

Photoelectron spectroscopy of the anions, CH_3NH^- and $(\text{CH}_3)_2\text{N}^-$ and the anion complexes, $\text{H}^-(\text{CH}_3\text{NH}_2)$ and $(\text{CH}_3)_2\text{N}^-[(\text{CH}_3)_2\text{NH}]$

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Abstract

The photoelectron spectra of the negative ions, CH_3NH^- and $(\text{CH}_3)_2\text{N}^-$, as well as the anion complexes, $\text{H}^-(\text{CH}_3\text{NH}_2)$ and $(\text{CH}_3)_2\text{N}^-[(\text{CH}_3)_2\text{NH}]$ have been measured. The adiabatic electron affinities of CH_3NH and $(\text{CH}_3)_2\text{N}$ were determined to be 0.432 ± 0.015 and 0.504 ± 0.030 eV, respectively. The vertical detachment energies of $\text{H}^-(\text{CH}_3\text{NH}_2)$ and $(\text{CH}_3)_2\text{N}^-[(\text{CH}_3)_2\text{NH}]$ were determined to be 1.157 ± 0.025 and 1.1 ± 0.1 eV, respectively, while the anion–neutral dissociation energies of $\text{H}^-(\text{CH}_3\text{NH}_2)$ and $(\text{CH}_3)_2\text{N}^-[(\text{CH}_3)_2\text{NH}]$ were found to be 0.40 and 0.6 eV, respectively. These species are compared with their unmethylated counterparts, NH_2^- , $\text{H}^-(\text{NH}_3)$, and $\text{NH}_2^-(\text{NH}_3)$. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The amidogen and methyl-substituted amidogen radicals and cations play important roles in organic, organometallic, and biological chemistry, and numerous studies have been reported [1–7]. In the case of their anions, however, only NH_2^- has received significant attention, it having been studied by anion photoelectron spectroscopy [8–10]. Very little information is available on the other two anions in this family, CH_3NH^- and $(\text{CH}_3)_2\text{N}^-$. Likewise, no information is available

on the anion–molecule complexes, $\text{H}^-(\text{CH}_3\text{NH}_2)$ and $(\text{CH}_3)_2\text{N}^-[(\text{CH}_3)_2\text{NH}]$. These are analogs to $\text{H}^-(\text{NH}_3)$ and $\text{NH}_2^-(\text{NH}_3)$, both of which have been studied by anion photoelectron spectroscopy [11–13]. Here, we extend previous work on NH_2^- , $\text{H}^-(\text{NH}_3)$, and $\text{NH}_2^-(\text{NH}_3)$, by measuring the anion photoelectron spectra of their methyl-substituted analogs, CH_3NH^- , $(\text{CH}_3)_2\text{N}^-$, $\text{H}^-(\text{CH}_3\text{NH}_2)$, and $(\text{CH}_3)_2\text{N}^-[(\text{CH}_3)_2\text{NH}]$.

2. Experimental

Anion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency laser beam and energy-analyzing the resultant photodetached electron. This

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is a direct approach to determining electron binding energies, and it is governed by the following energy-conserving relationship:

$$h\nu = \text{EBE} + \text{EKE}, \quad (1)$$

where $h\nu$ is the photon energy, EBE is the electron binding energy, and EKE is the measured electron kinetic energy.

Our negative ion photoelectron spectrometer has been described previously [14]. Briefly, anions are mass-selected with a 90° magnetic sector, photodetachment is accomplished with 2.540 eV (488 nm) photons from an argon ion laser which is operated intra-cavity, and electrons are energy-analyzed with a hemispherical electron energy analyzer having a resolution of ~ 25 meV. The photoelectron spectra in this study were calibrated with the well-known photoelectron spectrum [10] of NH_2^- .

In these experiments, negative ions and their complexes were generated in a supersonic expansion ion source in which low energy electrons were injected directly into the expanding jet in the presence of a weak magnetic field. A gas mixture of $\sim 10\%$ monomethylamine in ammonia was used to produce the anions, CH_3NH^- and $\text{H}^-(\text{CH}_3\text{NH}_2)$, while a mixture of $\sim 10\%$ dimethylamine in ammonia was used to generate $(\text{CH}_3)_2\text{N}^-$ and $(\text{CH}_3)_2\text{N}^-(\text{CH}_3)_2\text{NH}$. In both cases, these gas mixtures were expanded through a $20 \mu\text{m}$ nozzle orifice.

3. Results and discussion

3.1. The molecular anions, CH_3NH^- and $(\text{CH}_3)_2\text{N}^-$

The photoelectron spectra of NH_2^- , CH_3NH^- and $(\text{CH}_3)_2\text{N}^-$ are presented in Fig. 1. The photoelectron spectrum of NH_2^- is dominated by a single peak which is assigned as the origin transition. The maximum of this peak in our NH_2^- photoelectron spectrum occurs at an electron binding energy of 0.768 ± 0.010 eV which is in excellent agreement with the accepted value for the adiabatic electron affinity of the amide radical (0.771 ± 0.005 eV) [10]. Much weaker features at higher electron binding energies are

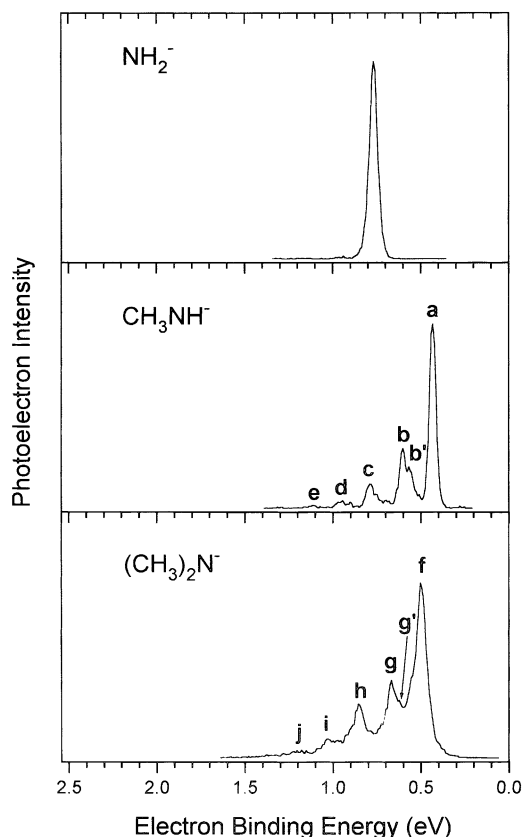


Fig. 1. The anion photoelectron spectra of NH_2^- , CH_3NH^- and $(\text{CH}_3)_2\text{N}^-$, each measured with 2.540 eV photons.

attributed to the symmetric stretch and bend of neutral NH_2 .

There are five resolved and one partially resolved features (labeled **a**, **b**, **b'**, **c**, **d** and **e**) present in the photoelectron spectrum of CH_3NH^- , a monomethyl-substituted analog to NH_2^- . We assigned the most prominent peak (**a**) in the spectrum as the origin transition. The maximum of this peak occurs at an electron binding energy of 0.432 ± 0.015 eV, and we interpret this to be the adiabatic electron affinity (EA) of the CH_3NH radical. The maxima of peaks **b** (EBE = 0.603 eV), **c** (EBE = 0.791 eV), **d** (EBE = 0.945 eV) and **e** (EBE = 1.106 eV) are separated from the maximum in peak **a** by 0.171 eV (1379 cm^{-1}), 0.359 eV (2896 cm^{-1}), 0.513 eV (4138 cm^{-1}) and 0.674 eV (5436 cm^{-1}), respectively, with intervals between

peaks, **b–a**, **c–b**, **d–c**, and **e–d** being 1379, 1517, 1242 and 1298 cm^{-1} , respectively.

Peak **b** is separated from the origin peak **a** by 1379 cm^{-1} , and we assign it as the symmetric deformation (umbrella) vibration [15] of the methyl group in neutral CH_3NH . In hydrocarbons [16], the methyl group's umbrella motion usually occurs in the range 1370–1390 cm^{-1} . The frequency of this band can be altered considerably, however, when an adjacent electronegative atom is present, its range then extending from 1260 to 1450 cm^{-1} . In the closely related molecule, CH_3NH_2 , this vibration is in fact observed [17] at 1430 cm^{-1} , while in the CH_3NH radical [3], it is computed to occur at 1435 cm^{-1} . We attribute the slightly smaller than expected **b–a** spacing that we observe to the effect of peak-pulling by the nearby shoulder peak, **b'**. The maximum of peak **b'** occurs at $\text{EBE} = 0.569$ eV, and its separation from peak **a** is 0.137 eV (1105 cm^{-1}). We assign peak **b'** as being due to the C–N stretching vibration of neutral CH_3NH , since this same vibration [17] in the related molecule, CH_3NH_2 occurs at 1044 cm^{-1} . Based on the similar intervals between adjacent peaks, **b–a**, **c–b**, **d–c**, and **e–d** and on the decreasing intensities of these peaks with increasing electron binding energy, we assign peaks, **c**, **d**, and **e** primarily as overtones of the methyl group deformation vibration. To the extent that these intervals are uneven, it is probably due to the excitation of additional (unresolved or overlapping) vibrational modes in the neutral.

There are five resolved and one partially resolved features (labeled **f**, **g**, **g'**, **h**, **i** and **j**) present in the photoelectron spectrum of $(\text{CH}_3)_2\text{N}^-$, a dimethyl-substituted analog to NH_2^- . We assigned the most prominent peak **f** in the spectrum as the origin transition. The maximum of this peak occurs at an electron binding energy of 0.504 ± 0.030 eV, and we interpret this to be the adiabatic electron affinity of the $(\text{CH}_3)_2\text{N}$ radical. The maxima of peaks **g** ($\text{EBE} = 0.667$ eV), **h** ($\text{EBE} = 0.855$ eV) and **i** ($\text{EBE} = 1.026$ eV) and **j** ($\text{EBE} = 1.189$ eV) are separated from the maximum in peak **f** by 0.163 eV (1315 cm^{-1}), 0.351 eV (2831 cm^{-1}), 0.522 eV (4210 cm^{-1}) and 0.685 eV (5525 cm^{-1}), respectively, with the intervals between peaks, **g–f**, **h–g**, **i–h**, and **j–i** being 1315, 1516, 1379, and 1315 cm^{-1} ,

respectively. The maximum intensity of peak **g'** is located at $\text{EBE} = 0.624$ eV, and it is separated from peak **f** by 0.120 eV (968 cm^{-1}). This spectrum closely resembles that of CH_3NH^- , except for its peaks being shifted to slightly higher EBE and broadened due to the presence of more modes. Because of the close similarity between these spectra, we assign the peaks in the spectrum of $(\text{CH}_3)_2\text{N}^-$ in the same way as in the spectrum of CH_3NH^- , i.e., peak **g** is due to the symmetric deformations of the methyl groups in neutral $(\text{CH}_3)_2\text{N}$, peaks **h**, **i**, and **j** are primarily overtones of this vibration, and feature **g'** is due to the C–N stretching vibration in neutral $(\text{CH}_3)_2\text{N}$. Again, to the extent that the observed intervals are uneven, it is probably due to the excitation of additional (unresolved or overlapping) vibrational modes in the neutral.

The single, narrow peak dominating the spectrum of NH_2^- indicates that the structures of neutral NH_2 and its anion are very similar. While the photoelectron spectra of CH_3NH^- and $(\text{CH}_3)_2\text{N}^-$ also suggest a degree of structural similarity between their neutrals and corresponding anions (as well as one another), the rich Franck–Condon profiles exhibited by these two spectra indicate greater structural differences between their neutrals and anions than between neutral NH_2 and its anion. Clearly, the basis of these differences are the methyl groups. The excess electrons on CH_3NH^- and $(\text{CH}_3)_2\text{N}^-$ must distort the methyl groups' umbrella geometries. Upon photodetachment, these methyl group umbrellas snap back to their original neutral configurations, 'plucking' the affected vibrations, which then appear in their photoelectron spectra. Also, since methyl groups are weak providers of electronic charge, they weakly distort the neighboring C–N bond, giving rise to the excitation of this vibration upon photodetachment.

3.2. The anion–molecule complexes, $\text{H}^-(\text{CH}_3\text{NH}_2)$ and $(\text{CH}_3)_2\text{N}^-[(\text{CH}_3)_2\text{NH}]$

The photoelectron spectrum of $\text{H}^-(\text{CH}_3\text{NH}_2)$ is presented in Fig. 2, along with the photoelectron spectrum of $\text{H}^-(\text{NH}_3)$ for comparison. Our previous photoelectron studies of $\text{H}^-(\text{NH}_3)$ found it

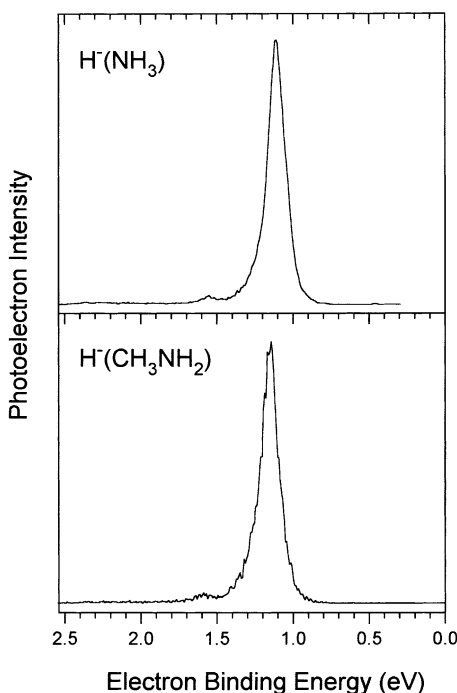


Fig. 2. The anion photoelectron spectra of $\text{H}^-(\text{NH}_3)$ and $\text{H}^-(\text{CH}_3\text{NH}_2)$, both measured with 2.540 eV photons.

to be a anion–molecule complex, with the dominant peak in its spectrum (centered at $\text{EBE} = 1.109$ eV) arising due to the photodetachment of electrons from the solvated hydride ion chromophore within the $\text{H}^-(\text{NH}_3)$ complex [11,12]. This value was taken to be its vertical detachment energy, VDE. A much weaker intensity peak centered at $\text{EBE} = 1.541$ eV was separated from the main peak by 0.432 eV (3484 cm^{-1}), and it was attributed to the excitation of stretching modes in the ammonia solvent. (The symmetric and asymmetric stretches of NH_3 occur at 3336 and 3443 cm^{-1} , respectively.) Since we were probably accessing the neutral $\text{H}(\text{NH}_3)$ potential surface near its dissociation asymptote, with only a shallow van der Waals well nearby, the spectral shift between the center of the dominant peak in the spectrum of $\text{H}^-(\text{NH}_3)$, i.e., its VDE, and the electron affinity of the hydrogen atom ($\text{EA}[\text{H}] = 0.754$ eV) is a measure of the interaction energy between H^- and NH_3 . This value, which is also the anion–neutral dissociation energy of $\text{H}^-(\text{NH}_3)$, is ~ 0.36 eV.

There is a strong similarity between the photoelectron spectra of $\text{H}^-(\text{NH}_3)$ and $\text{H}^-(\text{CH}_3\text{NH}_2)$. In the spectrum of $\text{H}^-(\text{CH}_3\text{NH}_2)$, the most prominent peak occurs at an electron binding energy of 1.157 ± 0.025 eV, which we take to be its VDE. There is also a weaker intensity peak at $\text{EBE} = 1.590$ eV, which is separated from the prominent peak by 0.433 eV (3492 cm^{-1}). The spacings between the major and minor peaks in both spectra are nearly identical. We assign the minor peak in the $\text{H}^-(\text{CH}_3\text{NH}_2)$ spectrum to an excitation of NH_2 stretching modes in CH_3NH_2 . In monomethylamine [17], this occurs at $\sim 3427\text{ cm}^{-1}$. We describe $\text{H}^-(\text{CH}_3\text{NH}_2)$ as an ion–molecule complex composed of an intact hydride ion solvated by a molecule of monomethylamine. Based on the spectral shift between its dominant peak and the EA of the hydrogen atom, the interaction energy between H^- and CH_3NH_2 is ~ 0.40 eV. This implies that monomethylamine binds slightly more strongly to the hydride anion than does ammonia.

Fig. 3 presents the photoelectron spectrum of $(\text{CH}_3)_2\text{N}^-[(\text{CH}_3)_2\text{NH}]$ along with that of $\text{NH}_2^-(\text{NH}_3)$ for comparison. Our previous photoelectron studies of $\text{NH}_2^-(\text{NH}_3)$ found it to be an anion–molecule complex, with the dominant peak in its spectrum (centered at $\text{EBE} = 1.311$ eV) arising due to the photodetachment of electrons from the solvated NH_2^- chromophore within the $\text{NH}_2^-(\text{NH}_3)$ complex [13]. This value was taken to be its vertical detachment energy. A weaker intensity peak centered at $\text{EBE} = 1.754$ eV was separated from the main peak by 0.443 eV (3573 cm^{-1}), and it was attributed to the excitation of stretching modes in the ammonia solvent. The spectral shift between the center of the dominant peak in the $\text{NH}_2^-(\text{NH}_3)$ spectrum and the center of the NH_2^- spectrum is a measure of the interaction energy between NH_2^- and NH_3 , and its value is ~ 0.54 eV.

As was the case for the spectra of $\text{H}^-(\text{NH}_3)$ and $\text{H}^-(\text{CH}_3\text{NH}_2)$, there is also a substantial similarity between the photoelectron spectra of $\text{NH}_2^-(\text{NH}_3)$ and $(\text{CH}_3)_2\text{N}^-[(\text{CH}_3)_2\text{NH}]$. The spectrum of $(\text{CH}_3)_2\text{N}^-[(\text{CH}_3)_2\text{NH}]$ is dominated by a single broad peak, the maximum of which occurs at an EBE of 1.1 ± 0.1 eV. We take this value to be its

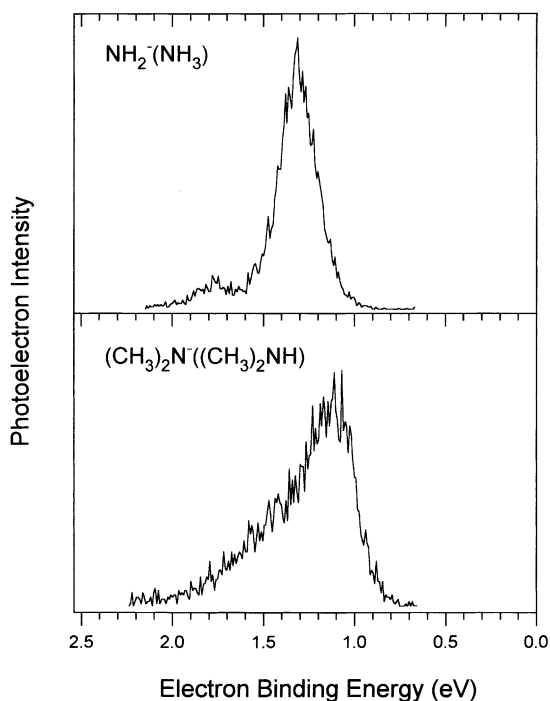


Fig. 3. The anion photoelectron spectra of $\text{NH}_2^-(\text{NH}_3)$ and $(\text{CH}_3)_2\text{N}^-[(\text{CH}_3)_2\text{NH}]$, both measured with 2.540 eV photons.

VDE, and we describe $(\text{CH}_3)_2\text{N}^-[(\text{CH}_3)_2\text{NH}]$ as an anion–molecule complex composed of an intact $(\text{CH}_3)_2\text{N}^-$ anion solvated by a molecule of dimethylamine. The broadening toward the high EBE side of the $(\text{CH}_3)_2\text{N}^-[(\text{CH}_3)_2\text{NH}]$ spectrum is due to several vibrational excitations already evident in the spectrum of its chromophore, $(\text{CH}_3)_2\text{N}^-$ (it has the same gross profile) plus excited intermolecular modes of the complex itself. Based on the spectral shift between its VDE and the EA of the $(\text{CH}_3)_2\text{N}$ radical, the interaction energy between $(\text{CH}_3)_2\text{N}^-$ and $(\text{CH}_3)_2\text{NH}$ is ~ 0.6 eV. The interaction energy between $(\text{CH}_3)_2\text{N}^-$ and

$(\text{CH}_3)_2\text{NH}$ is slightly stronger than that between NH_2^- and NH_3 .

Acknowledgements

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