

Photoionization mass spectrometric studies of N-methyl formamide and N,N'-dimethyl formamide in the 7–18 eV photon energy range

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ABSTRACT

A photoionization mass spectrometric study of N-methyl formamide and N,N'-dimethyl formamide has been made using synchrotron radiation over the photon energy range 8–20 eV. Photoion yield curves were measured for the parent ion in both species and for six fragment ions in N-methyl formamide. Assignments of the fragment ions and the pathways of their formation by dissociative photoionization were made on the basis of ion appearance energies in conjunction with thermochemical data and the results of electron impact mass spectral studies. Our results illuminate aspects of the effects of methylation of formamide on ionization energies and dissociative ionization channels, as well as on the relative order of analogous molecular orbitals. The principal dissociative ionization process in both compounds involves HCO-loss. This neutral product may be formed in an electronic excited state. A comparison between the ionization properties, in particular the heats of formation of the cations, of the methyl derivatives of formamide and acetamide, shows that the ionization energies of the latter require re-investigation.

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1. Introduction

UV and VUV radiation are among the important energy sources impinging on prebiotic and biotic species in astrophysical sites. It is within this exobiological context that we have carried out VUV spectroscopy and photophysics studies on small prebiotic molecules [1], as well as on amino acids [2] and purines and pyrimidines [3], including nucleobases [4]. Such studies are necessary in order to be able to assess the fate of photon energy uptake and the degree of viability of these species and their cations in various sites in space. A recent photoion mass spectrometry (PIMS) study in the 10–20 eV photon energy range has been on formamide [5]. This species is observed in the ISM, in star-forming regions [6] and in the comet Hale-Bopp [7]. Formamide is the smallest and simplest model molecule of the peptide prototype $\text{NH}-\text{C}=\text{O}$ linkage. This molecule, its radical cation, and related methyl derivatives, can serve as models of intact and oxidized peptide groups.

The present work, on N-methyl formamide and N,N'-dimethyl formamide is an extension of the formamide study. These formam-

ide species could play a role in the synthesis of adenine and related molecules in astrophysical milieux [8] and it has been suggested that formamide condensation occurring in the presence of inorganic oxides can be involved in a pathway of prebiotic synthesis of purine and pyrimidine derivatives. Indeed, formamides form nucleobases in the presence of oxides when UV-irradiated [9a] or heated [9b]. N-methyl formamide has other functions besides its exobiological and astrophysical interest. It also has applications to studies of intercalation in clay minerals as promising routes to the preparation of new materials [10]. It has been recognized as a potential candidate for combination chemotherapy [11]. Indeed, formamides, especially N-methyl formamide, have an important biological role in antitumour activity [12]. N-methyl formamide is an experimental antineoplastic agent which undergoes metabolism to a chemically reactive hepatotoxic intermediate [13]. Their capacity for forming hydrogen bonds and the strong polarity of these formamides are important factors in their biological functions (dipole moments: formamide 3.73 ± 0.07 D; N-methyl formamide 3.83 ± 0.08 D; N,N'-dimethyl formamide 3.82 ± 0.08 D [14]), and these properties could presumably play a role in their chemical reactions in space.

We have carried out a photoionization mass spectrometric study of N-methyl formamide and N,N'-dimethyl formamide in the 8–20 eV photon energy range. The results of the previous study on formamide will be recalled insofar as they serve to illuminate aspects of the present study on the methyl derivatives, in

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particular the effect of methylation of formamide on ionization energies and dissociative ionization channels, as well as the relative order of analogous molecular orbitals. The results also permit a comparison between the ionization properties, in particular the heats of formation of the cations, of the methyl derivatives of formamide and acetamide and show that the ionization energies of the latter require re-investigation.

2. Experimental

Synchrotron radiation from the Berlin electron storage ring BESSY II was monochromatised by a 3 m normal incidence monochromator, and then focussed into a differentially pumped gas cell. The general experimental set-up is described in more detail elsewhere [15]. The N-methyl formamide and N,N'-dimethyl formamide vapours were introduced into the ionization chamber via a needle valve, with the sample at room temperature. Parent and fragment ions formed by photoionization were measured using a quadrupole mass spectrometer (Leybold Q200), and ion yield curves were obtained through photon energy scans with measuring intervals of 5 or 10 meV. The yield curves of the principal ions observed are normalized to the incident photon flux measured by detecting the fluorescence of a sodium salicylate coated window. Wavelength dependent photon flux changes are due to the grating transmission function and decreasing electron storage ring current. The yield curves are presented in appropriate figures. Spectral bandwidth of the incident monochromatic radiation was typically 0.2 nm. Ion appearance energies were determined mainly with the aid of semi-log plots of the ion yield curves. Measurements were made up to 20 eV but diminished grating reflectivity above 17 eV is responsible for enhanced noise in this spectral region and we limit our discussed results to those below 18 eV. The N-methyl formamide and N,N'-dimethyl formamide samples were commercial products (Sigma-Aldrich) of 98% stated purity.

We remark that our ion appearance energies correspond to *effective* thermochemical energy values since they are a function of instrumental detection sensitivity and also reflect effects of intrinsic thermal energy as well as energy deposition in fragment products (Eq. (1)). The kinetic energy shift has two main factors: limited detection sensitivity and the thermal energy stored in the parent neutral. Following Chupka [16], we contend that compensatory effects lead to appearance energies that reflect reasonably well their 0 K values. Our AEs are determined from semi-log ion yield plots in the threshold region by fitting straight lines to the noise and to the ion signal rise in this region. The photon energy at the intersection of these two lines is assigned to the measured AE value. Applying different fits, the precision is estimated by visual inspection of the variation of the intersection and is thus a function of the sharpness of the ion signal rise in threshold region.

The measured AE's are used to calculate enthalpies of formation of fragment ions m_1^+ ($\Delta_f H(m_1^+)$) for different possible fragmentation pathways, using Eq. (2):



$$AE + \Delta_f H_{\text{gas}}(M) - \sum [\Delta_f H_{\text{gas}}(m_i)] = \Delta_f H_{\text{gas}}(m_1^+) \quad (2)$$

The $\Delta_f H(m_1^+)$ values determined from alternative possible dissociation products are then compared to tabulated standard thermochemical enthalpies of formation, thus permitting assignment of particular fragmentation channels. If literature $\Delta_f H(m_1^+)$ values are not available, then our results provide new, upper limit, values of these entities.

3. Results

3.1. N-methyl formamide

3.1.1. Structural preliminaries

In an NMR study chiefly on N,N'-dimethyl formamide, Phillips [17] also reported briefly on N-methyl formamide. He remarked that the observation of a single methyl proton resonance for N-methyl formamide suggested that only one of two possible rotational isomers, *cis* and *trans*, is present. It is indeed the *trans* form which dominates in the vapour phase, [18] with a small amount of the *cis* conformer being present, as confirmed by Sugawara et al. [19], who studied the IR spectrum of vapour phase N-methyl formamide by Fourier Transform Spectroscopy. A more recent IR and NMR study of methyl formamide concludes that the *cis* form constitutes a 5% component in the gas phase at room temperature, 95% being in the *trans* form [20]. An *ab initio* calculation of the geometry of methyl formamide [21] found that the *cis* form lies 2 kcal/mol higher than the *trans*. A more recent calculation finds this difference in energy to be 1.4 kcal/mol [22]. The barrier to rotation about the amide C–N bond is ≈ 955 meV, [23], showing that this bond has partial double bond character, as in formamide [5]. One expected effect of ionization will be modification of the barrier to rotation about the N–C(carbonyl) bond with respect to the neutral species, in both N-methyl formamide and N,N'-dimethyl formamide. This aspect has not yet been studied, either experimentally or theoretically.

N-methyl formamide is generally agreed to have a planar structure, as has formamide [24]. Earlier *ab initio* calculations by Radom and Riggs [25] show that in the preferred conformation the rotational orientation of the methyl group is eclipsed with respect to the N–C bond. The barrier to internal rotation of the methyl group, in the *trans* isomer, is 37.3 meV, and 6.8 meV in the *cis* isomer [26].

3.1.2. Mass spectrum

In Table 1 we compare our mass spectrum of N-methyl formamide obtained by 20 eV photon impact, with mass spectra reported for 70 eV electron impact (EI) [27,28]. There is good agreement between the two EI mass spectra. We note that the same m/z peaks are present in both the photon impact and the electron impact mass spectra. Exceptions are $m/z = 18$ and 17, not reported in the EI-MS, where they were possibly neglected on the assumption that they derive from a water impurity, and $m/z = 27$, seen in the electron impact but not in our photon impact MS. We note that the neutralization–reionization mass spectrum of methyl formamide [29] is very similar to the 70 eV EI-MS [27,28] in the relative intensities of most of its mass peaks.

The most intense peak in the EI-MS is that of the parent ion, ($m/z = 59$), whereas in the photon impact mass spectrum it is that of the fragment ion at $m/z = 30$. A similar behaviour was observed for the analogous mass spectra of formamide [5] and N,N'-dimethyl formamide (see later). We point out that there may be differences, between the photon impact and electron impact studies, in the residence time in the ion formation region. There is also the possibility for electron impact to form autoionising triplet states, inaccessible by photon impact, which lead to enhanced parent ion formation in the EI case. We note also a basic difference in the energy transfer process in the two ionization techniques. In contrast to the absorption of photon energy, in electron impact ionization the approach of the electron can distort the neutral molecule before electron loss, thus making electron impact not a strictly vertical process [30].

Table 1N-methyl formamide mass spectra: C₂H₅NO. Ion assignments and appearance energies.

<i>m/z</i>	Photon impact	Electron impact 70 eV		Ion	Neutral	Ion appearance energies ^a (eV)
	20 eV	[27]	[(28)]			
59	33	183	(185)	CH ₃ NHCHO ⁺	–	9.55 ± 0.04
58	5	15	(15)	CH ₃ NH–C=O ⁺	H	11.15 ± 0.02
44	1	1	(2)	H–N=C–OH ⁺	CH ₃	11.32 ± 0.04
41	1	5	(6)	CH ₂ =N=CH ⁺	H ₂ O	(15.69)
31	2	4	(4)	CH ₃ O ⁺ or CH ₂ OH ⁺	H ₂ CN (11.70)	(15.23)
30	100	100	(100)	H ₂ C = NH ₂ ⁺	HCO	11.27 ± 0.03
29	17	23	(24)	HCO ⁺	CH ₄ N	12.4 [39]
28	59	62	(63)	HCNH ⁺	CH ₃ O CH ₂ OH CH ₃ O	(11.97) (11.54) (13.59)
				CNH ₂ ⁺	CH ₂ OH	(13.16)
27	–	5	(6)	HCN ⁺	CH ₃ OH	(14.86)
18	9	–		NH ₄ ⁺	HCCO	11.4 ± 0.1
17	3	–		NH ₃ ⁺	CH ₂ CO	11.40 ± 0.05
15	18	3	(13)	CH ₃ ⁺	H ₂ NCO	13.5 ± 0.1

^a In brackets, calculated minimum ion appearance energies from thermochemistry.

3.1.3. Parent ion *m/z* = 59. CH₃N(H)CHO⁺

3.1.3.1. Molecular orbital considerations. N-methyl formamide is a planar C_s molecule. Its electron configuration, as given by Kimura et al. [31], and based on analysis of their HeI photoelectron spectrum, is

$$\dots (9a')^2 (10a')^2 (1a'')^2 (11a')^2 (12a')^2 (2a'')^2 (13a')^2 (3a'')^2$$

Kimura et al. consider the 3a'' M.O. to be n_N and the 13a' to be n_O and that they have the same energy (IE = 9.86 eV), as might be expected on simple Hückel theory [32]. Brundle et al. [33] report these two M.O.'s as having different energies, 3a'' (π₂) IE(ad) = 9.79 eV and 13a' (n_O) IE(ad) = 10.05 eV. Our results (see below) favour the assignments of Brundle et al. which suggest that the first excited state of the ion lies 260 meV above the ion ground state. The question of the order of the molecular orbitals will be discussed later in more detail in a comparison between formamide and its methyl derivatives (Section 4). However, we note here that molecular orbital calculations of charge localization associated with the formation of the radical ions [34] show that electron density loss on ionization, which involves both oxygen and nitrogen atoms in formamide, comes mainly from the N atom in N-methyl formamide.

3.1.3.2. Ionization energy. Fig. 1a shows the ion yield curve as a function of photon excitation energy in the 9–15 eV region for the parent ion, *m/z* = 59. From this we obtain a value of 9.55 ± 0.04 eV for the ionization energy of N-methyl formamide. This is the only reported photoionization value and it is lower by several hundreds of meV than previously reported values, obtained by electron impact, 10.00 ± 0.05 eV [35] or by photoelectron spectroscopy (PES), 9.86 eV [31], 9.79 eV [33]. The value of Kimura et al. [31] is cited as a vertical IE, whereas that of Brundle et al. [33] is reported as the adiabatic IE, with 9.87 eV as IE(vert). Since the onset region of the PES curve (Fig. 3 of Brundle et al. [33]) is clearly far less abrupt than our parent ion yield curve onset (Fig. 1a), the onset energy is thus difficult to determine with precision from the PES. We are thus satisfied that there is no real conflict between the two measurements. Our own examination of the PES curve onset in Fig. 3 of Brundle et al. shows that an onset value of 9.60 ± 0.05 eV would be a reasonable estimate from this figure.

We therefore consider that our photon impact value, IE = 9.55 ± 0.04 eV, is the true, or close to the true, adiabatic IE. The difference in energy between the adiabatic and reported vertical IE values is thus of the order of 320 meV. In formamide the corresponding value is ~200 meV [5,36] and is compatible with this interval being associated with a CO stretching vibration, whose va-

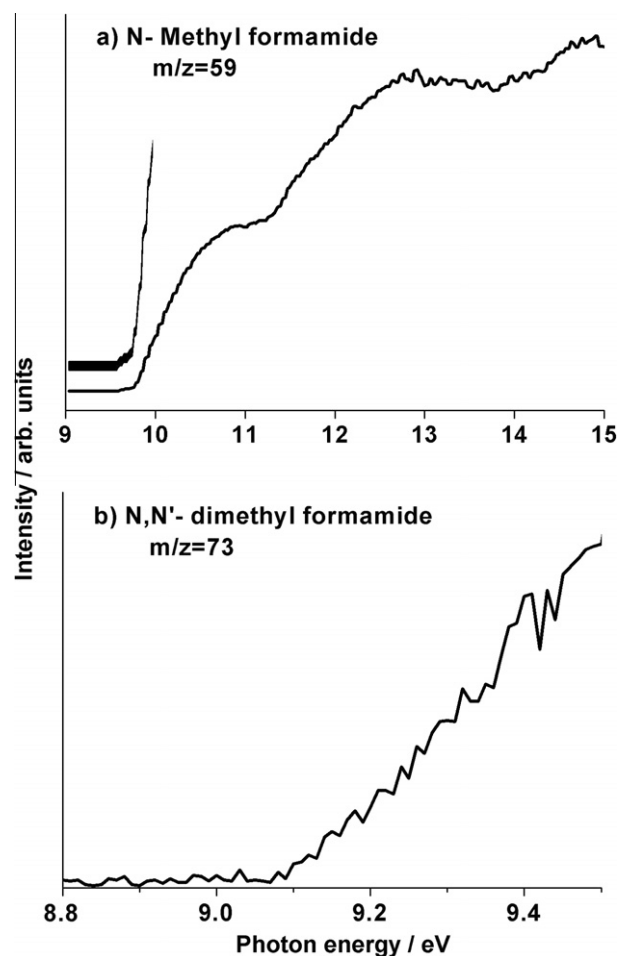


Fig. 1. (a) Photoion yield curve of N-methyl formamide: parent ion, *m/z* = 59, 9–15 eV. In the inset the ordinate scale has been expanded by a factor of 4 over the energy range 9–10 eV; (b) photoion yield curve of N,N'-dimethyl formamide: parent ion, *m/z* = 73, 8.8–9.5 eV.

lue in ground state neutral methyl formamide is 214 meV [37]. The ~320 meV value of the difference in energy between the adiabatic and reported vertical IE values could correspond to CH₃ stretching vibrations [37]. We note, however, that its value corresponds to the difference between the origin bands of the α and A series of PES

vibrational bands in the lowest energy photoelectron band profiles of N-methyl formamide (Fig. 2 of Brundle et al. [33]), and which is logically the difference between the energies of the π_2 and n_O molecular orbitals of this species (see below).

3.1.3.3. Heat of formation of the parent ion. The heat of formation of the methyl formamide ion (MeF^+) is given by the sum of the heat of formation of neutral methyl formamide (-1.938 ± 0.031 eV, [27]) and its ionization energy. With our value of the IE, we find $\Delta_f H(\text{MeF}^+) = 7.612 \pm 0.071$ eV. This is smaller than the value in the Lias et al. compilation [38], 7.855 eV, which was based on a value of the IE = 9.79 eV.

3.1.4. Fragment ions

3.1.4.1. $m/z = 58$. This ion is considered to be $\text{CH}_3\text{NH}-\text{C}=\text{O}^+$, formed by H-atom loss from the carbon atom bonded to oxygen in the methyl formamide ion. Its appearance energy $\text{AE} = 11.15 \pm 0.02$ eV (Fig. 2a) is essentially the same as the electron impact $\text{AE} = 11.2$ eV [39]. The dissociation energy is 1600 ± 60 meV. This is a little greater than the analogous C–H dissociation energy in formamide, 1070 meV, where from theory and experiment the reaction is reported to be slow and the H-loss is from a metastable ion. McGibbon et al. [29] show that $m/z = 58$ is a major ion in the metastable ion spectrum (MIS) of methyl formamide, being 60% of the intensity of the principal ion $m/z = 30$ (the only other ion reported in the MIS is $m/z = 41$, i.e. H_2O loss, at 10%). We note that our observed ratio of 5:1 for the peak intensities of $m/z = 58/41$ is very similar to the ratio 6:1 reported for the MIS by McGibbon et al. [29]. We can speculate that at higher energies the H-loss could also occur from the N–H and from the CH_3 group.

From our AE for $m/z = 58$ we obtain the heat of formation $\Delta_f H(\text{CH}_3\text{NH}-\text{C}=\text{O}^+) = 6.95$ eV. The literature value [30] is $\Delta_f H(\text{CH}_3\text{NH}-\text{C}=\text{O}^+) = 6.59$ eV. This is about 360 meV less than our value but it is based on the proton affinity of methyl isocyanate in which it is assumed, following calculations [40] that the protonation occurs at the N atom. It is possible that H-loss proceeds via an energy barrier and tunnelling.

3.1.4.2. $m/z = 44$. This ion can be thought of as initially being the formynitrenium ion $\text{H}-\text{N}=\text{C}(\text{H})=\text{O}^+$, formed by loss of the methyl radical from the parent ion. The $m/z = 44$ ion is weak but its yield curve was measured (Fig. 2b), the appearance energy being 11.32 ± 0.04 eV. It is similarly weak in the electron impact mass spectra (Table 1), as noted also by Hop et al. [41]. Other possible assignments of $m/z = 44$ is to the most stable isomer of CH_2NO^+ composition, isomer $\text{H}_2\text{N}-\text{C}=\text{O}^+$, and to the isomer HNCOH^+ which is calculated to lie 819 meV above $\text{H}_2\text{N}-\text{C}=\text{O}^+$, (and several eV above the $\text{H}-\text{N}=\text{C}(\text{H})=\text{O}^+$ ion) [41]. The $\text{H}_2\text{N}-\text{C}=\text{O}^+$ and HNCOH^+ ions could be formed by H-atom migration. We note that there is a large barrier between the two isomers $\text{H}_2\text{N}-\text{C}=\text{O}^+$ and HNCOH^+ [41]. It is logical to consider that the reaction involves a simple fission of the methyl–nitrogen bond in the parent ion, after isomerisation. We note that the metastable ion spectrum of methyl formamide contains no ion of $m/z = 44$ but that a fragment ion of this m/z value is seen in the EI-MIS of the isomer $\text{CH}_3\text{N}(\text{H})-\text{C}-\text{OH}^+$ [29]. This makes it likely that in N-methyl formamide there has occurred isomerisation of the parent ion by migration of an H-atom from carbon to oxygen, followed by cleavage of the methyl group, so as to form the ionic species $\text{H}-\text{N}=\text{C}-\text{OH}^+$.

From the appearance energy of $m/z = 44$, and the appropriate thermochemical values, we calculate the heat of formation of $m/z = 44$ ion as $\Delta_f H = 7.87 \pm 0.07$ eV. This is in reasonable agreement with the reported heat of formation of the $\text{H}-\text{N}=\text{C}-\text{OH}^+$ ion $\Delta_f H(\text{H}-\text{N}=\text{C}-\text{OH}^+) = 8.027$ eV [29] and thus supports our preferred ion assignment. It also excludes the $\text{H}-\text{N}=\text{C}(\text{H})=\text{O}^+$ ion, whose heat of formation is of the order of 12.6 eV [41]. However,

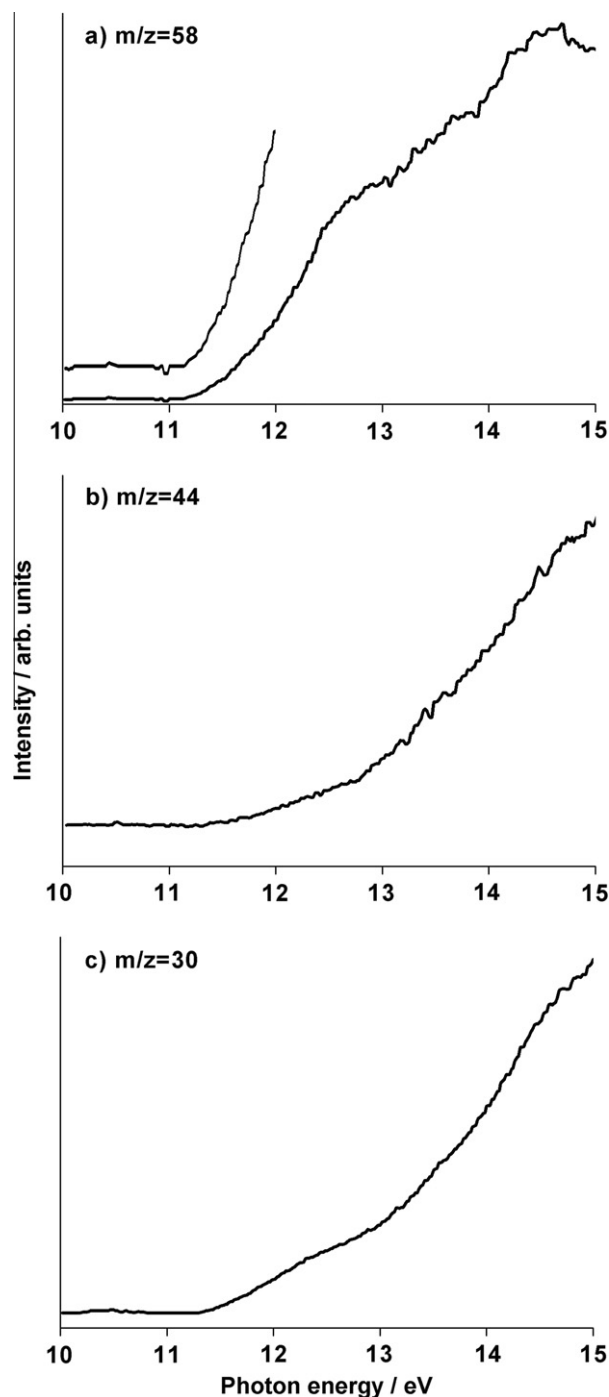


Fig. 2. Photoion yield curves of N-methyl formamide: (a) fragment ion $m/z = 58$, 10–15 eV. In the inset the ordinate scale has been expanded by a factor of 3 over the energy range 10–12 eV; (b) fragment ion $m/z = 44$, 10–15 eV; (c) fragment ion $m/z = 30$, 10–15 eV.

it is also compatible with $\Delta_f H(\text{H}_2\text{N}-\text{C}=\text{O}^+) = 6.995$ eV [39]. In a further study, McGibbon et al. conclude that loss of CH_3 leads to the formation essentially of the $\text{H}-\text{N}=\text{C}-\text{OH}^+$ ion with perhaps some co-generation of $\text{H}_2\text{N}-\text{C}=\text{O}^+$ [42].

3.1.4.3. $m/z = 41$. This fragment ion has the elemental composition $\text{C}_2\text{H}_3\text{N}^+$ and is formed by a H_2O loss process. Loss of H_2O in the parent ion competes with H-loss so that the daughter $m/z = 41$ ion is most likely to be $\text{CH}_2=\text{N}=\text{CH}^+$ rather than CH_3NC^+ , according to McGibbon et al. [29]. This implies that the two H atoms forming

H₂O come from CH₃ and N respectively, and not from the central carbon atom which must be the source of the H-loss in forming $m/z = 58$. As mentioned above, we note that our observed ratio of peak intensities of $m/z = 58$ and 41, $I(58)/I(41) = 5$ is similar to the value 6 as reported for this ratio in the metastable ion spectrum of N-methyl formamide by McGibbon et al. [29].

The calculated appearance energy AE ($\text{CH}_2=\text{N}=\text{CH}^{\circ+}$) = 15.691 eV is based on the following thermochemical values: $\Delta_f H(\text{CH}_2=\text{N}=\text{CH}^{\circ+}) = 11.253$ eV [30], $\Delta_f H(\text{MeF}) = -1.938$ eV [27], $\Delta_f H(\text{H}_2\text{O}) = 2.5$ eV [38].

If the $m/z = 41$ ion were CH_3NC^+ , the calculated appearance energy would be 17.516 eV, based on $\Delta_f H(\text{CH}_3\text{NC}^+) = 13.078 \pm 0.041$ eV [43].

3.1.4.4. $m/z = 31$. This fragment ion could have 3 different assignments: (a) CH_3O^+ (methoxy), (b) CH_2OH^+ (protonated formaldehyde), in both cases with H_2CN as neutral product, and (c) CH_3NH_2^+ , with CO as the neutral product.

Based on (a) $\Delta_f H(\text{CH}_3\text{O}^+) = 10.90$ eV, (b) $\Delta_f H(\text{CH}_2\text{OH}^+) = 7.37$ eV [30], and $\Delta_f H(\text{H}_2\text{CN}) = 2.39 \pm 0.43$ eV [3], the calculated appearance energies are $\text{AE}(\text{CH}_3\text{O}^+) = 15.23 \pm 0.45$ eV and $\text{AE}(\text{CH}_2\text{OH}^+) = 11.70 \pm 0.45$ eV.

If $m/z = 31$ is CH_3NH_2^+ , the resulting calculated $\text{AE}(\text{CH}_3\text{NH}_2^+) = 9.52$ eV, based on $\Delta_f H(\text{CH}_3\text{NH}_2^+) = 8.725$ eV [38] and $\Delta_f H(\text{CO}) = -1.145$ eV [38]. In this case the AE is equal to the ionization energy of N-methyl formamide and this dissociative ionization channel would be in competition with the non-dissociative parent ionization. The photoionization yield curve of the parent ion does not support this dissociative ionization channel as being of significance in the ionization threshold region.

3.1.4.5. $m/z = 30$. We consider the $m/z = 30$ fragment ion to be $\text{H}_2\text{C} = \text{NH}_2^+$ and the neutral product to be HCO (or COH). Although the dissociation is in principle a simple C–N bond rupture process, it involves reorganisation such as a 1,2-H-shift from the methyl group to the N atom.

The observed appearance energy in the ion yield curve (Fig. 2c) is 11.27 ± 0.03 eV. This AE leads to the following values for the heat of formation of the $\text{H}_2\text{C} = \text{NH}_2^+$ ion: $\Delta_f H(\text{H}_2\text{C} = \text{NH}_2^+) = 8.894$ eV if the neutral product is HCO, and 9.509 eV if it is COH. The literature value for the heat of formation of $\text{H}_2\text{C} = \text{NH}_2^+$ is 7.720 ± 0.083 eV [30]. McGibbon et al. [29] estimate that the barrier for formation of the $\text{H}_2\text{C} = \text{NH}_2^+$ ion by loss of HCO cannot be much greater than 560 meV. Our AE gives a maximum barrier of $8.894 - 7.720 = 1174 \pm 123$ meV for the reaction forming the preferred HCO product in its ground state or, if HCO is formed in the $^2A'$ excited state, which is at 1150 meV above the ground state of HCO [44], a quasi-zero energy barrier in the latter case.

Although $\text{H}_2\text{C} = \text{NH}_2^+$ is the only CH_4N^+ ion to have been investigated directly by experiment, the compilation of Lias et al. [38] gives a value $\Delta_f H(\text{CH}_3\text{NH}^+) = 8.632$ eV for the heat of formation of the CH_3NH^+ ion which, in principle, can be formed by rupture of the N–C(carbonyl) bond. This value is also compatible with our appearance energy for $m/z = 30$. In this case a barrier of 262 meV is implied, if the neutral product is HCO. However, the appearance energy indicates 1.72 eV as the dissociation energy for the simple N–C bond rupture. This is lower than that expected for either a single or partial double N–C bond [44,45], so that some form of atomic rearrangement must occur in the formation of the fragment ion. The small value of the dissociation energy indicates that the skeletal rearrangement occurs at the level of the parent molecular ion before dissociation, rather than in the CH_4N^+ fragment ion itself which was proposed by Loudon and Webb in their study of the nature of the CH_4N^+ ion formed by electron impact on

methylated formamides [39]. We therefore reject CH_3NH^+ as an assignment of $m/z = 30$.

3.1.4.6. $m/z = 29$. We consider a number of possibilities for assignment of the $m/z = 29$ fragment ion.

- HCO^+ : the dissociation reaction $\text{HCO}^+ + \text{CH}_4\text{N}$, corresponding to the cleavage of the central carbon–nitrogen bond, would be the charge switch reaction to that forming $m/z = 30$. The computed appearance energy for the $\text{HCO}^+ + \text{CH}_4\text{N}$ dissociation reaction is 12.09 eV, based on $\Delta_f H(\text{H}_2\text{C}=\text{NH}_2) = 1.591$ eV [30] for neutral $\text{H}_2\text{C}=\text{NH}_2$ and $\Delta_f H(\text{HCO}^+) = 8.56$ eV [38].
- CH_3N^+ : In the dissociation reaction $\text{CH}_3\text{N}^+ + \text{CH}_2\text{O}$, the CH_3N^+ ion is either (i) HCNH_2^+ [$\Delta_f H = 10.67$ eV] or (ii) CH_2NH^+ [$\Delta_f H = 10.84$ eV] [30].

CH_2O is taken to be formaldehyde H_2CO [$\Delta_f H = 1.126$ eV]. For HCNH_2^+ the computed thermochemical minimum appearance energy is 13.74 eV, and for CH_2NH^+ it is 13.91 eV.

In their electron impact study of N-methyl formamide, Loudon and Webb [39] observed $\text{AE}(m/z = 29) = 12.4$ eV. This is lower than the computed appearance energies for HCNH_2^+ and CH_2NH^+ . It is 301 meV higher than our computed $\text{AE}(\text{HCO}^+)$ so that we can conclude that the $m/z = 29$ fragment ion is indeed HCO^+ and that the dissociation reaction corresponds to the charge switch reaction of $m/z = 30$.

Stevenson's rule [47] considers that cleavage of a single bond in an odd electron ion can lead to two complementary charge-switch reactions. In the present case there is simple cleavage of the central carbon–nitrogen bond in methyl formamide, after H-shift from methyl to nitrogen, to form $m/z = 29$ $\text{HCO}^+ + \text{H}_2\text{C}=\text{NH}_2$ and the corresponding charge switch reaction $m/z = 30$ $\text{H}_2\text{C}=\text{NH}_2^+ + \text{HCO}$. Since $\text{IE}(\text{H}_2\text{C}=\text{NH}_2) = 6.29 \pm 0.03$ eV [30]; $\text{IE}(\text{HCO}) = 8.12 \pm 0.04$ [27], these ionization energies would be in favour of the $m/z = 30$ reaction relative to the $m/z = 29$ reaction, as indeed is confirmed by the relative intensities of the $m/z = 30$ and $m/z = 29$ fragment ions in both the 20 eV photon impact and 70 eV electron impact mass spectra (Table 1).

3.1.4.7. $m/z = 28$. That the $m/z = 28$ ion is due to impurities of ionized CO or N_2 is unlikely in view of the similar relative intensities of the $m/z = 28$ and $m/z = 30$ ions in both the photon impact and electron impact mass spectra (Table 1). We now consider the following possible assignments for $m/z = 28$:

- CO^+ , resulting from the dissociation reaction $\text{CO}^+ + \text{CH}_3\text{NH}_2$. The calculated appearance energy of CO^+ is 14.67 eV, based on $\Delta_f H(\text{CO}^+) = 12.87$ eV and $\Delta_f H(\text{CH}_3\text{NH}_2) = -0.238$ eV.
- H_2CN^+ , resulting from the dissociation reaction $\text{H}_2\text{CN}^+ + \text{CH}_3\text{O}$. There are two possible structures for the fragment ion, HCNH^+ and CNH_2^+ , and two possible structures for the neutral product, CH_3O and CH_2OH . The respective calculated appearance energies are as follows:
 - $\text{HCNH}^+ + \text{CH}_3\text{O}$: $\text{AE} = 11.97$ eV, based on $\Delta_f H(\text{HCNH}^+) = 9.865$ eV [30] and $\Delta_f H(\text{CH}_3\text{O}) = 0.161$ eV [38],
 - $\text{HCNH}^+ + \text{CH}_2\text{OH}$: $\text{AE} = 11.54$ eV, based on $\Delta_f H(\text{CH}_2\text{OH}) = -0.268$ [38],
 - $\text{CNH}_2^+ + \text{CH}_3\text{O}$: $\text{AE} = 13.59$ eV, based on $\Delta_f H(\text{CNH}_2^+) = 11.492$ eV [38],
 - $\text{CNH}_2^+ + \text{CH}_2\text{OH}$: $\text{AE} = 13.16$ eV.

On comparative thermochemical grounds it is unlikely that CO^+ is the $m/z = 28$ fragment ion. We consider the most probable assignment of the ion to be HCNH^+ , but we cannot exclude CNH_2^+ . Deute-

rium substitution studies of methyl formamide would be useful in deciding between these two possibilities.

3.1.4.8. $m/z = 27$. We did not observe a $m/z = 27$ ion in the 20 eV photon impact mass spectrum but it appears weakly in the 70 eV electron impact mass spectrum (Table 1). A possible assignment is to the HCN^+ ion, with CH_3OH as neutral product. The minimum thermochemical calculated appearance energy of HCN^+ would be

14.86 eV. However, the formation of HCN^+ would involve complex rearrangements of the parent ion before dissociation and thus suggests a high energy barrier not accessible to 20 eV photons but accessible to 70 eV electrons. The latter have been found to mimic to some extent the excitation characteristics of 30–35 eV photons, leading to similar mass spectra [48].

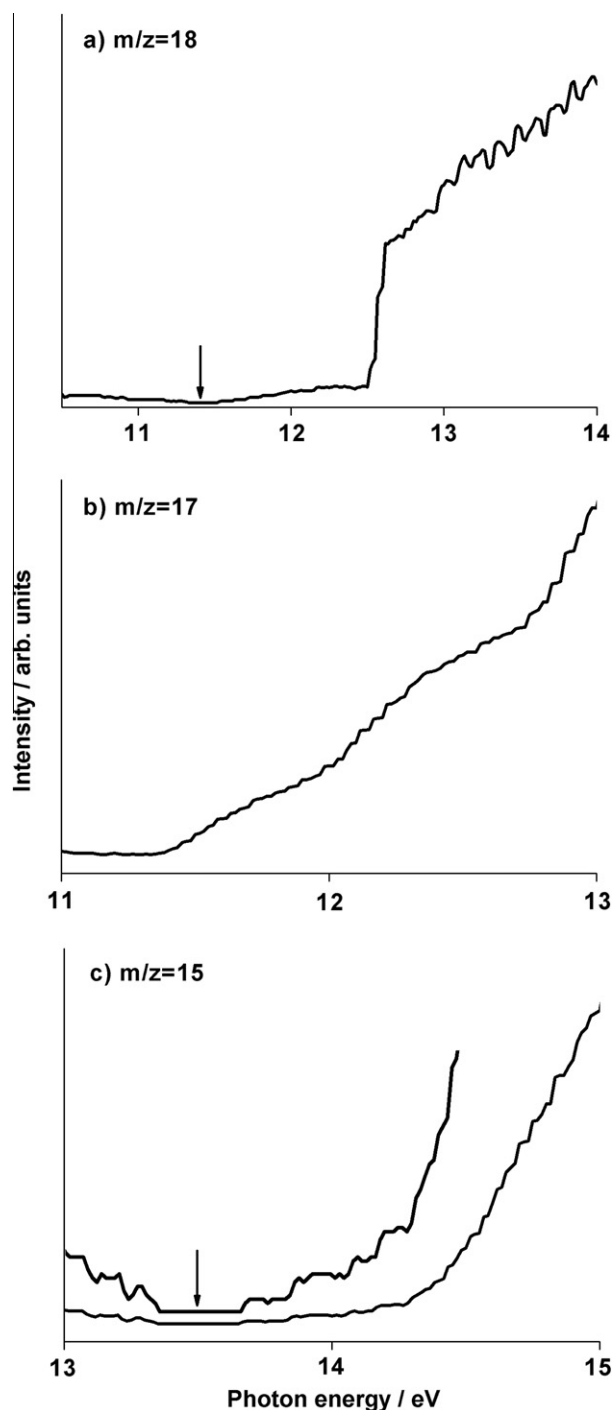


Fig. 3. Photoion yield curves of N-methyl formamide: (a) fragment ion $m/z = 18$, 10.5–14 eV. The arrow indicates the appearance energy of NH_4^+ at 11.4 ± 0.1 eV. The rising signal in the 12.6 eV region is due to H_2O^+ from a water impurity. (b) Ion $m/z = 17$, 11–13 eV. (c) Fragment ion $m/z = 15$, 13–15 eV. In the inset the ordinate scale has been expanded by a factor of 2.5 over the energy range 13–14.5 eV. The arrow indicates the appearance energy of CH_3^+ at 13.5 ± 0.1 eV.

3.1.4.9. $m/z = 18$. The $m/z = 18$ ion yield curve revealed the presence of water as an impurity by a sharp rising ion signal at 12.61 eV, the ionization energy of H_2O (Fig. 3a). There is a very weak ion signal below 12.6 eV, with an appearance energy of 11.4 ± 0.1 eV. We first considered the possibility of assigning this low energy $m/z = 18$ signal to the fragment ion H_2O^+ resulting from the dissociation of the parent ion into $\text{H}_2\text{O}^+ + \text{CH}_3\text{NC}$. However, a maximum appearance energy of the $m/z = 18$ ion of 12.61 eV would lead to $\Delta_f H(\text{H}_2\text{O}^+) = 8.98$ eV, based on $\Delta_f H(\text{CH}_3\text{NC}) = 1.69 \pm 0.08$ [27]. This value of the heat of formation of H_2O^+ is much smaller than the known thermochemical value $\Delta_f H(\text{H}_2\text{O}^+) = 10.104$ eV [38] so that H_2O^+ is not the correct assignment for a $m/z = 18$ fragment ion. A more reasonable assignment would be to the NH_4^+ ion. The dissociation reaction to give $\text{NH}_4^+ + \text{HCCO}$ would require considerable re-organization of the parent ion, involving multiple hydrogen transfer. Such processes could be facilitated by hyperconjugation, which would create a more labile electronic system. The appearance energy $\text{AE}(\text{NH}_4^+) = 11.4 \pm 0.1$ eV, giving a value of $\Delta_f H(\text{NH}_4^+) = 7.62 \pm 0.22$ would therefore be compatible with the known $\Delta_f H(\text{NH}_4^+) = 6.53$ eV [38], using $\Delta_f H(\text{HCCO}) = 1.84 \pm 0.091$ eV [38].

3.1.4.10. $m/z = 17$. The $m/z = 17$ ion is assigned to NH_3^+ resulting from the dissociation to $\text{NH}_3^+ + \text{CH}_2\text{CO}$. The ion yield curve (Fig. 3b) provided an appearance energy $\text{AE} = 11.40 \pm 0.05$ eV. This leads to $\Delta_f H(\text{NH}_3^+) = 10.00 \pm 0.08$ eV, based on $\Delta_f H(\text{CH}_2\text{CO}) = -0.539$ eV [30]. This value for the heat of formation of NH_3^+ is 321 ± 80 meV above the known $\Delta_f H(\text{NH}_3^+) = 9.679$ eV [38]. This may reasonably be considered as corresponding to the energy barrier in the formation of NH_3^+ which, as in the case of the formation of NH_4^+ , discussed above, requires considerable re-organization of the parent ion, involving multiple hydrogen transfer.

3.1.4.11. $m/z = 15$. We consider two possible assignments for $m/z = 15$, (a) NH^+ , (b) CH_3^+ . The appearance energy for $m/z = 15$ in the ion yield curve (Fig. 3c) is $\text{AE} = 13.5 \pm 0.1$ eV. In case (a) the dissociation would give $\text{NH}^+ + \text{C}_2\text{H}_4\text{O}$. There are three possible structures for the neutral product, (i) acetaldehyde ($\Delta_f H(\text{CH}_3\text{CHO}) = -1.718$ eV), (ii) Ethanol ($\Delta_f H(\text{CH}_2=\text{CHOH}) = -1.295$ eV) and Ethylene oxide ($\Delta_f H = -0.545$ eV) [38]. The derived heats of formation of NH^+ are $\Delta_f H(\text{NH}^+) = 13.28 \pm 0.13$ eV, 12.86 ± 0.13 eV and 12.11 ± 0.13 eV, respectively. These values are well below the known $\Delta_f H(\text{NH}^+) = 17.391$ eV, so that $m/z = 15$ is not NH^+ . The estimated thermochemical onset for NH^+ would be at (i) 18.15 eV and (ii) 18.04 eV.

The alternative assignment (b) involves the dissociation to $\text{CH}_3^+ + \text{H}_2\text{NCO}$. This is the charge switch reaction to the formation of $m/z = 44$ (Table 1). Using the $\text{AE} = 13.5 \pm 0.1$ eV, and $\Delta_f H(\text{CH}_3^+) = 11.342$ eV [49] we can estimate $\Delta_f H(\text{H}_2\text{NCO}) = 0.22 \pm 0.13$ eV. There are eleven isomers of this neutral species. The NH_2CO isomer has an *ab initio* calculated $\Delta_f H = -0.156 \pm 0.043$ eV, whereas the *ab initio* calculated heat of formation of the formaldiminoxy radical isomer CH_2NO is $\Delta_f H = 1.627$ eV [50]. The nine other isomers have intermediate values of their calculated heats of formation, so that our estimated $\Delta_f H(\text{H}_2\text{NCO}) = 0.22 \pm 0.13$ eV is within the calculated range.

3.2. N,N'-dimethyl formamide

3.2.1. Structure

In an NMR study of N,N'-dimethyl formamide, Phillips [17] observed 2 different proton resonances for the H-atom bonded to the C atom of the carbonyl group. There would have been a single signal if there was free rotation about the C–N bond, the observation thus showed that there is restricted rotation about the C–N bond, implying a partial double bond character of the C–N amide bond. The barrier to rotation about this bond is ≈ 855 meV [51]. Neutral and ionized dimethyl formamide are both calculated to be planar [34], this being compatible with gas-phase electron diffraction data on neutral dimethyl formamide [52]. A more recent electron diffraction study invokes a possible small non-planarity [53]. In this study we treat the molecule as having a planar nitrogen configuration. The methyl groups have local C_{3v} symmetry and have barriers to internal rotation of the order of 169 ± 13 meV for the *cis* methyl, and 117 ± 26 meV for the *trans* methyl (*cis* and *trans* defined with respect to the formyl hydrogen) according to an NMR study [54]. The greater *cis* barrier than *trans* is surprising since one would expect rotation of the *trans* methyl to be sterically more restricted by the carbonyl oxygen than that of *cis* methyl by the formyl hydrogen. *Ab initio* calculations support this relative order of the *cis* and *trans* methyl internal rotation barriers [55] but the physical reasons for this order remain obscure [56], although repulsive interactions are expected to play a role [57].

3.2.2. Mass spectrum and appearance energy measurements

The mass spectrum of dimethyl formamide was measured at 20 eV photon excitation (Table 2). Photoion yield measurements were made only for the parent ion, $m/z = 73$. In our discussion of the mass spectrum we will take into account both electron impact [39,58], and photon impact [59] measurements of fragment ion appearance energies. The PIMS measurements of Arimura and Yoshikawa [59] were made for ions whose $m/z = 73, 72, 58, 44$ and 30 in the restricted photon energy range 8.85–13 eV.

In Table 2 we compare our 20 eV photon impact mass spectrum with the 70 eV electron impact mass spectra of N,N'-dimethyl formamide reported by of NIST [27] and by Gilpin [28]. The major ion is $m/z = 30$ in the photon impact spectrum and the $m/z = 73$ parent ion in the electron impact spectra. This behaviour is analo-

gous to that in observed comparisons between 20 eV photon impact and 70 eV electron impact mass spectra of formamide [5] and N-methyl formamide, as discussed previously in Section 3.1.3.

3.2.3. $m/z = 73$: parent ion $(CH_3)_2NCHO^+$

3.2.3.1. Molecular orbital considerations. N,N'-dimethyl formamide is a planar C_s molecule. Its electron configuration, as given by Bieri et al. [61], and based on their HeI photoelectron spectrum, is

$$\dots (1a'')^2 (12a')^2 (13a')^2 (2a'')^2 (14a')^2 (15a')^2 (3a')^2 (16a')^2 (4a'')^2$$

Published analyses of the HeI photoelectron spectrum of N,N'-dimethyl formamide give the lowest IE as being due to loss of an electron from a π M.O. ($4a''$) and they place the n_O orbital $16a'$ as being 300–500 meV above the π orbital [33,61,62].

3.2.3.2. Ionization energy. The $m/z = 73$ ion yield curve in the 8.8–9.4 eV photon excitation region is given in Fig. 1b. From this we determine the ionization energy of N,N'-dimethyl formamide as $IE = 9.05 \pm 0.01$ eV. This agrees with the previous PIMS values of 9.12 ± 0.06 eV [59] and 9.12 ± 0.02 eV [60], and is slightly lower than the HeI photoelectron spectrum value of the adiabatic $IE = 9.14$ eV reported by Brundle et al. [33]. Photoelectron spectroscopy vertical values of the ionization energy have been reported: $IE(\text{vert}) = 9.25$ eV [33], 9.4 eV [61], 9.25 eV [62]. There is a change of slope in the $m/z = 73$ ion yield curve at 9.45 ± 0.05 eV, which could be associated with the n_O M.O. adiabatic IE. The difference with our adiabatic π IE is 400 ± 60 meV (3226 cm^{-1}) and it agrees with the assignment of the photoelectron spectrum by Brundle et al. [33] that places the latter at ≥ 9.4 eV.

We note that in formamide the lowest orbital is a σ orbital and the π orbital is at 330 meV above, while in N-methyl formamide the corresponding two molecular orbitals are in the same order as in N,N'-dimethyl formamide, according to Brundle et al. [33].

3.2.3.3. Heat of formation of the parent ion. The heat of formation of the N,N'-dimethyl formamide radical cation (DMeF^+), derived from our ionization energy and from the heat of formation of the neutral $\Delta_f H(\text{DMeF}) = -1.987 \pm 0.018$ eV [27], is $\Delta_f H(\text{DMeF}^+) = 7.063 \pm 0.028$ eV. The literature value is 7.140 V [38], based on $IE = 9.13 \pm 0.02$ eV.

Table 2
N,N'-dimethyl formamide mass spectra: C_3H_7NO . Ion assignments and appearance energies.

m/z	Photon impact 20 eV	Electron impact 70 eV		Ion	Neutral	Ion appearance energies (eV)
		[27]	[(28)]			
74	3	5		$^{13}\text{C}^{12}\text{C}_2\text{H}_7\text{NO}^+$		
73	42	112	(182)	$\text{C}_3\text{H}_7\text{NO}^+$		9.05 ± 0.01
72	3	11	(13)	$\text{C}_3\text{H}_6\text{NO}^+$	H	10.77 ± 0.08 [59]
58	5	7	(9)	$\text{C}_2\text{H}_4\text{NO}^+$	CH_3	10.77 ± 0.08 [59]
56	2	3	(2)	$\text{C}_3\text{H}_6\text{N}^+$	OH	
45	3	3	(4)	$\text{C}_2\text{H}_7\text{N}^+$	CO	
44	100	100	(100)	$\text{C}_2\text{H}_6\text{N}^+$ see text	HCO	10.59 ± 0.08 ; 12.2 ± 0.3 [59]
43	13	13	(11)	$\text{C}_2\text{H}_5\text{N}^+$	H_2CO see text	
42	43	47	(44)	$\text{C}_2\text{H}_4\text{N}^+$	CH_3O	
41	1	9	(5)			
40	-	9				
39	-	3				
38	-	1				
31	2	0.5	(1)			
30	34	28	(25)	CH_4N^+	$\text{C}_2\text{H}_3\text{O}$	11.9 ± 0.02 [59]
29	8	18	(11)	HCO^+	$\text{C}_2\text{H}_6\text{N}$	14.5 [39]; 14.3 ± 0.1 [58]
28	27	32	(22)	$\text{HCNH}^+/\text{CNH}_2^+$	See text	
27	6	6	(4)	$\text{HCN}^+/\text{HNC}^+$	See text	
18	30	18		NH_4^+	See text	
17	2	-				
15	11	18	(20)	CH_3^+	CH_3NHCO	

3.2.4. Fragment ions

3.2.4.1. $m/z = 72$. This fragment ion is assigned to the $\text{C}_3\text{H}_6\text{NO}^+$ ion formed by loss of a hydrogen atom from the parent cation. Three structures are listed in Lias et al. [38] for the fragment ion of elemental formula $\text{C}_3\text{H}_6\text{NO}^+$. Their heats of formation are given by Holmes et al. [30] as: protonated acrylamide $\Delta_f H = 5.482$ eV, protonated methoxyacetonitrile $\Delta_f H = 7.627$ eV and protonated 2-azetidinone $\Delta_f H = 6.031$ eV. We can add three more $\text{C}_3\text{H}_6\text{NO}^+$ structures, protonated 2-hydroxy-propanenitrile, protonated 3-hydroxy-propanenitrile, and protonated isocyanate-ethane [27]. Formation of any of these six structures is unlikely, because considerable skeletal re-organization would be required. Other, more likely structures involving loss of a H-atom from the parent ion can be conceived, e.g. H-atom ejection from one of the methyl groups or from the carbonyl carbon in $\text{N,N}'$ -dimethyl formamide.

The appearance energy of the $m/z = 72$ fragment ion has been reported as 11.35 eV in an electron impact experiment [39] and 10.77 ± 0.08 eV in a PIMS measurement [59]. Using the latter value we determine the heat of formation of ($m/z = 72$) = 6.541 eV. This certainly excludes protonated methoxyacetonitrile as an assignment for $m/z = 72$. We note that Arimura and Yoshikawa [59] tentatively propose that H-loss is from the carbonyl carbon in the reaction forming $m/z = 72$. This appears to us to be the most probable H-loss process, and it is the assignment to which we adhere.

3.2.4.2. $m/z = 58$. We assign the $m/z = 58$ ion to $\text{C}_2\text{H}_4\text{NO}^+$, resulting from loss of a methyl group from the parent ion. The PIMS appearance energy of this ion is 10.77 ± 0.08 [59]. From this we determine the heat of formation of the $\text{C}_2\text{H}_4\text{NO}^+$ ion as $\Delta_f H = 7.27$ eV. This value is 680 meV above that reported for $\Delta_f H(\text{CH}_3\text{NHCO}^+) = 6.591$ eV [30], which indicates that there is a considerable energy barrier in this dissociative ionization channel. One possibility is that, (as suggested also as a possibility in the case of CH_3 loss in N -methyl formamide (Section 3.1.4.2)), there has been isomerisation of the parent dimethyl formamide ion by migration of an H-atom from the carbonyl carbon to the oxygen atom, followed by cleavage of a methyl group, so as to form the ionic species $\text{CH}_3\text{—N}=\text{C—OH}^+$. However, we cannot follow up this possibility, for lack of thermochemical data on this ion.

3.2.4.3. $m/z = 44$. The $m/z = 44$ ion is the major fragment ion in the photon ionization mass spectrum (Table 2). We assign it to $\text{C}_2\text{H}_6\text{N}^+$ formed by loss of HCO from the parent ion. The electron impact appearance energy of the $m/z = 44$ ion is reported as 11.6 eV [39]. The photon impact appearance energy is 10.59 ± 0.08 eV, with a second threshold reported to exist at 12.2 ± 0.3 eV [59].

From the first threshold appearance energy we determine the heat of formation of the $m/z = 44$ ion as = 8.167 eV. If the dissociation process involved a simple rupture of the bond between the N atom and the carbonyl carbon atom, the resulting ion would be the dimethyl-nitrenium ion $(\text{CH}_3)_2\text{N}^+$. However, this ion is considered to have a heat of formation $\Delta_f H((\text{CH}_3)_2\text{N}^+) = 10.477$ eV [30], which is 2.31 eV above the derived $\Delta_f H = 8.167$ eV. Furthermore, the $(\text{CH}_3)_2\text{N}^+$ ion produced by photoionization of the neutral molecule is very unstable and has been found to fragment on the timescale of a photoionization experiment [63]. Indeed, in 70 eV electron impact experiments which sought to observe an ion of $(\text{CH}_3)_2\text{N}^+$ structure no ion of $m/z = 44$ was found above the error limit [64]. The results of the collisional activation experiments of Levens and McLafferty [64] suggest that ions of initial structure $(\text{CH}_3)_2\text{N}^+$ rearrange to $\text{CH}_3\text{NH}=\text{CH}_2^+$ faster than the 10^{-5} s drift time in their apparatus. This is followed by H-loss and H_2 -loss, as well as CH_4 and C_2H_2 loss, according to the amount of internal energy in the fragment ion.

We note that the NIST compilation gives $\Delta_f H(\text{CH}_3)_2\text{N}^+ = 6.674$ eV [27]. The value $\Delta_f H(\text{CH}_3)_2\text{N}^+ = 10.477$ eV given by

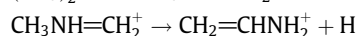
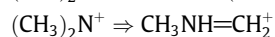
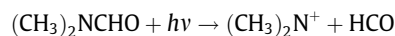
Holmes et al. [30] seems more reliable and is based in part on the results of G3 level calculations and on a value $\text{IE}(\text{CH}_3)_2\text{N} = 9.01$ eV [63] (see also later).

Seven isomers of $\text{C}_2\text{H}_6\text{N}^+$ are discussed by Holmes et al. [30] of which, as mentioned above, $(\text{CH}_3)_2\text{N}^+$ has the highest heat of formation, 10.477 eV, which is 3.586 eV above that of the lowest energy isomer $\text{CH}_3\text{CHNH}_2^+$. The calculated energy difference is 3.337 eV [30]. Our value $\Delta_f H(\text{C}_2\text{H}_6\text{N}^+) = 8.167$ eV is compatible, as an upper limit, with five of the other six isomers, whose heats of formation, based in some cases on calculated values, are given by Holmes et al. [30] as: 6.891 eV ($\text{CH}_3\text{CHNH}_2^+$), 7.306 eV ($\text{CH}_2\text{CH}_2\text{NH}_2^+$), 7.523 eV ($\text{CH}_3\text{NHCH}_2^+$), 7.710 eV ($\text{CH}_2\text{CHNH}_2^+$), 8.176 eV (cyclic $\text{CH}_2\text{—NH}_2\text{—CH}_2^+$). The formation of the cyclic isomer is unlikely, since a high entropy of activation would be necessary. The heat of formation of the sixth isomer, $\text{CH}_3\text{CH}_2\text{NH}^+$, is not known. We consider that $\text{CH}_3\text{NHCH}_2^+$ would be the most favoured isomer from the structural viewpoint. If the neutral product was COH rather than HCO, the heat of formation of the $\text{C}_2\text{H}_6\text{N}^+$ ion would be $\Delta_f H(\text{C}_2\text{H}_6\text{N}^+) = 9.397$ eV, which is 1.874 eV above that of the $\text{CH}_3\text{NHCH}_2^+$ isomer.

The second appearance energy onset, at 12.2 ± 0.3 eV, would give $\Delta_f H(\text{C}_2\text{H}_6\text{N}^+) = 9.777$ eV, with HCO as neutral product, which is 700 meV below the literature value for $\Delta_f H((\text{CH}_3)_2\text{N}^+)$, but above the heats of formation of five other isomers of $\text{C}_2\text{H}_6\text{N}^+$. The energy difference between the first and second thresholds is 1.61 ± 0.38 eV. We note that the HCO radical has a $^2A''$ excited state at 1.15 eV above the ground state [44], so that the second threshold could correspond to formation of a fleeting $\text{C}_2\text{H}_6\text{N}^+ + \text{HCO}(^2A'')$. If, however, the neutral product was COH, the second onset would give $\Delta_f H(\text{C}_2\text{H}_6\text{N}^+) = 10.392 \pm 0.380$ eV. In this case the fragment ion could well be $(\text{CH}_3)_2\text{N}^+$, whose $\Delta_f H((\text{CH}_3)_2\text{N}^+) = 10.477$ eV.

Thus we tentatively suggest that at the first onset, the $m/z = 44$ ion is $\text{CH}_3\text{NHCH}_2^+$, resulting from rupture of the N to carbonyl C bond and a 1,2-H-shift from a methyl group to the nitrogen atom, and that at the second onset the ion is the dimethyl amidogen cation $(\text{CH}_3)_2\text{N}^+$, formed by simple rupture of the N to carbonyl C bond. This is supported by an estimation of the strength of the N—C(carbonyl) bond, assuming simple bond cleavage, as $D(\text{N—C}) = \text{AE}(12.2 \pm 0.3 \text{ eV}) - (\text{IE}((\text{CH}_3)_2\text{NHCO}) = 9.05 \pm 0.01 \text{ eV}) = 3.15 \pm 0.31 \text{ eV}$, which is a reasonable value [45,46] for a N—C single bond. This also suggests that there is no prior isomerisation of the parent dimethyl formamide ion by migration of an H-atom from the carbonyl carbon to the oxygen atom so as to form the COH product before rupture of the nitrogen to carbonyl carbon bond. However, at the first onset, the corresponding value of the estimated dissociation energy is 1.54 eV, which is too low for a simple N—C rupture, thus confirming that more complex processes are occurring at this onset, such as H-shifts.

3.2.4.4. $m/z = 43$. The $m/z = 43$ fragment ion is most assignable to the $\text{C}_2\text{H}_5\text{N}^+$ ion, probably as the structure $\text{CH}_2=\text{CHNH}_2^+$ [65]. A possible dissociation is to $\text{C}_2\text{H}_5\text{N}^+ + \text{H}_2\text{CO}$, by rupture of the N to carbonyl carbon bond and H-atom shift from a methyl group to the carbonyl carbon. This process has an estimated minimum appearance energy of 9.421 eV. However, the $\text{CH}_2=\text{CHNH}_2^+$ ion could also be created in a secondary dissociation by loss of a H-atom from the $\text{CH}_3\text{NH}=\text{CH}_2^+$ ion which results by rapid rearrangement of the $m/z = 44$ $(\text{CH}_3)_2\text{N}^+$ ion initially formed, as mentioned above, with loss of HCO in the primary dissociation channel. The dissociative ionization process can be considered to be:



The estimated minimum appearance energy for $m/z = 43$ $\text{CH}_2=\text{CHNH}_2^+$ by this process is 13.242 eV.

Two other possible sets of dissociation products to produce an ion of $m/z = 43$ can be considered, but are much less likely than the dissociative ionization pathways discussed above: (i) $\text{CH}_3\text{CO}^+ + \text{CH}_4\text{N}$ and (ii) $\text{NCHO}^+ + \text{C}_2\text{H}_6$. The channel giving CH_3CO^+ would involve considerable skeletal re-organization and we disregard it. The NCHO^+ pathway would involve rupture of the two $\text{N}-\text{CH}_3$ bonds and the subsequent recombination $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$. The most likely structure of the ion formed by this pathway is HNCO^+ . The minimum appearance energy for such a process can be estimated as $\text{AE} = 11.656 \text{ eV}$ for HNCO^+ , and 13.78 eV for HCNO^+ .

3.2.4.5. $m/z = 42$. This is the second most intense fragment ion. It can be assigned to $\text{C}_2\text{H}_4\text{N}^+$. It can be formed by a similar pathway as that discussed above for formation of $\text{CH}_2=\text{CHNH}_2^+$ ($m/z = 43$) but in which the dissociation of the $\text{CH}_3\text{NH}=\text{CH}_2^+$ ion involves molecular hydrogen loss. In an assessment of experimental data on dissociation of the $\text{C}_2\text{H}_6\text{N}^+$ system, Barone et al. [66,67] conclude that the transition state for loss of H_2 does not involve rupture of a bond to nitrogen. The collisional activation study of Levens and McLafferty [64] showed that hydrogen loss occurred from the $\text{CH}_3\text{NH}=\text{CH}_2^+$ ion, but involves extensive scrambling of all hydrogen atoms. Two different channels of similar energy for H_2 -loss from the $\text{CH}_3\text{NH}=\text{CH}_2^+$ ion, suggested by Barone et al., do involve loss of hydrogen from the N atom:

- (a) $\text{CH}_3\text{NH}=\text{CH}_2^+ \rightarrow \text{CH}_2\text{NCH}_2^+ + \text{H}_2$; estimated minimum $\text{AE}(\text{CH}_2\text{NCH}_2^+) = 11.59 \text{ eV}$.
- (b) $\text{CH}_3\text{NH}=\text{CH}_2^+ \rightarrow \text{CH}_3\text{NCH}^+ + \text{H}_2$; estimated minimum $\text{AE}(\text{CH}_3\text{NCH}^+) = 11.27 \text{ eV}$.

High internal energies in the $\text{CH}_3\text{NH}=\text{CH}_2^+$ ion are reported to favour H-loss and low internal energies favour H_2 -loss [63,64]. We note, however, that the intensities of the $m/z = 42$ and 43 ions relative to that of the $m/z = 44$ ion are very similar in the 20 eV photon impact and 70 eV electron impact mass spectra (Table 2). This indicates that the internal energies of the $\text{CH}_3\text{NH}=\text{CH}_2^+$ ion are similar although formed in two very different excitation processes.

3.2.4.6. $m/z = 30$. The $m/z = 30$ fragment ion, which has a substantial intensity in the 20 eV photon impact mass spectrum (Table 2), was assigned by Arimura and Yoshikawa to CH_4N^+ [59], with the neutral product having the elemental formula $\text{C}_2\text{H}_3\text{O}$. The photon impact appearance energy of the ion is $\text{AE} = 11.9 \pm 0.02 \text{ eV}$ [59]. From this we determine the heat of formation $\Delta_f H(\text{CH}_4\text{N}^+) = 10.037 \text{ eV}$, assuming that the neutral product is the acetyl radical CH_3CO whose $\Delta_f H = -0.124 \text{ eV}$ [27]. A possible structure for CH_4N^+ is CH_2NH_2^+ , whose reported heat of formation is $\Delta_f H(\text{CH}_2\text{NH}_2^+) = 7.72 \pm 0.08 \text{ eV}$ [30]. This value is about 2.3 eV below $\Delta_f H(\text{CH}_4\text{N}^+) = 10.037 \text{ eV}$. We note that CH_3CO has an excited electronic state at 2.32 eV in the gas phase, (2.07 eV in Ar matrix) [27], so that it is conceivable that if CH_3CO is the neutral product it is formed in an excited state.

Two other, but less probable, sets of ionic and neutral products are worth considering. They are both charge-switch reactions of possible pathways considered above in forming the $m/z = 43$ ion:

- (i) $\text{CH}_2\text{O}^+ + \text{C}_2\text{H}_5\text{N}$: estimated minimum $\text{AE} = 12.484 \text{ eV}$ ($\text{CH}_2=\text{NCH}_3$ neutral); 11.821 eV ($\text{CH}_3\text{CN}=\text{NH}$ neutral); 12.039 eV ($\text{CH}_2=\text{CHNH}_2$ neutral).
- (ii) $\text{C}_2\text{H}_6^+ + \text{CHNO}$: estimated minimum $\text{AE} = 11.552 \text{ eV}$ (HNCO neutral); 14.899 eV (HCNO neutral).

Since the experimental $\text{AE}(m/z = 30) = 11.90 \pm 0.02 \text{ eV}$, this eliminates CH_2O^+ as $m/z = 30$, but allows C_2H_6^+ as a possible assignment if the neutral product is HNCO .

3.2.4.7. $m/z = 29$. We assign the $m/z = 29$ ion to HCO^+ , with $\text{C}_2\text{H}_6\text{N}$ as the neutral product. Lack of synchrotron radiation beam time prevented us from measuring the ion yield curves of the $m/z = 29$ and $m/z = 28$ fragment ions. Electron impact studies give the appearance energy of $m/z = 29$ as 14.5 eV [39] or $14.3 \pm 0.1 \text{ eV}$ [58]. This dissociation channel could constitute the charge switch reaction forming the principal fragment ion $m/z = 44$, which we assigned above to $\text{CH}_3\text{NHCH}_2^+$ at its appearance energy first onset, and to the $(\text{CH}_3)_2\text{N}^+$ ion at the second onset (see previous discussion on $m/z = 44$). Using $\text{AE}(m/z = 29) = 14.3 \text{ eV}$, we obtain $\Delta_f H(m/z = 29) = 10.81 \text{ eV}$. Literature values are $\Delta_f H(\text{HCO}^+) = 8.56 \text{ eV}$ and $\Delta_f H(\text{COH}^+) = 9.98 \text{ eV}$ [38]. The much greater relative intensity of the $m/z = 44$ to $m/z = 29$ ions (Table 2) is not consistent with Stevenson's rule [47] for a charge switch reaction forming the dimethyl amidogen ion as $m/z = 44$ since the ionization energy $\text{IE}(\text{HCO}) = 8.10 \pm 0.05 \text{ eV}$ [38] ($\text{IE}(\text{COH})$ is not known) is smaller than $\text{IE}((\text{CH}_3)_2\text{N}) = 9.01 \pm 0.02 \text{ eV}$ [63,68]. However, another value for the ionization energy of a $\text{C}_2\text{H}_6\text{N}$ species is reported to be 5.17 eV [27]. This is most probably the ionization energy of the CH_3NHCH_2 entity [30]. Thus we confirm, as discussed previously, that a certain proportion of the parent ions are capable of isomerisation to $\text{CH}_3\text{NHCH}_2\text{CHO}$, by H transfer from a methyl group to the nitrogen atom, before rupture of the nitrogen to carbonyl carbon bond occurs. The resulting dissociations to $\text{CH}_3\text{NHCH}_2^+ + \text{HCO}$ and $\text{CH}_3\text{NHCH}_2 + \text{HCO}^+$ are consistent with Stevenson's rule.

Another possible assignment for $m/z = 29$, to the ions HCNH_2^+ or CH_2NH^+ , with acetaldehyde CH_3CHO as neutral product, can be disregarded since the appearance energy of $m/z = 29$ would give $\Delta_f H(\text{HCNH}_2^+/\text{CH}_2\text{NH}^+) \approx 14.1 \text{ eV}$, far greater than the literature values $\approx 10.8 \text{ eV}$ [30].

3.2.4.8. $m/z = 28$. We remark that the $m/z = 28$ ion, which is quite intense (Table 2), is not due to a nitrogen (air) impurity, since we observe no ion signal at $m/z = 32$ and $m/z = 16$. Furthermore, the relative intensity of the $m/z = 28$ ion is similar to that in the electron impact mass spectra [27,28]. Possible assignments of the $m/z = 28$ fragment ion are (i) CO^+ , (ii) HCNH^+ , (iii) CNH_2^+ , as in the analogous case of N-methyl formamide.

- (i) Dissociation to $\text{CO}^+ + \text{C}_2\text{H}_7\text{N}$. The calculated minimum $\text{AE}(\text{CO}^+) = 14.365 \text{ eV}$ with $\text{C}_2\text{H}_5\text{NH}_2$ as neutral product, or 14.66 eV if the neutral is $(\text{CH}_3)_2\text{NH}$.

Much more probable is dissociation to HCNH^+ or CNH_2^+ .

- (ii) Dissociation to $\text{HCNH}^+ + \text{C}_2\text{H}_5\text{O}$. The calculated minimum $\text{AE}(\text{HCNH}^+) = 11.168 \text{ eV}$ (CH_3CHOH as neutral product) or 11.717 eV (CH_3OCH_2 as neutral product).
- (iii) Dissociation to $\text{CNH}_2^+ + \text{C}_2\text{H}_5\text{O}$. Calculated minimum $\text{AE}(\text{CNH}_2^+) = 13.427 \text{ eV}$ (CH_3CHOH as neutral product) or 13.976 eV (CH_3OCH_2 as neutral product).

A very probable pathway to formation of HCNH^+ or CNH_2^+ is loss of CH_4 from the unstable $(\text{CH}_3)_2\text{N}^+$ $m/z = 44$ ion [64]. This would lead to the calculated minimal appearance energies $\text{AE}(\text{HCNH}^+) = 11.516 \text{ eV}$ and $\text{AE}(\text{CNH}_2^+) = 13.775 \text{ eV}$.

3.2.4.9. $m/z = 27$. Although the $m/z = 27$ fragment ion is only weakly seen in the mass spectra of N,N'-dimethyl formamide (Table 2) its assignment is worth consideration. An immediate suggestion is that it is the fragment ion HCN^+ or HNC^+ , which are species of definite exobiological interest. These could result from H-loss from HCNH^+ . The reaction pathway would involve multiple steps so that the designation of the neutral product(s) is not evident. The assignment of $m/z = 27$ to C_2H_3^+ is much less probable since much more skeletal rearrangement would be necessary for its formation.

3.2.4.10. $m/z = 18$. The $m/z = 18$ fragment ion is quite intense (Table 2). Unfortunately there is no reported appearance energy for this ion. Possible assignments are $\text{H}_2\text{O}^+(\text{C}_3\text{H}_5\text{N})$, and $\text{NH}_4^+(\text{C}_3\text{H}_3\text{O})$. Since we do not observe $m/z = 16$ and $m/z = 17$ is very weak in the mass spectra (Table 2), the strong $m/z = 18$ signal is not due to a water impurity.

If $m/z = 18$ results from the dissociation $\text{H}_2\text{O}^+ + \text{C}_2\text{H}_5\text{CN}/\text{C}_2\text{H}_5\text{NC}$, we find, using the appropriate thermochemical values [38], that the estimated minimum appearance energy $\text{AE}(\text{H}_2\text{O}^+) = 12.625 \text{ eV}$ ($\text{C}_2\text{H}_5\text{CN}$ as neutral) or 13.556 eV ($\text{C}_2\text{H}_5\text{NC}$ as neutral).

We consider now the more probable assignment, NH_4^+ for $m/z = 18$. If $\text{C}_3\text{H}_3\text{O}$ is $\text{CH}_2=\text{CHCO}$ ($\Delta_f H = 0.746 \text{ eV}$ [38]), and using $\Delta_f H(\text{NH}_4^+) = 6.53 \text{ eV}$ [27], we can estimate the appearance energy of the NH_4^+ ion as $\text{AE} = 7.771 \text{ eV}$. This is rather low, in fact below the IE of the parent ion. However, there is another possible process leading to a more reasonable value for the appearance energy of the NH_4^+ ion. This involves another pathway for dissociation of the unstable $m/z = 44$ ($\text{CH}_3)_2\text{N}^+$ ion, that involving acetylene loss [66]: $\text{C}_2\text{H}_6\text{N}^+ \rightarrow \text{NH}_4^+ + \text{C}_2\text{H}_2$. The thermochemically estimated minimum appearance energy by this pathway is $\text{AE}(\text{NH}_4^+) = 10.878 \text{ eV}$, which is about 1.83 eV above the ionization energy of $\text{N,N}'$ -dimethyl formamide.

The MNDO calculations of Barone et al. [66,67] suggest that in this pathway, $\text{C}_2\text{H}_6\text{N}^+$ is the $\text{CH}_2=\text{CH}-\text{NH}_3^+$ ion which is reached after a series of isomerisations. This pathway is in competition with the molecular hydrogen loss channel from $\text{C}_2\text{H}_6\text{N}^+$, leading to the formation of the $m/z = 42$ ion (Table 2).

3.2.4.11. $m/z = 15$. The $m/z = 15$ fragment ion has a very significant intensity in both the photon and electron impact mass spectra (Table 2). A reasonable assignment is to the methyl cation CH_3^+ , with CH_3NHCO as the neutral species formed by rupture of a methyl carbon to nitrogen bond. This channel constitutes the charge switch reaction to that forming the $m/z = 58$ ion (Table 2). The ionization energy of CH_3 is $9.84 \pm 0.01 \text{ eV}$ [27]. Since the $m/z = 15$ ion is more than twice as intense as is the $m/z = 58$ ion in the mass spectra (Table 2), we conclude, from Stevenson's rule concerning charge-switch reactions [47], that the IE of the $\text{C}_2\text{H}_4\text{NO}$ neutral species (unreported in the literature) is substantially greater than that of the methyl radical.

4. Ionization energies and M.O. orders: trends

Our measurements of the ionization energies of the two highest energy filled molecular orbitals, the π and σ M.O.'s, of the series of molecules formamide, N-methyl formamide and $\text{N,N}'$ -dimethyl formamide provide more precise information on their adiabatic energy values (Table 3). They confirm the general conclusions of previous experimental and theoretical studies of the effects of methylation on ionization energies and M.O. orders of these molecules, in particular that there is an inversion in the order of the formamide σ and π orbitals on methyl substitution. This interpretation of photoelectron spectra concerning the energy order behaviour of the π and σ orbitals on methylation of formamide was compatible with the results of an early MINDO/3 calculation [69].

Table 3
Ionization energies (eV) of electrons in the highest energy occupied σ and π molecular orbitals.

M.O.	Formamide	N-methyl formamide	$\text{N,N}'$ -dimethyl formamide
σ	10.220 ± 0.005 [5]	10.05	9.45 ± 0.05
π	10.55 ± 0.01 [5]	9.55 ± 0.04	9.05 ± 0.01

The energy shifts in the σ molecular orbital are 170 meV and 770 meV in going from formamide to N-methyl formamide and $\text{N,N}'$ -dimethyl formamide, respectively. The corresponding shifts to lower ionization energies for the π M.O. are 1000 meV and 1500 meV , respectively. The π orbital is thus found to be much more susceptible to perturbation by N-methyl groups than the $\sigma(\text{n}_o)$ orbital. The more important lowering of the energy of ionization from the π orbital can be interpreted in terms of a hyperconjugative effect, i.e. from the greater interaction of the π components of the methyl groups with the π M.O. as compared with the $\sigma(\text{n}_o)$ orbital [24], so destabilising the π state. Hyperconjugation will also tend to reinforce molecular planarity. The effects of methylation can also be related to the results of *ab initio* molecular orbital calculations of charge localization associated with the formation of the radical cations of the formamide species [34]. These calculations show that electron loss on ionization, which involves both oxygen and nitrogen atoms in formamide, comes mainly from the N atom in N-methyl formamide and that on ionization of $\text{N,N}'$ -dimethyl formamide, there is a small increase in electron loss from the N atom [34].

We note, however, that in the *ab initio* calculations of Baldwin and Welham [34] the charge distributions in formamide and N-methylated analogues were determined from Mulliken population analysis. Although the Mulliken method of population analysis has been criticised [70] it has certainly been used successfully for small molecular ions [71]. A possible factor on the σ M.O. concerns the effect on hyperconjugation of changes in bond angles, and therefore on partial electron donation by the methyl groups [72]. By this donation, methyl groups can increase the electron density on the nitrogen atom, so that the lone pair electrons are less bound to nitrogen in the methylated compound. In going from ammonia to trimethylamine the ionization energy decreases by about 2.33 eV ; the change in bond angle from 106° to 110° is estimated to be responsible for about 1.78 eV of that decrease, due to the ability of the lone pair electrons of the nitrogen atom to take up more p character, adding to the ease of electron removal, while electron donation effects the remaining 0.55 eV of the IE decrease. In formamide the $\text{H}-\text{N}-\text{C}$ angles are 118.5° and 120.5° [73] while in N-methyl formamide the $\text{Me}-\text{N}-\text{C}$ angle is 121.4° [74]. These angles are close to those of sp^2 hybridized bonds. The bond angle modification on N-methyl substitution in formamide is therefore only likely to be a minor contributor to the 170 meV decrease in the energy of ionization from the σ orbital. Steric effects may be more important in going to $\text{N,N}'$ -dimethyl formamide, where the energy for the σ M.O. ionization is 770 meV less than in formamide (Table 3). However, in $\text{N,N}'$ -dimethyl formamide, the $\text{Me}-\text{N}-\text{C}$ angle, 120.3° [53], is also close to that of sp^2 hybridized bonds, so that the effect of bond angle on the ease of ionization would be expected to be not more important in the dimethyl compound.

5. Heats of formation, effects of methyl substitution: relation with number of atoms

Empirical generic equations for the calculation of heats of formation of homologous series of odd electron organic cations have been developed [75] and have been extended to both odd and even electron C_nH_m hydrocarbon cations [76]. These are size dependent relations. Holmes and Lossing [77] have shown that substitution of a functional group such as the methyl radical at the formal charge-bearing sites in both odd and even electron ions has, to a first approximation, a simple ion size effect on the heat of formation of the ions. They found a linear relation between the heat of formation of the ion and $\ln(n)$, where n is the number of atoms in the ion. Their study did not involve cations containing nitrogen atoms. Fig. 4, straight line α , shows that this relation holds well for the

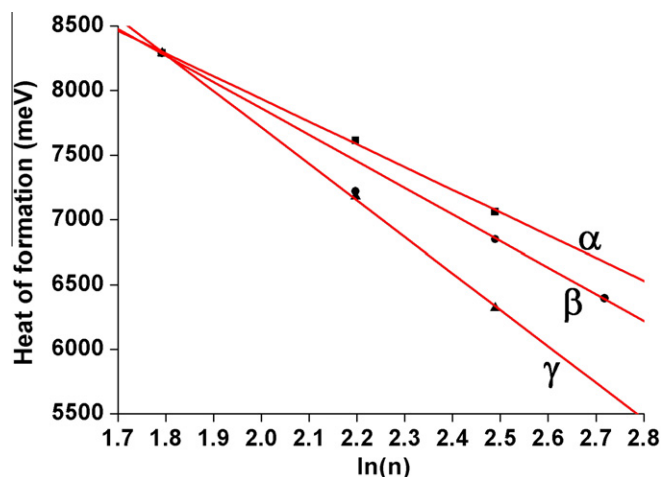


Fig. 4. Heats of formation of cations as a function of $\ln(n)$ where n is the number of atoms in the ion: formamide, N-methyl formamide and N,N'-dimethyl formamide (line α); formamide, acetamide, N-methyl acetamide and N,N'-dimethylacetamide (lines α and γ).

Table 4
Size effect on cation heats of formation of related formamides and acetamides.

Cation	No. atoms (n)	$\ln n$	Heat of formation (eV)	Reference
Formamide	6	1.792	8.29	[5]
N-methyl formamide	9	2.197	7.612 ± 0.071	Present study
N,N'-dimethyl formamide	12	2.489	7.063 ± 0.028	Present study
Acetamide	9	2.197	7.220 ± 0.078	[27]
			7.181	[38]
N-methyl acetamide	12	2.489	6.321 ± 0.062	[30]
			6.849	[38]
N,N'-dimethyl acetamide	15	2.718	6.394 ± 0.030	[38]

set of nitrogen-bearing cations of formamide, N-methyl formamide and N,N'-dimethyl formamide, using our values for $\Delta_f H$ of these ions. This is consistent with the principal charge-bearing site (location of greatest charge density) being the nitrogen atom in these three species [34].

We found it of interest to extend this size effect study to the related acetamide ions. The heats of formation of the cations of the series formamide, acetamide, N-methyl acetamide and N,N'-dimethyl acetamide [27,30,38] are also shown in Fig. 4.

A comparison of methyl formamide and acetamide cations shows that methyl substitution on the carbon atom of formamide leads to greater stability as compared with substitution on the nitrogen atom (N-methyl formamide). This behaviour extends to the heats of formation of N-methyl acetamide and N,N'-dimethyl acetamide cations in comparison with the analogous mono- and di-methyl derivatives of formamide (Table 4).

However, there are ambiguities in the reported heats of formation of the cations acetamide and its alkyl derivatives. Fig. 4 shows that a straight line (γ) can be drawn for the relation between $\ln n$ and $\Delta_f H(\text{formamide}^+)$, the NIST [27] or Lias et al. [38] values for $\Delta_f H(\text{acetamide}^+)$, and the Holmes et al. value for $\Delta_f H(\text{N-methyl acetamide}^+)$ [30], but a different straight line, (β), can be drawn that links $\Delta_f H(\text{formamide}^+)$ and the Lias et al. values for $\Delta_f H(\text{N-methyl acetamide}^+)$ [38] and $\Delta_f H(\text{N,N'-dimethyl acetamide}^+)$ [38].

We remark (a) that the Holmes et al. [30] $\Delta_f H(\text{N-methyl acetamide}^+)$ is based on the Watanabe et al. [60] PIMS value IE (N-

methyl acetamide) = 8.90 ± 0.02 eV and (b) the Lias et al. value $\Delta_f H(\text{N-methyl acetamide}^+) = 6.849$ eV is based on an IE (N-methyl acetamide) = 9.3 eV, considered as the onset of a He I PES band of N-methyl acetamide. Although the reference of this PES study is not specified by Lias et al. [38], it is presumably the article of Sweigart and Turner [78]. Examination of Fig. 2 of this article shows that the onset in the PES of N-methyl acetamide has been overvalued by Lias et al. and that a band onset can be chosen that is indeed compatible with the Watanabe et al. [60] value 8.9 eV. However, extrapolation, to $\ln n = 2.708$, of straight line γ in Fig. 4 predicts a value $\Delta_f H(\text{N,N'-dimethyl acetamide}^+) = 5.69$ eV, which is considerably lower than the Lias et al. value $\Delta_f H(\text{N,N'-dimethyl acetamide}^+) = 6.394 \pm 0.030$ eV [38]. The latter is based on the Watanabe et al. [60] PIMS value IE(N,N'-dimethyl acetamide) = 8.81 ± 0.03 eV [60]. A value $\Delta_f H = 5.69$ eV implies IE(N,N'-dimethyl acetamide) = 8.12 eV. We note that the PES of N,N'-dimethyl acetamide, (Fig. 2 of [78]) is compatible with a lowest value of 8.3 eV for the IE of this species.

These results call for new measurements of the heats of formation of N-methyl acetamide and N,N'-dimethyl acetamide. This essentially boils down to new measurements of the ionization energies of these methyl derivatives of acetamide. Until these studies are carried out, it is not possible to fully confirm that the heats of formation of the methyl derivatives of acetamide conform to the Holmes and Lossing relation with ion size [75].

6. Conclusion

The photoion mass spectrometry study of N-methyl formamide and N,N'-dimethyl formamide was carried out using monochromatized synchrotron radiation over the photon energy range 8–20 eV. The photoion mass spectra at 20 eV excitation energy of these two species were similar to their respective electron impact mass spectra observed with 70 eV electrons. Photoion yield curves of N-methyl formamide were measured for the parent ion and six fragment ions, and for the parent ion of N,N'-dimethyl formamide. The PIMS study of Arimura and Yoshikawa [59] provided appearance energies for several fragment ions of the latter. The ionization energy of N-methyl formamide was determined as $IE = 9.55 \pm 0.04$ eV, improving on higher values obtained by photoelectron spectroscopy. For N,N'-dimethyl formamide our PIMS $IE = 9.05 \pm 0.01$ eV improves slightly on the previous PIMS values $IE = 9.12 \pm 0.02$ eV [60]. For both of these species the ground state of the ion is a π state, which lies below the first excited σ state, in contrast to the energy order in formamide. This effect of methylation on the relative energies of these molecular orbitals is related to hyperconjugation effects and changes in charge localization on ionization.

The fragment ions were identified and the pathways of their formation were proposed on the basis of their appearance energies, aided by thermochemical data and the published results of electron impact mass spectral studies. The principal fragment ion in N-methyl formamide is $\text{H}_2\text{C}=\text{NH}_2^+$ and in N,N'-dimethyl formamide it has the elemental formula $\text{C}_2\text{H}_6\text{N}^+$, with HCO being the neutral product in both cases. At least two isomers of $\text{C}_2\text{H}_6\text{N}^+$ may be involved in the species formed at the two appearance energies for $m/z = 44$ in the dimethyl derivative and much of the discussion of the $m/z = 44$ ion, as well as some other fragment ions, involves the existence and fate of the dimethyl-nitrenium ion $(\text{CH}_3)_2\text{N}^+$. Overall, the chief dissociative photoionization processes in N-methyl formamide involve neutral loss of H, H_2O , CH_3 , H_2CN , HCO, CH_2NH_2 , CH_3O , CH_3OH , HCCO and H_2NCO . These include both small stable molecules as well as some free radicals. The main neutral products in the case of N,N'-dimethyl formamide are likewise H, CH_3 , OH, CO, HCO, H_2CO , CH_3O , $\text{C}_2\text{H}_3\text{O}$ and $\text{C}_2\text{H}_6\text{N}$. In both species it is pos-

sible that HCO, in the principal neutral loss channels, can be formed in its first excited electronic state $1^2A''$. Some simple bond cleavages are shown to lead to charge-switch reactions, in agreement with Stevenson's rule [47]. Isomerisation of the parent ion is considered to occur in some of the fragmentation reactions of both species. Many of the ions proposed as fragment ions must result from molecular rearrangements. If several different dissociation pathways of the parent ion are possible, the relative abundance of a particular fragment ion of this type will depend on the relative activation energy and the stability of the products of the rearrangement reaction as compared to those factors in other possible reaction pathways. Isomerisation of the parent ion, if it exists, will play an important role in determining which reaction pathways are available. Isotopic studies needed to clarify many of the proposed reactions in the present study.

Heats of formation were derived for all ions detected in the mass spectra and are compared with literature values where they exist; the values determined are often new or revised with respect to previous publications.

A comparative study was made of the heats of formation of the cations of formamide and its related methyl derivatives, N-methyl formamide, acetamide, N,N'-dimethyl formamide, N-methyl acetamide and N,N'-dimethyl acetamide. This study, as a function of the number of atoms in the species, was carried out in the spirit of the work of Holmes and Lossing [77] who established empirical rules for homologous series of cations, relating their heats of formation to size of the ion. We show that a simple relation holds for the cations of the series formamide, N-methyl formamide and N,N'-dimethyl formamide, but that there are ambiguities in the relation for the analogous series formamide, acetamide, N-methyl acetamide and N,N'-dimethyl acetamide. It is shown that the reported heats of formation for the acetamide series require re-investigation and this points, in particular, for a need to determine more precisely the ionization energies of N-methyl acetamide and N,N'-dimethyl acetamide.

Finally, we make some applications of our results to astrophysical and exobiological issues. H Ly- α emission, which is important in the VUV in both the solar system and in the interstellar medium (ISM), has an energy of 10.2 eV, which is above the ionization energy 9.55 ± 0.04 eV of N-methyl formamide as well as that, 9.05 ± 0.01 eV, of N,N'-dimethyl formamide. The ionization yield of these two species at 10.2 eV, and at the HI limit 13.6 eV in the ISM, can be estimated by using a rule of thumb valid for many molecules [1d,79]. We thus estimate, for N-methyl formamide, the total ionization yield for formamide would be 9% at 10.2 eV and 58% at 13.6 eV. The corresponding values for N,N'-dimethyl formamide are 16% and 65% respectively. The N-methyl formamide and N,N'-dimethyl formamide ions are stable up to 11.15 eV (H-loss channel, Table 1) and 10.59 eV (HCO-loss, Table 2) respectively. These energies are respectively 2.45 eV and 3.01 eV below the HI limit at 13.6 eV. These results should be integrated into models concerning the presence and possible survival of these prebiotic molecules in space. They particularly concern the conditions for observational searches for N-methyl formamide and N,N'-dimethyl formamide in the ISM and in comets, where these species would be subject to UV and VUV irradiation.

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