope. The $NaND_2$ spectrum shows similar peaks for ND_2 asymmetric stretch (2432 cm^{-1}), ND_2 symmetric stretch (2359 cm^{-1}), ND_2 bend (1130 cm^{-1}) and lattice modes (397 cm^{-1}, 336 cm^{-1}, 230 cm^{-1}, 173 cm^{-1} and 102 cm^{-1}).

Mass Spectrometry Data Analysis

Calibration runs of 100% pure Ar, N_2, ND_3, NH_3, H_2 and D_2 were carried out in order to ascertain the fragment peak ratios, Table S1. For partially deuterated species (ND_2H, NDH_2, HD), fragmentation patterns were linearly interpolated from their wholly hydrated or deuterated isotopologues. The ammonia species were presumed to be statistically scrambled such that the following relationships were true:

$$f_{NH_3} = (1 - D_{am})^3 f_{am}$$

$$f_{NDH_2} = (1 - D_{am})^2 D_{am} f_{am}$$

$$f_{ND_2H} = (1 - D_{am}) {D_{am}}^2 f_{am}$$

$$f_{ND_3} = {D_{am}}^3 f_{am}$$

Where f_i refers to the fraction of isotopologue i and f_{am} and D_{am} are the total fraction of ammonia species and the deuteration fraction of those species as defined by:

$$f_{am} = f_{NH_3} + f_{NDH_2} + f_{ND_2H} + f_{ND_3}$$

$$D_{am} = \frac{\frac{1}{3} f_{NDH_2} + \frac{2}{3} f_{ND_2H} + f_{ND_3}}{f_{NH_3} + f_{NDH_2} + f_{ND_2H} + f_{ND_3}}$$

As such, for the ammonia species, the two parameters f_{am} and D_{am} were used instead of the four fractional components in order to reduce the number of parameters fitted.

Histograms were fitted to linear combinations of the fragmentation patterns in Table S1, *i.e.* $\sum f_i \boldsymbol{F_i}$, where $\boldsymbol{F_i}$ is the fragmentation pattern for species *i* with some modifications. The modifications to the fragmentation patterns of Table S1 were for the ions where an extra H or D atom had been gathered before detection. These are (including all isotopologues): H_3^+, H_2D^+, HD_2^+, D_3^+, NH_4^+, NDH_3^+, $ND_2H_2^+$, ND_3H^+, ND_4^+. These fragmentation fractions were modified according to the concentrations of H or D species going into the mass spectrometer. As way of example, the m/z peak at 18 for NH_4^+ for a 50/50 mixture of NH_3 and ND_3 would be split into two peak contributions of equal heights at m/z 18 and m/z 19 corresponding to NH_4^+ and NDH_3^+ respectively (similar modifications would be carried out for NDH_2, ND_2H and ND_3). A Levenberg-Marquardt least-squares algorithm was used to minimise the error for the fits.

References

(1) A. Liu and Y. Song, In Situ High-Pressure Study of Sodium Amide by Raman and Infrared Spectroscopies, *J. Phys. Chem. B*, 2011, **115**, 7–13.

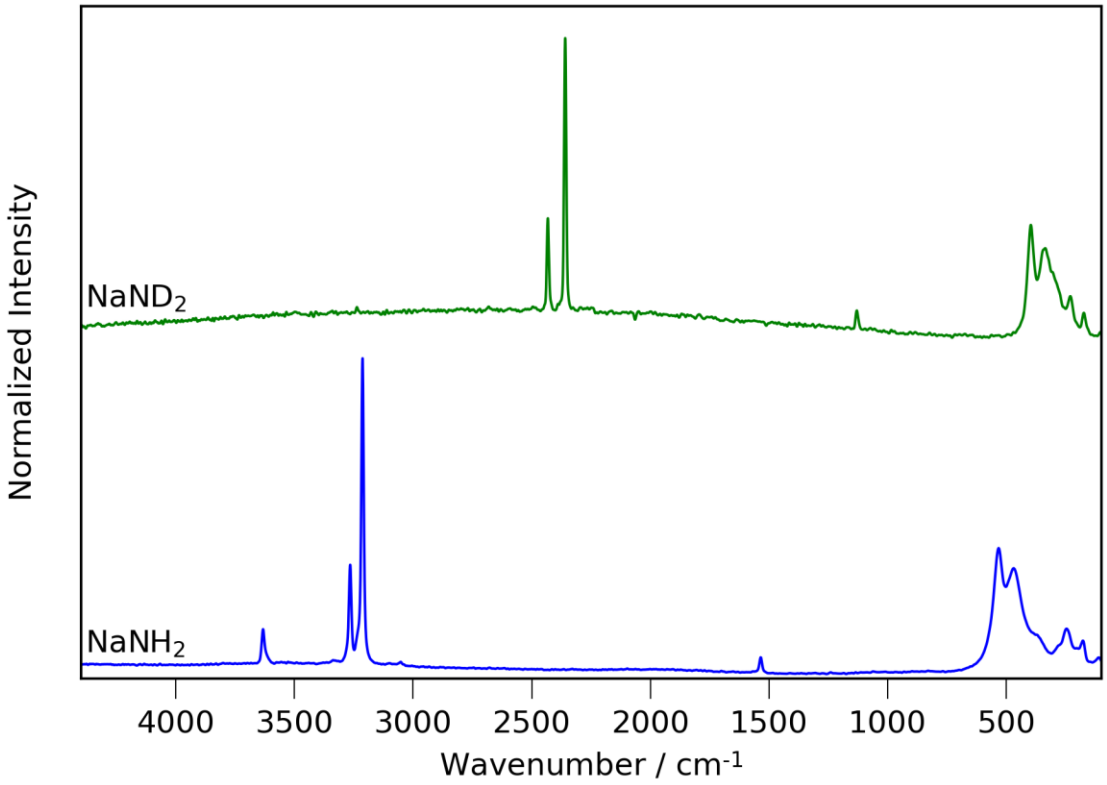

Figure S1: Normalized Raman plot of $NaNH_2$ and $NaND_2$ starting materials.

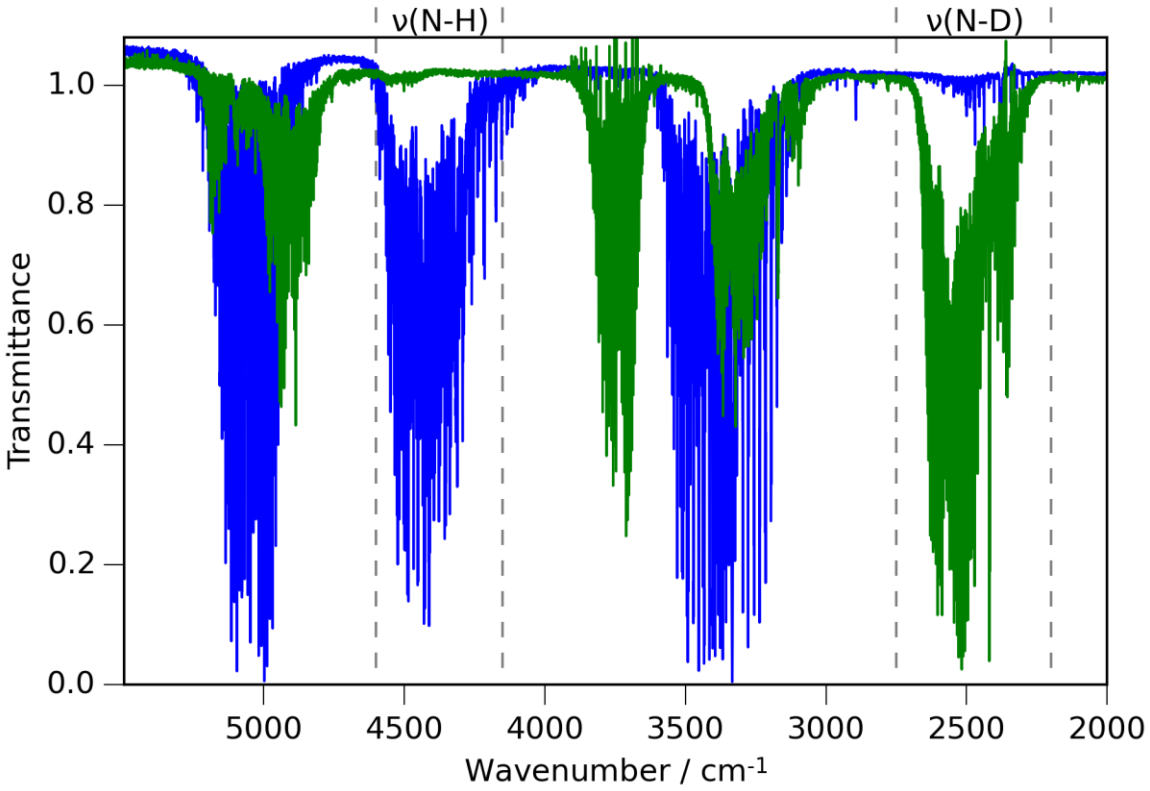

Figure S2: Infrared raw (background-subtracted) gas-phase spectra from the blank reactor at 0 minutes (shown in blue, *i.e.* all ammonia peaks are due to NH_3) and 100 minutes (shown in green, all ammonia peaks due to ND_3). Peak areas calculated for the regions shown within grey dashed lines.

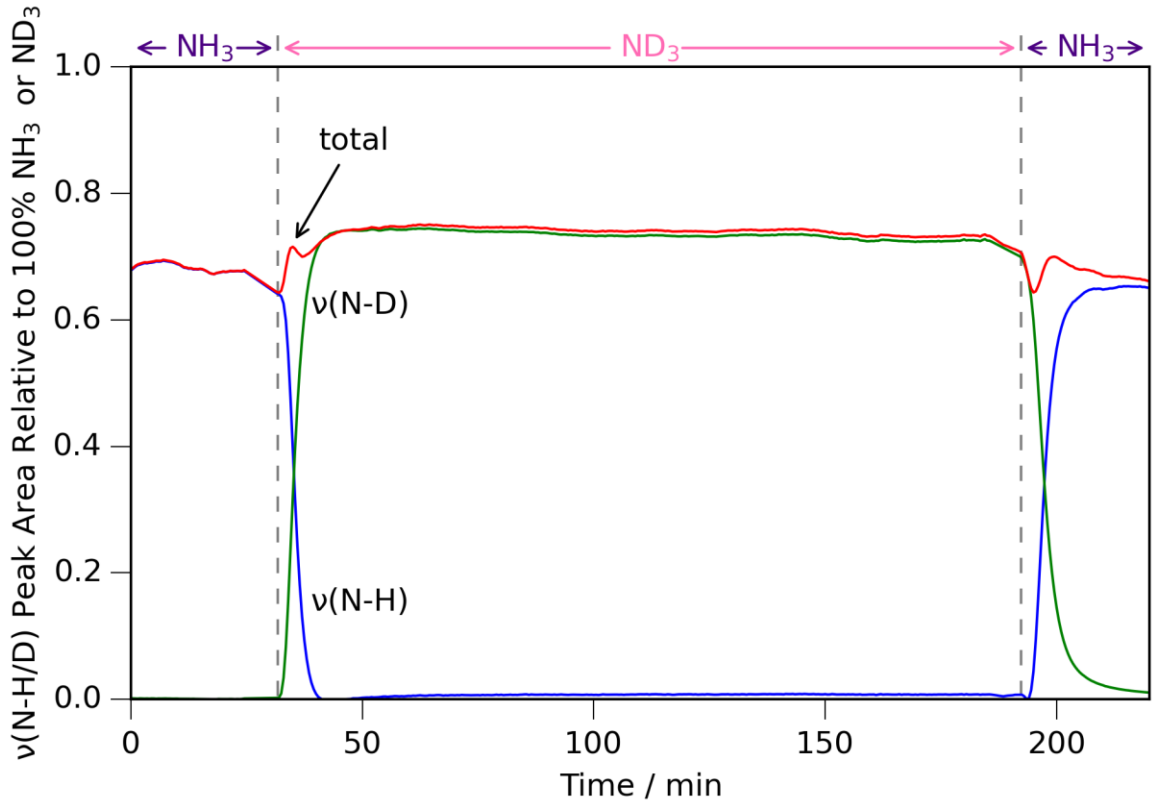

Figure S3: Infrared ν(N-H) and ν(N-D) peak areas relative to 100% NH_3 or ND_3 for the blank reactor run under 25 sccm NH_3 and subsequently 25 sccm ND_3.

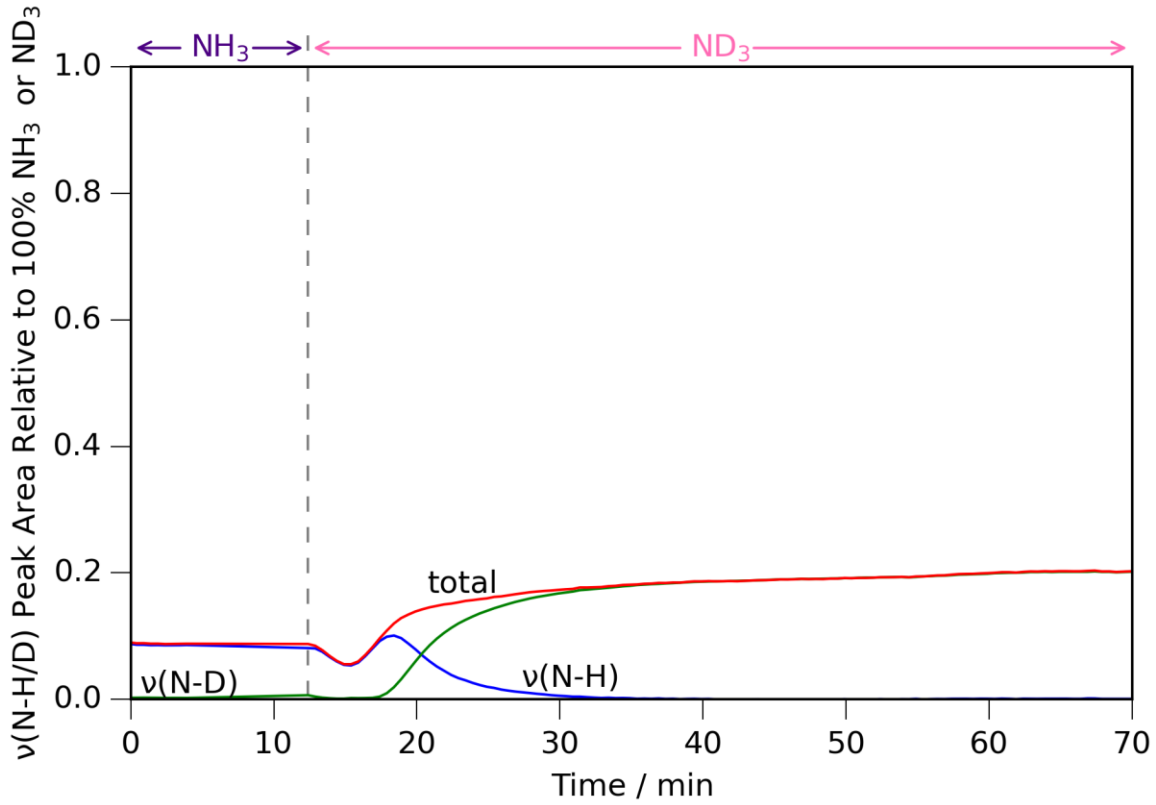

Figure S4: Infrared ν(N-H) and ν(N-D) peak areas relative to 100% NH_3 or ND_3 for $NaNH_2$ run under 25 sccm NH_3 and subsequently 25 sccm ND_3.

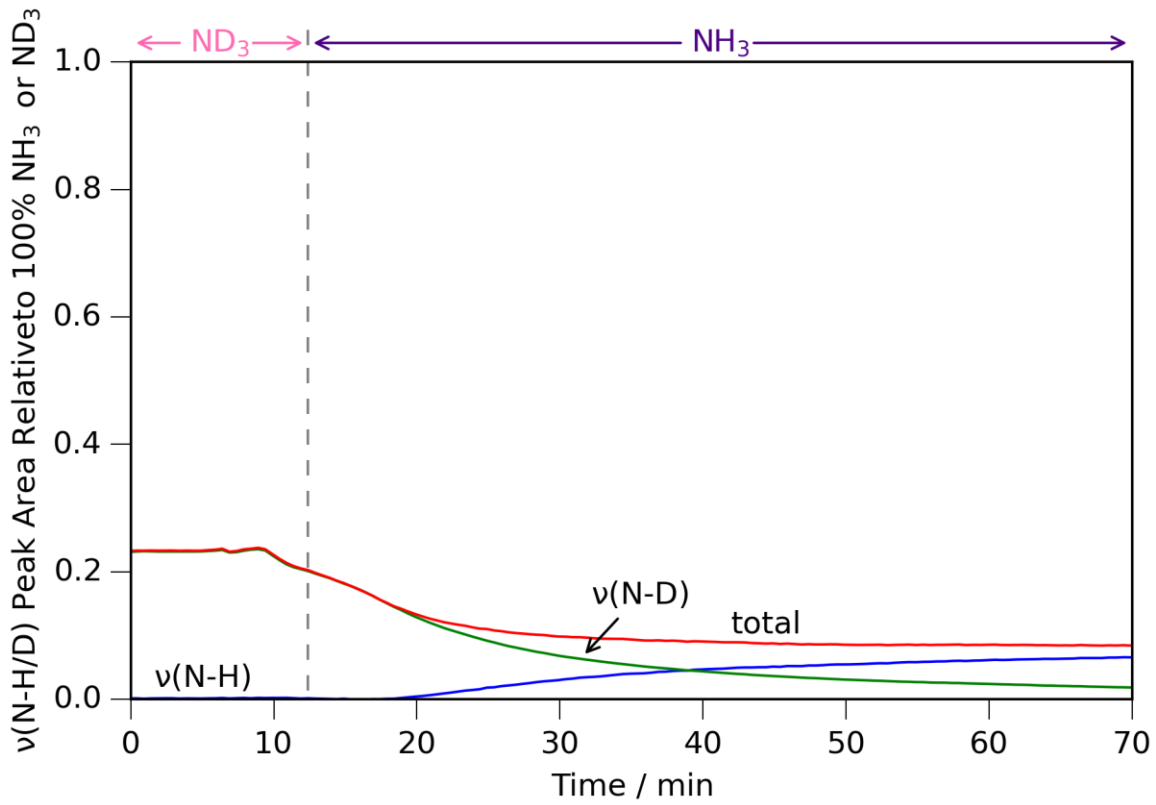

Figure S5: Infrared ν(N-H) and ν(N-D) peak areas relative to 100% NH_3 or ND_3 for $NaND_2$ run under 25 sccm ND_3 and subsequently 25 sccm NH_3.

Table S1: Mass Spectrometry Fragmentation Patterns for Pure Gases

Gas (pure)	m/z	Fraction	Associated Fragment
Ar	40	0.8768	$^{40}Ar^{+}$
	36	0.0026	$^{36}Ar^{+}$
	20	0.1206	$^{40}Ar^{++}$
N_2	29	0.0072	$^{14}N^{15}N^{+}$
	28	0.9369	$^{14}N_2^{+}$
	14	0.0559	$^{14}N^{+}$
ND_3	28	0.0151	N_2^{+}
	22	0.0126	ND_4^{+}
	20	0.5459	ND_3^{+}
	18	0.3816	ND_2^{+}
	16	0.0116	ND^{+}
	14	0.0051	N^{+}
	4	0.0092	D_2^{+}
	2	0.0189	D^{+}
NH_3	28	0.0168	N_2^{+}
	18	0.0269	NH_4^{+}
	17	0.5259	NH_3^{+}
	16	0.3754	NH_2^{+}
	15	0.0175	NH^{+}
	14	0.0066	N^{+}
	2	0.0142	H_2^{+}
	1	0.0168	H^{+}
D_2	6	0.0068	D_3^{+}
	4	0.9802	D_2^{+}
	2	0.0130	D^{+}
H_2	3	0.0072	H_3^{+}
	2	0.7151	H_2^{+}
	1	0.2777	H^{+}