Internal conversion mediated by specific nuclear motions: The nitrogen inversion in amines

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To investigate the influence of amine structure on the internal conversion from S_2 to S_1, three aliphatic amines containing the same number of degrees of freedom, but with different degree of N-substitution, were investigated with femtosecond time-resolved mass spectrometry. As N-substituents lower the excitation energies, and the excitation in all cases is by a 200 nm photon, the S_1 density-of-states in the Franck–Condon region will be high for the more N-alkylated amine. This, according to standard models, should lead to faster internal conversion. The experimental results are in contrast to this, indicating non-ergodic behavior and a coupling of the states by very few molecular vibrations. This was further investigated by substituting differing numbers of hydrogen atoms with deuterium in two amines, one primary and one tertiary, thus freezing the degrees of freedom while altering the N-substituent mass. In both case, deuteration resulted in a significantly longer lifetime of the initially excited state, confirming the importance of the N-inversion motion in the description of the dynamics of internal conversion.

1. Introduction

The amino group is an important functional group in organic chemistry, and it appears multiple places in all living organisms as a building block in proteins and nucleotide bases. Small aliphatic amines are the simplest available model system for understanding internal conversion of the photophysical processes and conformational dynamics of nitrogen-containing systems.

An interesting feature of simple amines is that all the low lying excited state, like those of ammonia, are expected to be of the Rydberg type, as explored in a long series of examinations of the photophysics of amines [1]. The lowest excited state is of the 3s Rydberg type, followed by three 3p type states, two of which are nearly degenerate. Several studies have been made on different aspects of the conformational dynamics in excited amines [2–9].

A study of ten different aliphatic amines combining femtosecond time-resolved mass spectrometry (TR-MS) and calculations [4] found that the degree of N-alkylation has an effect on the photophysics of the amine, reflected in the decay time of the ion currents. Amines with a given degree of N-alkylation showed the same behavior, though no absolute conclusion about the connec-

tion between structure and photophysics was made. This study also established computationally that the vibrational mode corresponding to planarization around the nitrogen is the principal motion taking the wave-packet out of the Franck–Condon area.

A later study of N,N-dimethylisopropylamine (DMIPA) using Rydberg fingerprint spectroscopy established the photophysics of this tertiary amine [5]. Using both time-resolved mass spectrometry and photoelectron spectroscopy, the decay time of the parent ion current was shown be the same as that of the initially excited singlet 3p Rydberg state, reflecting the rate of internal conversion to the lower singlet 3s Rydberg state. The initial rise and following decay time of the 3s state match that of the α-cleavage fragment ion, which is formed on the ion surface after ionization [5]. We can clearly rule out the involvement of triplet states as calculations indicate that the triplet states differ in energy by approximately 0.3 eV, which no longer matches the photoelectron peaks. Moreover, there are no molecular features in aliphatic amines that would drive an ultrafast intersystem crossing; neither by an El Sayed mechanism nor by a heavy-atom effect.

From standard statistical models (Fermi's Golden Rule), the density of states is expected to play the greatest role in deciding the rate of non-radiative transitions such as internal conversion. Larger molecules should thus undergo faster internal conversion than smaller. However, this is not always the case. A series of examinations on cycloketones [10–13] show that cyclobutanone undergoes faster internal conversion than cyclopentanone and

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cyclohexanone. This is explained by a coupling of the excited states by very few specific degrees of freedom [13], corresponding to vibrational movement involving the cyclic structure. This behavior is referred to as non-ergodic internal conversion [10], and we have recently explored the occurrence of this phenomenon in a variety of systems [14].

In the excitation of the smallest amines, one vibrational mode stands out: the wagging motion related to planarization around the nitrogen atom [15,16]. This mode is interesting as the structure in the Franck–Condon region is pyramidal, but moving out of the Franck–Condon region, planarization occur, and the Rydberg minimum structure is planar and cation-like [17]. If the Rydberg states of aliphatic amines are coupled by a vibrational mode, this would be the likely candidate.

In order to investigate the influence of amine structure on the photophysical processes following excitation, we initially studied three aliphatic amines containing the same number of degrees of freedom, but with different degree of N-substitution. The amines were pentylamine (PnA), N-methylbutylamine (MBA) and N,N-dimethylpropylamine (DMPA) - the structures are shown in Fig. 1.

As the results indicated that substituent mass in more important in determining the rate of internal conversion than the density of states, which would agree with coupling of the states by a planarization vibration, we further investigated two series of selectively deuterated amines, shown in Fig. 2 – thus freezing the number of degrees of freedom and changing nothing but the substituent mass.

2. Experimental

Pentylamine (99%) and N-methylbutylamine (96%) was purchased from Sigma–Aldrich and used without further purification. N,N-Dimethylpropylamine was synthesized by Eschweiler-Clarke reaction on propylamine in two equivalents formalin with formic acid and sodium formate. After the reaction, hydroxide was added to give an alkaline solution, and the upper phase was distilled over KOH. N-d-Pentylamine and N,N-d_2-pentylamine was made by stirring pentylamine with sodium and D_2O overnight, followed by distillation of the upper phase (until boiling point 80 °C). The deuterated dimethylisopropylamines were synthesized by dissolving isopropylamine in pyridine and adding ethyl chloroformate. This mixture was then put into water and extracted with diethyl ether, which was then dried with $MgSO_4$ and evaporated. The resulting carbamate was isolated by distillation on oil pump. The carbamate was then dissolved in THF and a small excess of $LiAlD_4$ in dry THF was added, and the mixture was refluxed overnight. KOH was added, giving a white suspension, from with the liquid was decanted, thus obtaining a THF solution of N-methyl-d_3-isopropylamine. Repeating the process gave N,N-dimethyl-d_6-isopropylamine. N-Methyl-d_3-N-methylisopropylamine was obtained by methylating the trideuterated amine in an Eschweiler–Clarke reaction as described for N,N-dimethylpropylamine.

The experimental setup for the TR-MS experiments consists of an ultrafast pulsed laser system and a vacuum chamber fitted with an ion time-of-flight spectrometer and has been described in detail elsewhere [18]. Briefly, a commercial 1 kHz titanium–sapphire amplifier (Spitfire, SpectraPhysics) seeded by a femtosecond
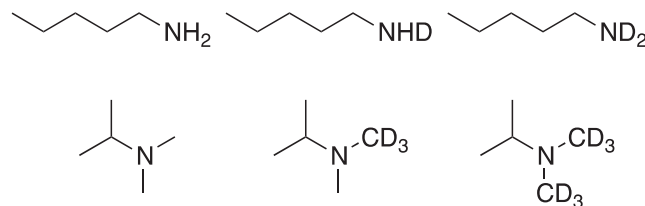
Fig. 1. The three amines studied: Pentylamine (PnA), N-methylbutylamine (MBA) and N,N-dimethylpropylamine (DMPA).

Fig. 2. The two series of deuterated amines studied: the primary PnA series (top) and the tertiary DMIPA series (bottom).

oscillator (Tsunami, SpectraPhysics) delivers 100 fs (fwhm) output pulses at 800 nm and 1.1 mJ. The pulses were split into two and one part was upconverted to the fourth harmonic in three steps of sum-frequency generation in beta barium borate (BBO) crystals to create the pump pulse at 200 nm. The other part was used to pump a TOPAS-C (Light Conversion) to create the 360 nm probe pulse. The pump and probe intensities were 270–300 nJ and 1.5 µJ, respectively. The pulse cross-correlation (FWHM) is about 140 fs.

The first excited state in amines is the $n_N \rightarrow 3s$ transition, and the second excited state is $n_N \rightarrow 3p$. The pump of 200 nm corresponds to the excitation to the $n_N \rightarrow 3p$ excitation. The probe pulse was chosen at 360 nm because this gave the most stable and powerful output from the TOPAS-C in this wavelength region. This gives a total of 9.6 eV for the $(1 + 1')$ pump–probe process. The vertical ionization potential of the primary amine PnA is 9.30 eV [19] and that of DMIPA is 8.20 eV [20]. No ionization potentials have been reported for DMPA or MBA. DMPA is expected to have an ionization potential very similar to that of DMIPA, while the secondary amine MBA is expected to have an ionization potential between the two others in value, which would be similar to other secondary amines (piperidine at 8.66 eV and diethylamine at 8.63 eV[21]).

The transients were fitted using an exponential decay function of the $a \cdot e^{\frac{-t}{\tau_0}}$ type, convoluted with the Gaussian instrument response function of 140 fs. In some cases, a small positive offset was added at positive time delays. The transients corresponding to the fragment ions of the tertiary amines were fitted using a delayed exponential function, $a \cdot \left(1 - e^{\frac{-t}{\tau_0}}\right) \cdot e^{\frac{-t}{\tau_1}}$, where the first time constant (τ_0) corresponds to the initial rise and the second time constant (τ_1) to the following decay.

The calculations were carried out using the GAUSSIAN 09 program package [22]. Vertical excitation energies were calculated using (TD-)B3LYP/6-31+G(2df,p) on minimum energy structures optimized on the same level of theory.

3. Results and discussion

3.1. Calculated excitation energies

The two lowest calculated vertical excitation energies were calculated for PnA, MBA and DMPA. The values are summarized in Table 1. A clear trend of decreasing excitation energies when going to more substituted amines is seen. This is in agreement with the general trend for energy levels in amines, observed for smaller amine systems both experimentally [23] and theoretically [24], as well as mirroring the trend in the vertical ionization potentials,
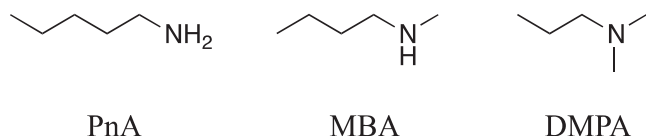
Table 1
Calculated (TD-B3LYP/6-31+G(2df,p)//B3LYP/6-31G(d)) vertical excitation energies for the amines PnA, MBA and DMPA. Values are in eV.

Amine	PnA	MBA	DMPA
S_1 (3s)	5.54	5.34	4.93
S_2 (3p)	6.34	5.84	5.47

see above. This trend is in agreement with the Rydberg nature of the states, with additional substitution on the nitrogen leading to greater stabilization of the cationic character of the Rydberg state compared to the neutral ground state.

3.2. Mass spectra

Mass spectra taken at pump–probe time delay $\Delta t = 0$ ps are shown in Fig. 3 for each of the amines. In each case, the spectrum shows a parent ion (m/z 87 in all cases) as well as a fragment, corresponding to loss of an alkyl radical by α-cleavage, the dominant mass spectroscopic fragmentation pathway for amines [25–27]. It

is evident that the intensity of the signal follows the degree of substitution: The tertiary amine is by far the best, the secondary in-between and the primary not very good in comparison, though the signal was still sufficient to obtain transients for both parent and fragment. For MBA, a smaller peak is seen above the parent ion at m/z 101, likely from a contamination of *N,N*-dimethylbutyl-amine in the sample. As we select the ions by mass in the detection, this is of no consequence for our data.

Mass spectra of the deuterated samples are shown in Fig. 4. The primary amines d2-PnA and d-PnA were present in the same sample and measured simultaneously. The α-cleavage fragment ions are visible at m/z 32 and 31, but the signal-to-noise was
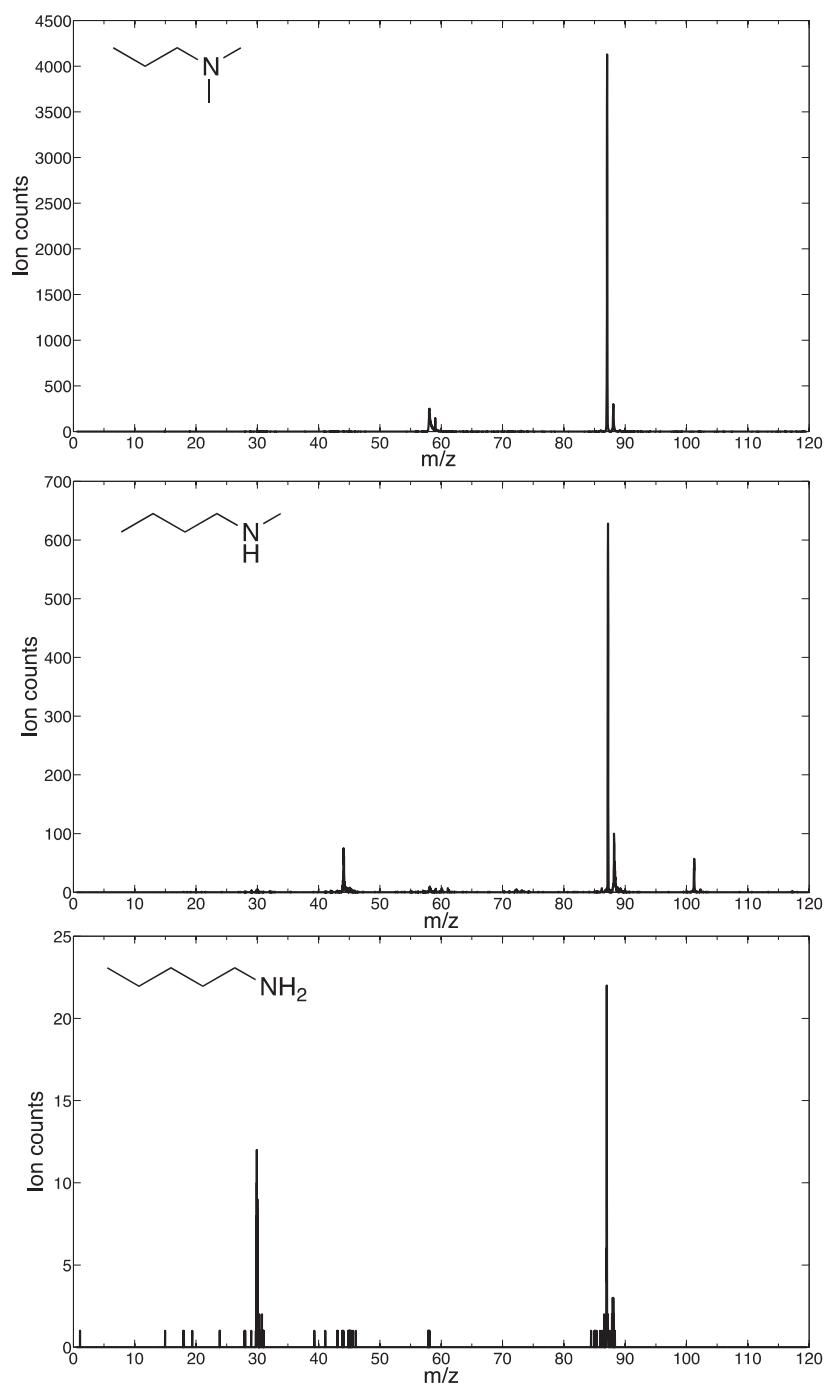

Fig. 3. Mass spectra for DMPA (top), MBA (middle) and PnA (bottom), all taken at $\Delta t = 0$ ps.
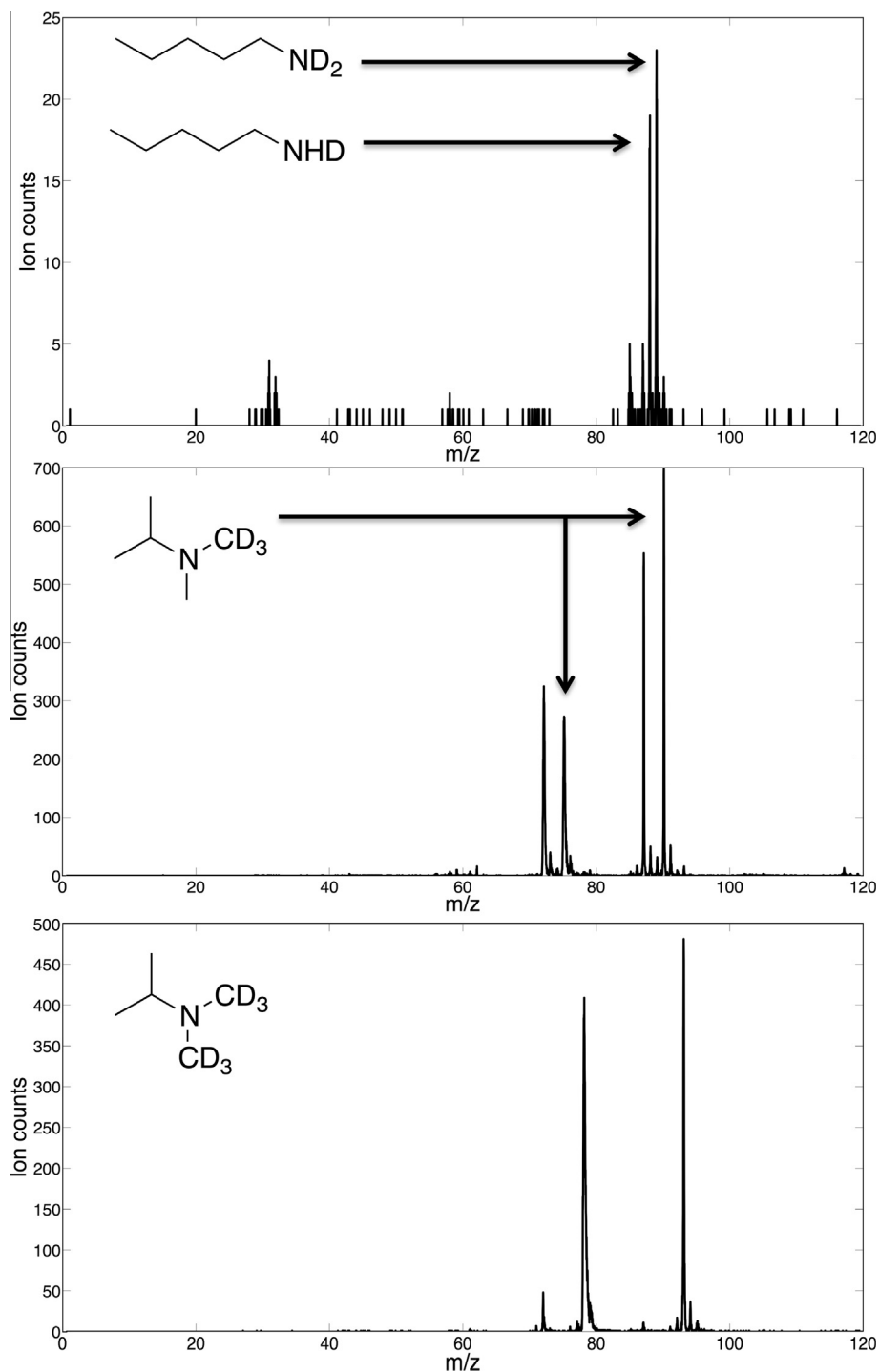
Fig. 4. Mass spectra of the deuterated amines shown in Fig. 2, with indication of the measured masses. Top: d2-PnA and d-PnA (m/z 89 and 88). Middle: d3-DMIPA. Parent (m/z 90) and fragment ion (m/z 75) are indicated by arrows. The two other peaks correspond to the undeuterated DMIPA parent and fragment ions. Botttom: D6-DMIPA, with parent (m/z 93) and fragment (m/z 78) peaks. The spectra of d3-DMIPA and d6-DMIPA were recorded at $\Delta t = 1$ ps.

insufficient to acquire meaningful data for these masses. The deuterated tertiary amines d6-DMIPA and d3-DMIPA both shows a parent and a fragment ion, as expected.

3.3. Time-resolved mass spectrometry

Transients associated with parent and fragment ions of PnA, MBA and DMPA are shown in Figs. 5 and 6 along with the fit to each transient. The time constants obtained from the fits are shown in Table 2.

The transients for DMPA closely resemble those obtained by Gosselin et al. [5]. The decay of the parent ion is mirrored by the rise time of the delayed exponential fit to the fragment, and the time constants are in reasonable agreement with those of the earlier study. For the tertiary amine, the parent ion results from ionization of the initially excited 3p state, and the fragment ion corresponds to the life-time of the S_1 excited state reached by
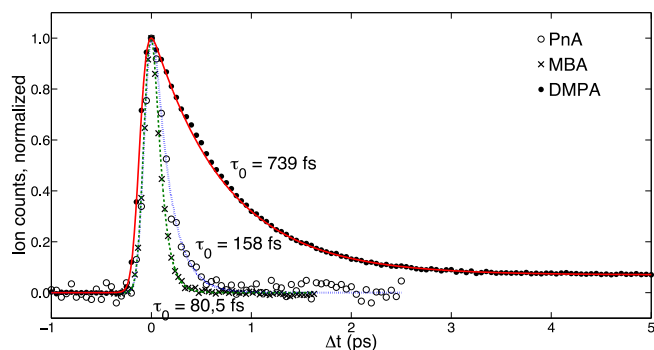
Fig. 5. Ion currents for the parent ions of DMPA (filled circles), MBA (crosses) and PnA (open circles), including the best fit to each (lines – red solid, green dashed and blue dotted, respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
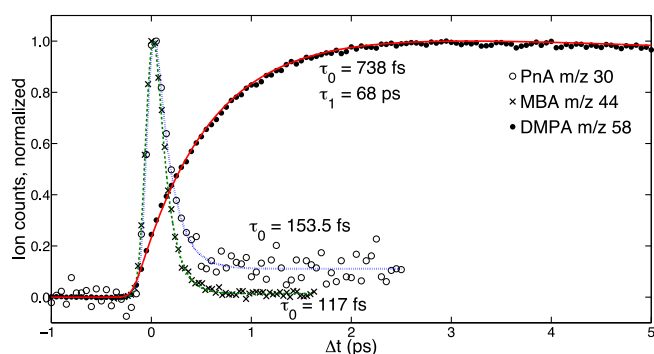

Fig. 6. Temporal evolution of ion currents for the fragment ions of DMPA, MBA and PnA (points), and the best fits (lines). The representation is the same as in Fig. 5.

Table 2
Time constants from the fit to the parent and fragment ion transients of the three amines PnA, MBA and DMPA. For the DMPA fragment, only the first time constant, corresponding to the rise that mirrors the parents decay, is shown. The time constants from the fits have an associated uncertainty of ±15%.

Amine	τ_0/fs	Amine	τ_0/fs	Amine	τ_0/fs
PnA m/z 87	158	MBA m/z 87	80.5	DMPA m/z 87	739
PnA m/z 30	154	MBA m/z 44	117	DMPA m/z 58	738

internal conversion. The 68 ps time constant given for the fragment fit in Fig. 6 corresponds to slow fluorescence decay from the S_1 state [5], which is not the focus of this paper.

For MBA and PnA, the time constants for the parent ion decay are found to be considerably shorter than for DMPA. In contrast to the long lived fragment from the tertiary amine, fragment ion current from both primary and secondary amine decays fast, in keeping with the fact that only tertiary amines have been found to display fluorescence [28,29]. In addition, they both seem to grow in simultaneously with their respective parent ions, a markedly different behavior from the tertiary amine. It seems that for MBA and PnA, both ions are formed by ionization from the same excited state, or that several states are excited simultaneously. We cannot conclude what happens from the present data - this is definitely a topic for future examination. Photoelectron spectroscopy would be a useful tool for establishing which excited states are in play.

In all cases, however, the parent ion reflects the dynamics of the initially excited state, and the time constant for its decay is ascribed to the life-time of the 3p state before internal conversion.

From standard density-of-states arguments, the rate of internal conversion should be fastest for the tertiary amine because the excited states are lower in energy, while in all cases the excitation energy is the same (200 nm), and so a higher density-of-states is reached in the tertiary amine. However, this is not what we find. Instead, the parent ion currents of the tertiary amines show a considerably slower decay than that of secondary and primary. However, if the states are coupled by specific motion, such as the nitrogen planarization mode (sometimes called the 'amine wag'), the mass of the nitrogen substituents would be expected to influence the rate of internal conversion, as heavier substituents are more difficult to move, resulting in slower vibrations, and thus slower internal conversion.

3.4. Labeling experiments

To test this hypothesis, we repeated the experiments on two series of selectively deuterated primary and tertiary amines (Fig. 2). In this way, we increase the weight of the substituents on nitrogen by replacing selected hydrogens with deuterium, either directly bonded to the nitrogen or on the *N*-methyl groups. The substituent mass is the only thing that changes; the number of degrees of freedom is constant.

The transients for the PnA series and the DMIPA series parent ions, respectively, are shown in Figs. 7 and 8 together with the best fits. The time constants obtained from the fit for the parent ions are shown in Table 3. Especially for the primary amines, the fitted time constants for the deuterated species are somewhat uncertain, as the signals did not level off in the range of pump–probe delays measured. However, it is still evident that substitution of one or two *N*-hydrogen(s) in PnA leads to a significant increase in the decay time for the parent ion current.

For the DMIPA series, the same effect is seen, though to a lesser degree, in keeping with a smaller relative increase in mass. For d3-DMIPA the parent ion transient is the only one studied that cannot be fitted by a monoexponential decay, but needs two exponential functions to describe it. This can be done with two different models: two parallel exponential functions (giving time constants of 540 fs and 1.81 ps) or two sequential exponential functions (time constants 481 fs and 1.76 ps). The time constants obtained from each method are very similar, the fits appear equally good, and we cannot decide that one model is better than the other.

We ascribe the need for more components to symmetry breaking by the asymmetric deuteration, which may lead to a perturbation of the wagging motion. Similar observations were made for diethyl amine previously [4]. This asymmetry is also present in both d-PnA and MBA, but a single exponential can fit both of these one reason for this could be that one of the wagging combinations
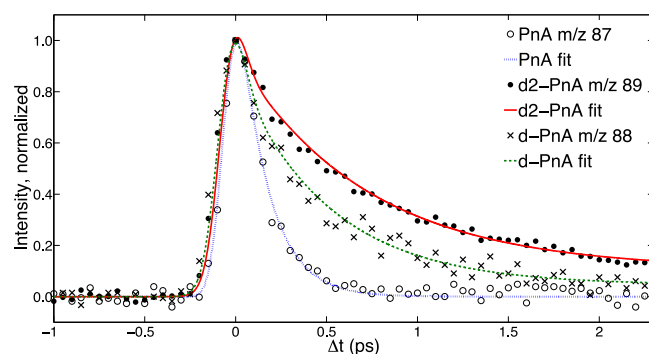

Fig. 7. Transients for the parent ions of the PnA series of amines. The data points are indicated (PnA: open circles, d-PnA crosses, d2-PnA filled circles), and the lines show the best fits.
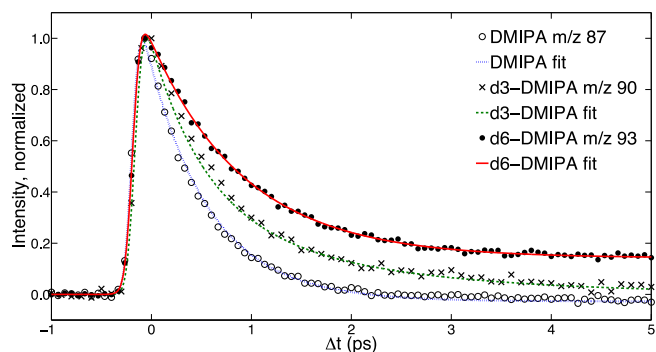
Fig. 8. Transients for the parent ions of the DMIPA series of amines. The data points are indicated (DMIPA: open circles, d3-DMIPA: crosses, d6-DMIPA: filled circles), and the lines show the best fit for DMIPA and d6-DMIPA, and a parallel biexponential fit for d3-DMIPA.

Table 3

Time constants for the two series of deuterated amines. All time constant are from fits to the parent ion except for D3-DMIPA, where the constant is obtained from the rise of the fragment ion (not shown). The time constants have an associated uncertainty of ±15%.

Primary	τ_0/fs	Tertiary	τ_0/fs
PnA	158	DMIPA	619
d-PnA	503	d3-DMIPA	756
d2-PnA	789	d6-DMIPA	936

is not in play. In the two latter cases the substituents differ significantly more compared to CH_3 versus CD_3. The fragment, however, behaves like the other DMIPA fragments and can be fitted by a delayed monoexponential. For DMIPA and d6-DMIPA the rise time of the fragment corresponds to the decay of the parent, as expected from Ref. [5]. The d3-DMIPA fragment can be fitted by the same model, giving a time constant of 756 fs, which is in between those obtained for DMIPA and d6-DMIPA.

4. Conclusions

TR-MS transients obtained for the parent and fragment ions of three aliphatic amines show that, contrary to the expectation based on a density-of-state argument, the initially excited 3p state undergoes internal conversion to 3s faster for the less substituted amines. This can be explained by a non-ergodic coupling of the states via specific nuclear motion. In the case of the amines, a likely vibration is the amine wag leading to planarization around nitrogen. The frequency of this vibration is strongly dependent on the mass of the *N*-substituent, thus explaining the observation. This is further supported by experiments performed on the deuterated amines d-PnA, d2-PnA, d3-DMIPA and d6-DMIPA, where deuteration on nitrogen or the nitrogen alkyl substituents is seen to dramatically decrease the rate of internal conversion.

Studies using photoelectron spectroscopy could add further to the understanding of the photophysics of simple amines, especially the different behavior observed for the fragment ions for the sec-

ondary and primary amines. We have recently performed such experiments using time-resolved photoelectron velocity map imaging on the amines from this study. The results point to the lowest excited states of the primary and secondary amines being predissociative by coupling with a σ^* state. In addition, it would be interesting to perform experiments with varying pump wavelengths to investigate the effect of the exact initial vibronic state and the related density-of-states.

References

[1] M.B. Robin, Higher Excited States of Polyatomic Molecules I, Academic Press, New York, 1974.
[2] R.A. Beecroft, R.S. Davidson, J. Chem. Soc., Perkin. Trans. II (1985) 1063.
[3] A.M. Halpern, B.R. Ramachandran, J. Phys. Chem. 96 (1992) 9832.
[4] T.I. Sølling, C. Kötting, A.H. Zewail, J. Phys. Chem. A 107 (2003) 10872.
[5] J.L. Gosselin, M.P. Minitti, F.M. Rudakov, T.I. Sølling, P.M. Weber, J. Phys. Chem. A 110 (2006) 4251.
[6] J.D. Cardoza, F.M. Rudakov, P.M. Weber, J. Phys. Chem. A 112 (2008) 10736.
[7] S. Deb, M.P. Minitti, P.M. Weber, J. Chem. Phys. 135 (2011) 044319.
[8] S. Deb, B.A. Bayes, M.P. Minitti, P.M. Weber, J. Phys. Chem. A 115 (2011) 1804.
[9] A.E. Boguslavskiy, M.S. Schuurman, D. Townsend, A. Stolow, Faraday Discuss. 150 (2011) 419.
[10] E.W.G. Diau, J. Herek, Z.H. Kim, A.H. Zewail, Science 279 (1998) 847.
[11] T.S. Kuhlman, T.I. Sølling, K.B. Møller, ChemPhysChem 13 (2012) 820.
[12] T.S. Kuhlman, S.P.A. Sauer, T.I. Sølling, K.B. Møller, J. Phys. Chem. A 137 (2012) 22A522.
[13] T.S. Kuhlman, M. Pittelkow, T.I. Sølling, K.B. Møller, Angew. Chem. Int. Ed. 52 (2013) 2247.
[14] T.I. Sølling, T.S. Kuhlman, A.B. Stephansen, L.B. Klein, K.B. Møller, ChemPhysChem 15 (2014) 249.
[15] D.P. Taylor, E.R. Bernstein, J. Chem. Phys. 103 (1995) 10453.
[16] M.J. Hubin-Franskin, J. Delwiche, A. Giulani, M.P. Ska, F. Motte-Tollet, I.C. Walker, N.J. Mason, J.M. Gingell, N.C. Jones, J. Chem. Phys. 116 (2002) 9261.
[17] R.S. Mulliken, J. Chem. Phys. 3 (1935) 506.
[18] N. Rusteika, K.B. Møller, T.I. Sølling, Chem. Phys. Lett. 461 (2008) 193.
[19] M. Takahashi, I. Watanabe, S. Ikeda, J. Phys. Chem. 87 (1983) 5059.
[20] S.F. Nelsen, J. Org. Chem. 49 (1984) 1891.
[21] D.H. Aue, H.M. Webb, M.T. Bowers, J. Am. Chem. Soc. 98 (1976) 311.
[22] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision B.01, Gaussian Inc., Wallingford, CT, 2009.
[23] E. Tannenbaum, E.M. Coffin, A.J. Harrison, J. Chem. Phys. 21 (1953) 311.
[24] A. Osted, J. Kongsted, O. Christiansen, J. Phys. Chem. A 109 (2005) 1430.
[25] R.S. Gohlke, F.W. McLafferty, Anal. Chem. 31 (1981) 1281.
[26] S. Hammerum, Tetrahedron Lett. 22 (1981) 157.
[27] R.D. Bowen, A. Maccoll, Org. Mass Spectrom. 20 (1985) 331.
[28] C.G. Freeman, M.J. McEwan, R.F.C. Claridge, L.F. Phillips, Chem. Phys. Lett. 8 (1971) 77.
[29] C.G. Cureton, K. Hara, C.V. O'Connor, D. Phillips, Chem. Phys. 63 (1981) 31.