

INNER SHELL ELECTRON ENERGY LOSS SPECTRA OF THE METHYL AMINES AND AMMONIA

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ABSTRACT

Electron energy loss spectroscopy has been used to obtain the inner shell excitation spectra of the methyl amines CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$ and $(\text{CH}_3)_3\text{N}$ for both the N 1s and C 1s regions. A spectrum of the N 1s region of NH_3 is also presented at higher resolution than previously published data. The C 1s spectra are all very similar and the discrete portions may be assigned to Rydberg transitions. However, features attributable to a σ^* shape resonance are observed just above the N 1s and C 1s ionization edges. The NH_3 spectrum is ascribed to Rydberg transitions. The N 1s spectra of the methyl amines, however, become increasingly dominated by a σ^* resonance in the continuum with increased methylation. The features in the inner-shell spectra are compared with the reported valence-shell optical absorption spectra and support the Rydberg assignment. The inner-shell spectra of $(\text{CH}_3)_3\text{N}$ and NH_3 are also compared with previously published inner shell electron energy loss spectra of NF_3 and the third row phosphorus analogues PF_3 , $\text{P}(\text{CH}_3)_3$ and PH_3 .

INTRODUCTION

Inner shell electron energy loss spectroscopy (ISEELS) provides an effective way of obtaining the core level electronic excitation spectra of gaseous molecules. These excitations occur at energies corresponding to the soft X-ray region of the electromagnetic spectrum [1,2]. In contrast to the valence region, excitation of core (inner shell) electrons into the unoccupied levels provides more definitive information for these levels due to the relative simplicity of the core spectra. Valence shell spectra are frequently complex [3], due to the close proximity of the originating orbitals, which can result in many overlapping transitions. However, the core levels are usually well separated and the transitions can usually be unambiguously assigned [4–7] as originating from a particular level.

In recent studies from this laboratory, the ISEELS spectra of several phosphorus containing compounds were compared [4,5] and the effects of

the ligand on the relative spectral intensities contrasted. Similar comparisons [6] have been made between the ISEELS spectra of $\text{Si}(\text{CH}_3)_4$ and earlier reported spectra of related silicon compounds. The ligand plays an important role in the observed intensity distributions. In contrast to ligands such as H and CH_3 , highly electronegative ligands, for example F, enhance the probability of transitions to virtual valence levels at the expense of those to Rydberg levels. This has also been observed in the ISEELS spectra of NF_3 [7]. Dehmer [8] has rationalized these differences by postulating the formation of an effective potential barrier by the electronegative ligands. Alternatively, these features can be understood in terms of shape resonances caused by the anisotropic nature of the molecular field [9–12]. This latter model is particularly useful in explaining the intensity distributions in molecules such as N_2 where there are no surrounding groups of electronegative ligands. As a continuation of earlier studies on ligand effects the ISEELS spectra of $(\text{CH}_3)_3\text{N}$, which is isoelectronic with NF_3 , are now reported, as well as the spectra of the other related methyl amines, $(\text{CH}_3)_2\text{NH}$ and CH_3NH_2 and also of NH_3 .

To date, the only previously reported inner shell electron excitation spectra of these molecules have been the ISEELS spectra of NH_3 and CH_3NH_2 reported by Wight and Brion [13] and a recent X-ray absorption spectrum of NH_3 [14]. However, there have been several studies on the valence electron excitation spectra. For example, Tannenbaum et al. [15] have reported the UV absorption spectra of the methyl amines up to ~ 8 eV. There have also been numerous studies on NH_3 [16]. The lowest excited states in the valence and inner-shell spectra have been assigned to transitions to levels of mainly $3s$ and $3p$ Rydberg character [13,15]. Salahub [17] has performed semi-empirical MO–CI calculations on these molecules and assigned the lowest valence excitations to HOMO (N lone pair) $\rightarrow \sigma^*$ transitions. However, ab initio calculations on NH_3 [18,19] and $(\text{CH}_3)_3\text{N}$ [19] support the Rydberg assignment. The spectra presented here provide further evidence for the assignment of the lowest electronic transitions to Rydberg levels.

EXPERIMENTAL

All the spectra were obtained using an ISEELS spectrometer situated at the University of British Columbia. The construction and operation of this spectrometer have already been described in detail [20]. The spectra were excited using a monochromated beam of electrons with an impact energy of 2500 eV. The inelastically scattered electrons thus obtained were sampled at a small angle ($\sim 1^\circ$) to suppress back scattering effects in the analyser that can lead to non-spectral background in the inner-shell spectra. Under these (small momentum transfer) conditions, it has been found that

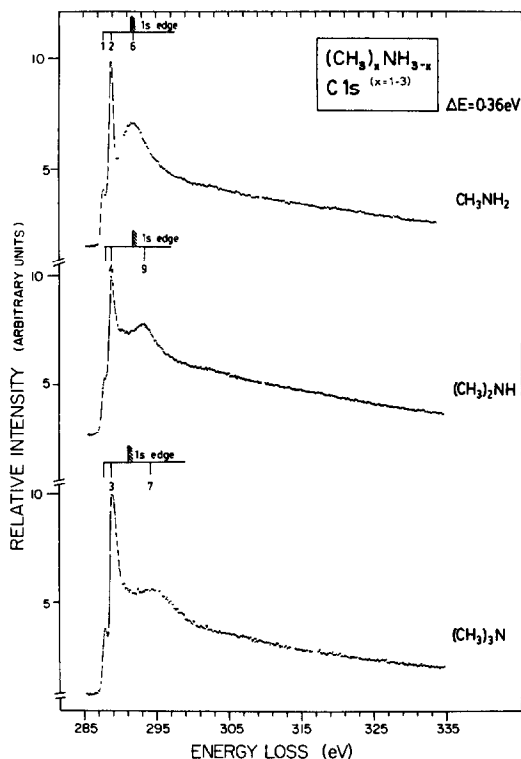


Fig. 1. Long range electron energy loss spectra of the C 1s region of the methyl amines.

spectra are dominated by dipole allowed transitions. The spectra obtained had typical resolutions of 0.14–0.36 eV FWHM. The C 1s spectra of the amines were calibrated against the $S\ 2p_{1/2} \rightarrow t_{2g}$ (184.54 eV) feature of SF_6 [21]. These C 1s spectra were used, except in the case of $(CH_3)_3N$, to internally calibrate the N 1s regions of the methyl amines. The N 1s spectra of $(CH_3)_3N$ and NH_3 were calibrated against the N_2 ($N\ 1s \rightarrow \pi^*$ ($\nu = 1$), 401.10 eV) and CO ($C\ 1s \rightarrow \pi^*$ ($\nu = 0$), 287.40 eV) features respectively [21]. The energy scales were established with the aid of a digital voltmeter of high accuracy (Datron 1071). All the samples were commercially obtained samples of high stated purity and used without further purification. No impurities were apparent in the spectra.

RESULTS AND DISCUSSION

Carbon 1s spectra

The long-range spectra of the C 1s region of the methyl amines are shown in Fig. 1. These spectra were obtained with a resolution of 0.36 eV FWHM.

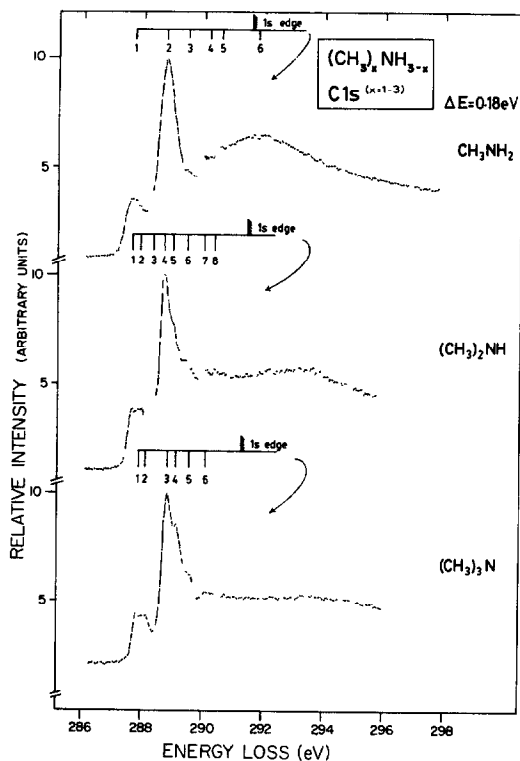


Fig. 2. Short range, high resolution electron energy loss spectra of the C 1s region of the methyl amines.

More detailed short-range spectra, recorded at a higher resolution (0.18 eV FWHM), are shown in Fig. 2. The assigned ionization edges for $(\text{CH}_3)_3\text{N}$ and CH_3NH_2 have been taken from X-ray photoelectron spectroscopy (XPS) [22,23]. As no value for the C 1s IP of $(\text{CH}_3)_2\text{NH}$ has been reported, its value was assumed to be the mean of the other two IPs. Table 1 summarizes the spectral data.

The spectra are similar to that for CH_4 [13,24,25] and the analysis can be considered in terms of that for a mono-substituted methane. The C 1s spectrum of CH_3NH_2 is virtually identical to that for C_2H_6 [26]. Similar observations were made for the C 1s spectra of $\text{P}(\text{CH}_3)_3$ and $\text{Si}(\text{CH}_3)_4$ [4,6].

Hitchcock and Brion have discussed the C 1s spectra of the methyl halides [20,27]. It is instructive to compare the analysis there with the spectra presented here. The methyl halides all possess a feature attributable to low-lying σ^* orbital [27]. However, the rest of the spectrum can be assigned solely to Rydberg transitions. In the amine spectra reported here there is a complete absence of any feature attributable to a low-lying σ^* feature. The discrete portions of the amine C 1s spectra reported here are similar to

TABLE 1
ENERGIES, TERM VALUES AND POSSIBLE ASSIGNMENTS FOR THE C 1s REGION OF THE METHYL AMINES

CH ₃ NH ₂				(CH ₃) ₂ NH				(CH ₃) ₃ N				Possible ^b assignment
Feature	Energy (eV)	T ^a (eV)		Feature	Energy (eV)	T ^a (eV)		Feature	Energy (eV)	T ^a (eV)		
1	287.70	3.90		1	287.61	3.82		1	287.84	3.42		3s
				2	287.85	3.58		2	288.08	3.18		3s + v
				3	288.3	3.1						
2	288.78 ^c	2.82		4	288.67 ^c	2.76		3	288.80 ^c	2.46		3p(x,y)
				5	288.95	2.48		4	289.07	2.19		3p(x,y) + v
3	289.46	2.14		6	289.46	1.97		5	289.51	1.75		3p(z)
4	290.21	1.39		7	290.03	1.40		6	290.06	1.20		4p(x,y)/3d
5	290.59	1.01		8	290.35	1.08						4p(z)
IP ^d	291.60	0		IP ^d	291.43	0		IP ^d	291.26	0		1s limit
6	291.8	-0.2		9	293.2	-1.8		7	294.3	-3.0		σ*
												shape-resonance

^aT = IP - Energy.

^b(CH₃)₂NH and CH₃NH₂ : C_s symmetry p(x, y) ≡ p_x, p(z) ≡ p_z.

^cCalibrated feature, estimated uncertainty ± 0.08 eV for CH₃NH₂, (CH₃)₂NH; ± 0.15 eV for (CH₃)₃N.

^dXPS; CH₃NH₂ from ref. 23, (CH₃)₃N from ref. 22; (CH₃)₂NH mean of other two values.

the remainder of the methyl halide spectra (above the σ^* level) and can be assigned solely to Rydberg features in an analogous manner. The assignments based upon these arguments [27] are shown in Table 1.

The post-edge behaviour is different in these two sets (i.e., the amines and methyl halides) of molecules. The methyl amines show a broad and fairly intense feature just beyond the ionization edge (Fig. 1). This is not the case for the methyl halides, nor for that matter methane [13,24]. However, ethane [26] shows similar behaviour to the molecules here. The difference between the C 1s spectra of methane [13] and ethane [26] is nicely illustrated in a recent paper by Hitchcock et al. [28] and clearly indicates a peak just beyond the edge for ethane. The continuum features can be attributed to a σ^* shape resonance [9–12] associated with the C–C bond in ethane [28] and with the C–N bond in the amines. In MO terms these can be thought of as excitations into a σ^* antibonding state [29]. Thus the major difference between the methyl halides and the molecules here is the location of the σ^* orbital. In the former they are low lying and in the discrete portion, whereas in the methyl amines they are in the continuum. The σ^* shape resonances will be discussed further below.

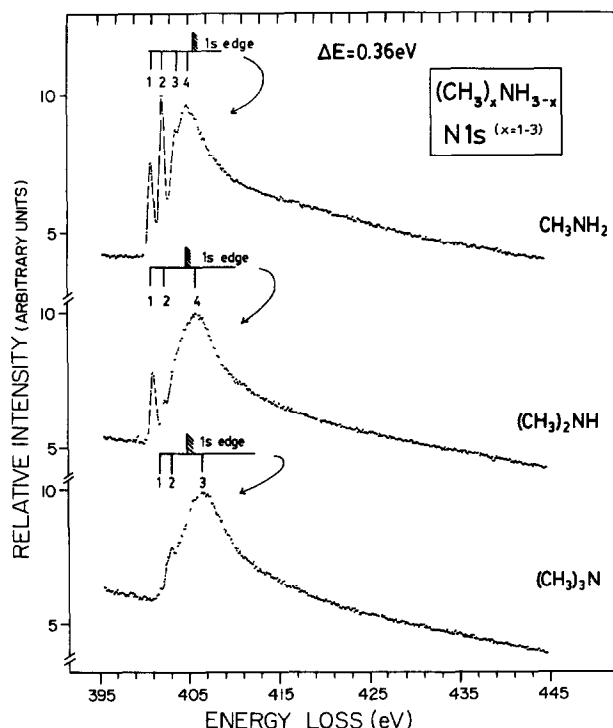


Fig. 3. Long range electron energy loss spectra of the N 1s region of the methyl amines.

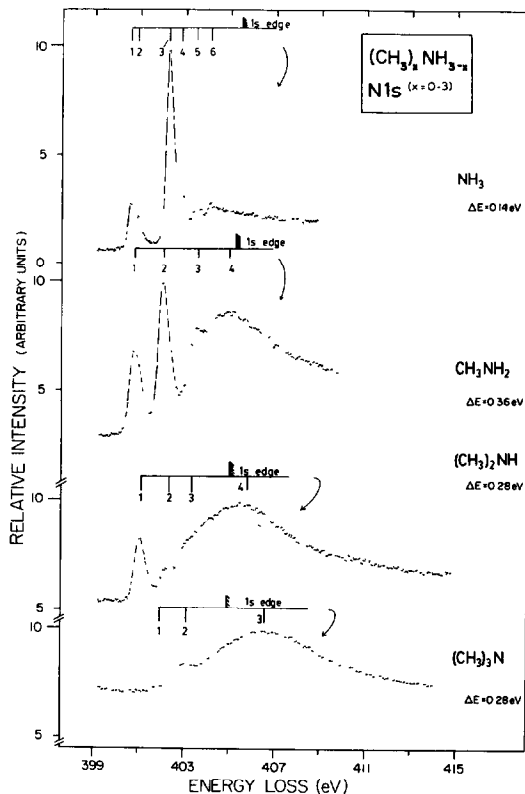


Fig. 4. Short range electron energy loss spectra of the N 1s region of ammonia and the methyl amines. The (differing) spectral resolution is indicated on each spectrum.

Nitrogen 1s spectra

Figure 3 shows the long-range N 1s spectra of the methyl amines. The spectral resolution is 0.36 eV FWHM. More detailed short-range spectra are shown in Fig. 4 along with a high-resolution spectrum (0.14 eV FWHM) of NH_3 . The 1s ionization edges are taken from XPS measurements [30]. On going from NH_3 to $(\text{CH}_3)_3\text{N}$ a gradual change in spectral features can be observed. The NH_3 spectrum is characteristic of a dominant (atomic-like) Rydberg spectrum with a largely structureless continuum of low intensity. In contrast, the $(\text{CH}_3)_3\text{N}$ spectrum shows little Rydberg structure and is dominated by a broad continuum feature that can be ascribed to a $\sigma^*(\text{N}-\text{C})$ shape resonance.

As stated above, the NH_3 spectrum can be assigned to transitions to the Rydberg levels and this spectrum has been published earlier [13,14]. There is no evidence of any distinct σ^* feature in the discrete portion, though Robin [16] has suggested that the $\text{HOMO} \rightarrow 3s$ feature in the valence shell

TABLE 2
ENERGIES, TERM VALUES AND ASSIGNMENTS FOR THE N 1s ENERGY LOSS SPECTRA OF NH₃

Feature	ISEELS			X-ray absorption			
	Present work		Assignment	Wight and Brion [13]		Assignment	
	Energy (eV) ^b	Term value (eV)		Energy (eV)	Assignment		
1	400.61	4.91	3s	400.6	3s	400.8	3s
2	400.92	4.60	3s + v	—			
3	402.29	3.23	3p(e)	402.2	3p(e)	402.4	3p(e)
4	402.85	2.67	3p(a ₁)	—		~ 403.0	3p(a ₁)
5	403.52	2.00	4s	403.5	3p(a ₁)	403.6	4s
6	404.14	1.38	4p/3d	404.1	4s/3d/4p(e)	404.1	4p(e)
IP ^a	405.52	0					

^aXPS from ref. 30.

^bEstimated uncertainty ± 0.08 eV.

UV spectrum is on top of a continuous valence shell transition, and Schwarz [31] suggests an admixture of valence antibonding character for the $n = 3$ Rydberg levels. Rather weak features in the NH_3 1s continuum (~ 14 eV above the edge) have been identified with a $\sigma^*(\text{N-H})$ shape resonance [32]. The NH_3 spectrum presented here is summarized in Table 2 along with possible assignments. The results of the earlier ISEELS work [13] and the X-ray absorption spectrum [14] are also shown. The energies of the spectral features in the different ISEELS spectra are in good agreement with each other and with the X-ray absorption spectrum, though in the latter the features are uniformly ~ 0.1 – 0.2 eV higher in energy. The assignments in the present work differ only slightly from the earlier ISEELS work [13]. This results from the much higher resolution achieved here. Features 1 and 2 are assigned to the $1s \rightarrow 3s$ transition plus vibrational component, thereby concurring with the suggestions of Wight and Brion [13]. No vibrational component is discernible at the resolution employed in the X-ray work [14]. Features 3 and 4 are assigned to the $3p(e)$ and $3p(a_1)$ Rydberg levels respectively, with a separation of ~ 0.6 eV, which agrees well with separation observed (< 0.6 eV) in the valence electron excitation spectrum [33]. No feature corresponding to feature 4 was observed in the earlier ISEELS work due to poorer resolution [13], however, it is seen in the X-ray spectrum [14]. On this basis feature 5 is now re-assigned to the $1s \rightarrow 4s$ transition consistent with the interpretation given by Schwarz [31] and also by Akimov et al. [14].

In comparing the ISEELS spectrum with the valence shell spectrum of the three amines and ammonia, two points can be noted. Firstly, there occurs a reversal in the intensity of the features associated with the $3s$ and $3p$ Rydberg levels. This reflects the s -level characteristics of the originating orbital in the core spectra which favour an $s \rightarrow p$ transition (dipole-allowed in the pure atomic case) over the $s \rightarrow s$ transition (dipole-forbidden in the pure atomic case), especially in a molecule as symmetrical as NH_3 [31]. The second point concerns the term values of the features. The term values are between 0.4 and 0.5 eV larger for the $3s$ and $3p$ features in the ISEELS spectra than for the corresponding features in the valence shell spectra [16]. This arises from the localized nature of the core-hole, and thus the newly promoted electron sees a centre approximating a $(Z + 1)$ core. Actually, this difference is quite small and it reflects the Rydberg nature of the final orbital in both spectra. Rydberg orbitals, being large and diffuse, are less sensitive to the location of the hole. In NF_3 , where the lowest unoccupied orbital is a σ^* antibonding orbital, the difference in term values between core and valence spectra is 2.17 eV [7].

Table 3 summarizes the spectral features of the N 1s region of the methyl amines. Of these only the spectrum of CH_3NH_2 has been previously reported [13]. As before, the first features of CH_3NH_2 are assigned as transitions to the $3s$ and $3p$ levels respectively. The term values are lower than those in NH_3

TABLE 3
ENERGIES, TERM VALUES AND POSSIBLE ASSIGNMENTS FOR THE N $1s$ REGION OF THE METHYL AMINES

CH_3NH_2			$(\text{CH}_3)_2\text{NH}$			$(\text{CH}_3)_3\text{N}$		
Feature	Energy (eV)	T^a (eV)	Feature	Energy (eV)	T^a (eV)	Feature	Energy (eV)	T^a (eV)
1	400.78	4.39	1	401.04	3.89	1	(401.8)	(3.0)
2 ^b	402.03	3.14	2 ^b	402.30	2.63	2 ^b	403.0	1.8
3	403.55	1.62	3	403.24	1.69	—	—	—
4	404.8	0.3	4	405.8	— 0.9	3	406.5	— 1.7
IP ^c	405.17		IP ^c	404.93		IP ^c	404.82	

^a $T = \text{IP} - \text{Energy}$.

^bCalibrated feature, estimated uncertainty ± 0.12 eV for CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$; ± 0.2 eV for $(\text{CH}_3)_3\text{N}$.

^cXPS from ref. 30.

3s
3p
3d etc.
 σ^* shape-resonance

which would be expected upon replacing an H ligand by an alkyl group [16] and once again the term values are ~ 0.5 eV higher than for the corresponding valence shell spectra [16]. A further difference between the spectra of CH_3NH_2 and NH_3 is that the relative intensity of the $\text{N } 1s \rightarrow 3p$ transition to that of the $\text{N } 1s \rightarrow 3s$ transition is less in CH_3NH_2 . However, the former transition to the $3p$ is still more intense. The major difference between CH_3NH_2 and NH_3 is the appearance of a broad feature at the edge for CH_3NH_2 . This previously unassigned feature [13] parallels that observed in the $\text{C } 1s$ spectrum and can be assigned to a $\sigma^*(\text{N}-\text{C})$ shape resonance [32]. The spectrum shows no evidence of any low-lying σ^* orbital below the ionization edge.

The spectrum of $(\text{CH}_3)_2\text{NH}$ (Figs. 3 and 4, Table 3) also shows transitions that can be assigned to the Rydberg levels. However, the intensity of the $\text{N } 1s \rightarrow 3s$ transition is now larger than that of the $\text{N } 1s \rightarrow 3p$ transition. However, the relative reduction in the $3p$ intensity is consistent with that observed on going from NH_3 to CH_3NH_2 . The first feature in the spectrum is at 401.04 eV, which is very close to the $\text{N } 1s \rightarrow \pi^*$ feature of N_2 (401.10 eV) [21]. The possibility of this feature arising from an N_2 impurity, however, can be discounted since the valence spectrum was run and no trace was found of the very intense N_2 ($X \rightarrow b^1\Pi_u$) feature at 12.93 eV [34]. The term values for the $3s$ and $3p$ levels are about ~ 0.3 eV larger than in the valence spectra [16]. As with CH_3NH_2 , the spectrum has a broad, intense feature that is assigned to a $\sigma^*(\text{N}-\text{C})$ resonance. In this case the feature is centred just above the edge. Once again the spectrum shows no evidence for any low-lying σ^* feature below the edge.

The spectrum of $\text{N}(\text{CH}_3)_3$ (Figs. 3 and 4, Table 3) shows very little Rydberg character. There is an indication of a weak feature, 1, with a term value of 3.0 eV, which is assigned to a transition to the $3s$ Rydberg level. The term value compares with one of 3.03 eV from the valence shell spectra. The broad feature 2 presumably encompasses transitions to the $3p$ Rydberg levels and higher. The lack of intensity for the $3s$ transitions is consistent with the arguments made above in the case of NH_3 . The spectrum is totally dominated by a $\sigma^*(\text{N}-\text{C})$ shape resonance, centred just above the edge.

GENERAL DISCUSSION

The spectra presented here all support the contention that there are no low-lying σ^* virtual orbitals, and that the lowest levels are Rydberg in nature. This agrees with the assignment of the valence shell spectra (below the first IP) as transitions to levels of predominantly Rydberg character [16,18,19]. In the ISEELS spectra the σ^* levels have been found to be at or only just above the ionization edges in the amines (Tables 1 and 3) and seemingly absent in NH_3 . For the valence spectra, transitions to the σ^*

TABLE 4
 RESONANCE ENERGY POSITIONS (δ) FROM EDGE AND C—N BOND LENGTHS
 (R) FOR THE METHYL AMINES

Molecule	$R(\text{\AA})^a$	$\delta(\text{eV})^b$	
		C 1s	N 1s
$(\text{CH}_3)_3\text{N}$	1.451 (3)	3.0	1.7
$(\text{CH}_3)_2\text{NH}$	1.462 (7)	1.8	0.9
$(\text{CH}_3)\text{NH}_2$	1.4714 (20)	0.2	− 0.3

^aFrom microwave spectroscopy. Landholt—Börnstein (New Series) II/7, Structure Data of Free Polyatomic Molecules, Springer-Verlag, Berlin, 1976.

^b δ = Resonance energy — IP = — Term value.

levels would be higher in the continuum than for the core spectra, since there would be no core hole to cause a large relaxation. The C 1s spectra are very similar and show an essentially constant $3s/3p$ intensity ratio. On the other hand, the Rydberg characteristics of the N 1s spectra change dramatically and certainly do not parallel the C 1s spectra. Indeed, the C 1s spectra could be solely interpreted in terms of a localized Rydberg structure based upon a CH_3X model compound. This phenomenon has also been noted in $\text{Si}(\text{CH}_3)_4$ [6] and $\text{P}(\text{CH}_3)_3$ [4].

A broad feature at or just above the edge is present in all of the methyl amine C 1s and N 1s spectra and is associated with the σ^* antibonding orbital formed by the C—N bond. In a multiple scattering picture it is also termed as a σ^* shape-resonance [9–12]. There has been much discussion recently on the relationship between bond length and the shape-resonance position (E_R) from the edge ($\delta = E_R - \text{IP}$). Hitchcock et al. [28] have demonstrated that a linear relationship is sufficient to describe the C—C bond length variation and shape-resonance position in a series of hydrocarbons. Sette et al. [32] have made a systematic study on a larger variety of systems. A study on some phosphorus compounds [5] also indicated that there is a relationship between bond length/type and resonance position. Table 4 lists the C—N bond lengths and resonance positions from the edge (δ). It is seen that as the bond length decreases the relative position of the resonance with respect to the edge moves to higher energy, as has been noted before [5,28,32]. The limited number of data points and the large error limits, however, do not allow the detailed nature of the relationship to be examined.

Finally, it is of value to compare the spectra of NF_3 [7], $(\text{CH}_3)_3\text{N}$ and NH_3 with their third row analogues PF_3 , $\text{P}(\text{CH}_3)_3$ and PH_3 [4]. In a later paper [4] the effects of the ligand on the P 2p spectra of some phosphorus compounds are compared to the effects on the Si 2p spectra

of silicon compounds. The ligand identity had a similar effect in both series. Briefly, the more highly electronegative ligands (e.g., F) enhance the probability of transitions to the σ^* virtual levels at the expense of transitions to the higher-lying Rydberg levels. The term values of the lowest σ^* orbitals were much larger in these compounds than those of compounds with less electronegative ligands such as H. The σ^* levels in third row hydrides still precede the Rydberg levels. However, the spectrum is much less dominated by the σ^* levels and relatively strong Rydberg transitions are observed. The effect of the electron donating CH_3 ligand leads to possible overlapping or mixed Rydberg-valence transitions. It is of interest to note, however, the complete absence of a $2p \rightarrow 4s$ Rydberg transition in the Si $2p$ spectrum of $\text{Si}(\text{CH}_3)_4$, implying that this spectrum consists essentially of transitions to valence orbitals. By contrast the C $1s \rightarrow 4s$ transition is clearly seen [6] in the C $1s$ ligand spectrum of $\text{Si}(\text{CH}_3)_4$. Features in the continuum spectra of $\text{Si}(\text{CH}_3)_4$ [6] and phosphorus compounds [4,5] are also present and can be identified in part with d -like σ^* shape resonances.

On comparing the ISEELS spectra of the phosphorus compounds with the spectra of the nitrogen compounds it should be remembered that in the former the $2p$ spectral region is being considered whereas the $1s$ region is being considered for the latter. However, important differences (or similarities) can still be noted. The effects of the ligands would appear to be very similar in both series. The major difference arises with the position of the σ^* antibonding orbitals which are high lying and in the continuum for the N compounds except when they have electronegative ligands. Thus the N $1s$ spectrum of NF_3 [7] has a very intense, low-lying N $1s \rightarrow \sigma^*$ transition and only weak transitions to the Rydberg levels. The NH_3 spectrum can be mostly ascribed to Rydberg transitions with the high-lying and weak σ^* (N—H) shape resonance approximately 14 eV into the continuum [32], whereas in PH_3 the σ^* transitions precede the relatively intense Rydberg transitions. The N $1s$ spectrum of $(\text{CH}_3)_3\text{N}$ is dominated by a N $1s \rightarrow \sigma^*$ shape resonance occurring just beyond the edge and shows little Rydberg character. As in $\text{Si}(\text{CH}_3)_4$ and $\text{P}(\text{CH}_3)_3$ [4,6], the ligand spectrum of $(\text{CH}_3)_3\text{N}$ shows the typical C $1s \rightarrow$ Rydberg transitions. Thus the N spectrum lends further support for the assignments previously given for $\text{P}(\text{CH}_3)_3$ and $\text{Si}(\text{CH}_3)_4$ [4,6], which indicate that the lowest Rydberg levels belong very much to the methyl group and have much C character. The assignment of the $(\text{CH}_3)_3\text{N}$ valence shell spectrum to Rydberg transitions [16,18,19] is consistent with the above discussion since the σ^* level is in the continuum (and at a higher energy since there would be no core hole). It is interesting to contrast the lack of intensity of transitions to Rydberg orbitals in the N $1s$ spectra of NF_3 and $(\text{CH}_3)_3\text{N}$. In the former molecule, NF_3 , this can be explained by the formation of a potential barrier resulting in enhanced (inner-well) virtual valence occupied states, and depleted (outer-well) Rydberg states [8–12]. However such a barrier should not exist in $(\text{CH}_3)_3\text{N}$,

where the ligands are in fact slightly electron donating in contrast to the highly electronegative F ligands in NF_3 . Thus the lack of Rydberg transitions in $(\text{CH}_3)_3\text{N}$ arises not from the formation of a barrier, but rather from the "localized" nature of the lowest Rydberg members, which appear to be highly concentrated around the methyl groups. This is consistent with the progressive reduction in Rydberg intensity for the N 1s spectra progressing along the series: $\text{NH}_3 \rightarrow \text{CH}_3\text{NH}_2 \rightarrow (\text{CH}_3)_2\text{NH} \rightarrow (\text{CH}_3)_3\text{N}$. No features attributable to *d*-like shape-resonances were noted in the N spectra, and this of course is in keeping with the fact that N is a row 2 (Li \rightarrow Ne) atom.

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