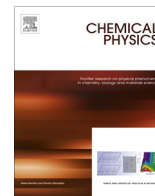




Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

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

Liv B. Klein, Theis I. Sølling*

Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100, Denmark

ARTICLE INFO

Article history:
Available online xxx

Keywords:
Amines
Internal conversion
Non-ergodicity
Time-resolved mass spectrometry

ABSTRACT

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.

© 2014 Published by Elsevier B.V.

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 connection

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 to 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

* Corresponding author. Present address: Maersk Oil Research and Technology Centre, TECH 2 Building, Level 1, Unit 107, Al Gharrafa Street, Al Rayyan, Education City, PO Box 210121, Doha, Qatar.

E-mail address: theis@kiku.dk (T.I. Sølling).

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 is 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 D₂O 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 MgSO₄ and evaporated. The resulting carbamate was isolated by distillation on oil pump. The carbamate was then dissolved in THF and a small excess of LiAlD₄ 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

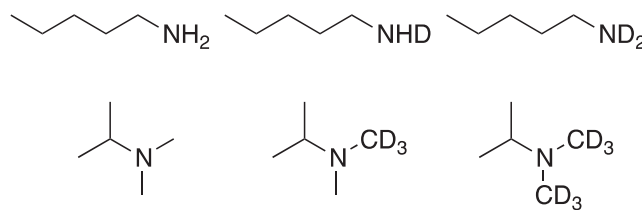


Fig. 2. The two series of deuterated amines studied: the primary PnA series (top) and the tertiary DMIPA series (bottom).

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 $a \cdot e^{-t/\tau_0}$ 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, $a \cdot (1 - e^{-t/\tau_0}) \cdot e^{-t/\tau_1}$, 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

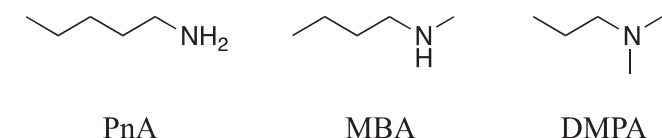


Fig. 1. The three amines studied: Pentylamine (PnA), *N*-methylbutylamine (MBA) and *N,N*-dimethylpropylamine (DMPA).

Download English Version:

<https://daneshyari.com/en/article/5373488>

Download Persian Version:

<https://daneshyari.com/article/5373488>

[Daneshyari.com](https://daneshyari.com)