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Photoelectron Spectra of Chloramine and Dichloramine

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The He I photoelectron spectra of chloramine, NH_2Cl, and dichloramine, $NHCl_2$, have been obtained from observation of the products of the gas-phase reaction of NH_3 and Cl_2. The NH_2Cl concentration was optimized in the presence of excess NH_3, and the $NHCl_2$, with excess Cl_2. Spectrum-stripping was used to remove NH_3 and Cl_2 bands and to separate the NH_2Cl and $NHCl_2$. The resulting "pure" spectra correlate well with calculated ab initio eigenvalues and molecular orbital properties. On the basis of observed ion fragmentation, a heat of formation of 16 kcal mol^{-1} is derived for NH_2Cl.

Introduction

The chloramines, which may be regarded as the ammonia molecule with successive chlorine substitution of hydrogen, have been known for a long time. However, only the explosive completely substituted compound NCl_3 has been extensively studied. The monosubstituted compound NH_2Cl, chloramine, though unable to be isolated in pure form, is easily prepared in the gas phase by the so-called chloramine generator reaction[1]

$$2NH_3(g) + Cl_2(g) \rightarrow NH_2Cl(g) + NH_4Cl(s)$$

where a nitrogen atmosphere is used, with chlorine, nitrogen, and ammonia mixed in the recommended ratio of 1:3:30. It has also been prepared by the reaction of aqueous NH_3 and NaOCl at 0 °C[2] and by the vapor reaction of Cl_2O above an aqueous NH_3 solution.[3] It has been characterized by studies of its infrared spectrum,[2] and its geometry has been determined by microwave spectroscopy.[3] Its inversion barrier has been studied theoretically[4] and compared to an approximate experimental value.[5]

Dichloramine, $NHCl_2$, is obtained in gaseous NH_3/Cl_2 mixtures containing relatively more chlorine than in the chloramine generator, but equilibria involving NH_3 and the three chloramines have the effect of severely limiting the dichloramine lifetime. Moore and Badger[2] noted that while NH_3 inhibits the decomposition of NH_2Cl, it seems to react rapidly with $NHCl_2$ via

$$NH_3(g) + NHCl_2(g) \rightleftharpoons 2NH_2Cl(g)$$

The more stable NCl_3 is also produced, particularly at higher Cl_2 concentrations. Dichloramine has been studied by infrared spectroscopy, and five of its six fundamental modes have been assigned.[2]

Of the above molecules only NH_3[6] and NCl_3[7] have been studied by photoelectron (PE) spectroscopy. The high-resolution ultraviolet PE spectroscopic technique is proving a useful means of studying small molecules of limited accessibility. Recent work on relatively long-lived closed-shell molecules include data on CH_2NH,[8] N_2H_2,[9] CH_2CO,[10] and NH_2Br.[11] In certain cases the PE spectrum of the transient molecule is considerably overlapped by those of background molecules, for which careful spectrum-stripping is required in order to reveal the complete spectrum of the species of interest.

We have used a numerical spectrum-stripping technique, as described earlier,[8] with time-averaged digitized spectra to obtain the He I photoelectron spectra of NH_2Cl and $NHCl_2$ from measurements on the NH_3/Cl_2 gas-phase reaction products.

Experimental Section

Chlorine (at −80 °C) and ammonia (at −80 °C), held in glass tubes, were admitted simultaneously through Teflon needle valves to an all-glass reaction chamber. The gaseous reaction products passed directly to the glass inlet nozzle placed in the ionization chamber of the photoelectron spectrometer. The spectrometer, specially designed for the study of transient species, consists of separately pumped ionization and analyzer chambers. The helium discharge lamp is of standard design, and the electron analyzer is a 150° double-hemispherical electrostatic-focusing type. The spectrometer is controlled by an on-line PDP 11/20 minicomputer which operates a repetitive 1024 point analyzer sweep voltage over any chosen range and counts and stores the pulses from the electron detection and amplification system.

Because of the reaction producing solid NH_4Cl, there were some difficulties with pressure stability. By varying the relative amounts of the two reactants, we were able to obtain spectra which indicated variously an excess of NH_3 or of Cl_2. The flow rate of the gases reacting at room temperature was sufficient to prevent the formation of NCl_3. Only when a cold trap held at −30 °C was included in the inlet system could NCl_3 be identified by its PE spectrum particularly from its isolated second band at 11.2 eV.[7]

We chose to record accurate spectra for mixtures containing maximized amounts of NH_2Cl with NH_3 present and mixtures containing maximized amounts of $NHCl_2$ with Cl_2 present. The time-averaged scans were of about 20-min duration and at a pressure measured at $(1-2) \times 10^{-4}$ Torr in the ionization chamber. A high count rate was obtained because the inlet nozzle operated with a stagnation pressure of about 1 Torr, for which an estimated pressure of $\sim 4 \times 10^{-2}$ Torr was produced in the ionization region near the nozzle.

Results

The He I spectra of four different mixtures of NH_3/Cl_2 reaction products are shown in Figure 1. In each case the spectrum was accumulated over a 20-min period with maximum counts in the region of 20 000 for an operational resolution of about 30 meV. In Figures 1a and 1b excess Cl_2 is observable, and Figures 1c and 1d show excess NH_3. Comparisons of these spectra indicate that at least two further molecular species are involved. It is clear from the absence of a sharp band at 11.2 eV that no NCl_3 is present in any of these mixtures.

On the assumption that only two molecules, apart from NH_3 and Cl_2, are contributing to the four spectra, the interactive stripping program[8] was then used to obtain spectra of the "pure" components. There are no precise numerical criteria applicable to this stripping procedure, so it can be questioned on the basis of the subjectivity of the visual judgments required. However, reasonable assumptions concerning the origin and nature of particular PE bands can be made in suitable cases.

In the spectra in Figures 1c and 1d, the extremely sharp second band (12.0 eV) is very likely to belong to only one of the molecules present, and since it is analogous to the sharp second band observed for NH_2Br,[11] it is assigned to the monochloro species NH_2Cl.

The third band (12.4 eV), which appears in each of Figures 1a–d, is more prominent in Figure 1a corresponding to the excess Cl_2 mixtures. Since the sharp second band of Figures 1c and 1d is not present in Figures 1a and 1b, this third band can then be associated with another species, which is likely to be $NHCl_2$.

Rather than stripping a pure Cl_2 spectrum from, say, Figure 1a, we have found that, due to small changes in operational resolution for gases of considerably different composition, more

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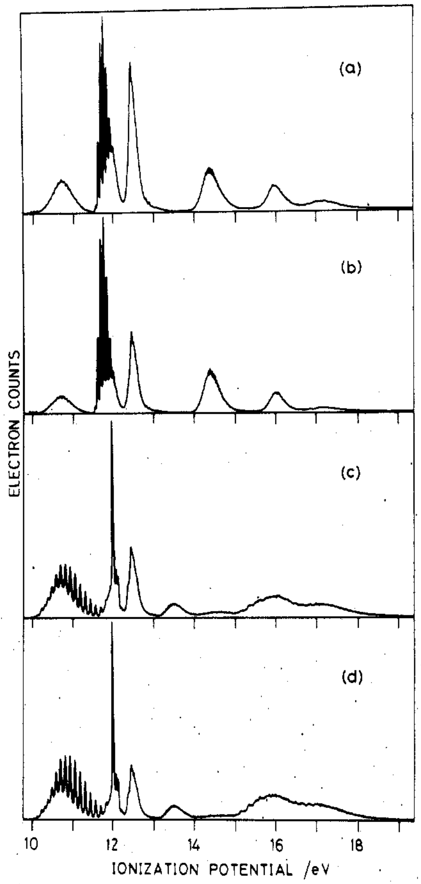

Figure 1. He I photoelectron spectra of NH_3/Cl_2 reaction mixtures. (a) and (b) show mostly $NHCl_2$ and excess Cl_2. (c) and (d) show both NH_2Cl and $NHCl_2$ with excess NH_3.

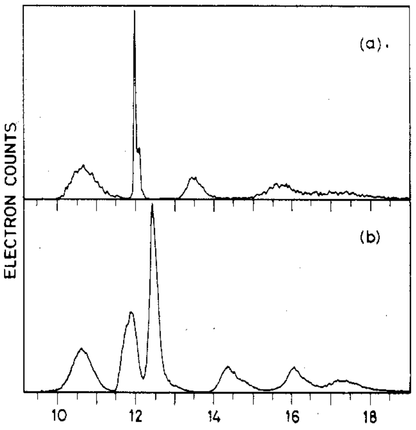

Figure 2. The stripped He I photoelectron spectra of (a) "pure" NH_2Cl and (b) "pure" $NHCl_2$.

Table I. Comparison of Experimental Vertical Ionization Potentials[a] and GAUSSIAN 70[b] Eigenvalues of NH_2Cl and $NHCl_2$ (in eV)

NH_2Cl (C_s)			$NHCl_2$ (C_s)		
IP	MO	$-\epsilon$	IP	MO	$-\epsilon$
10.60	10a′	9.66	10.52	12a′	10.21
11.95	3a″	10.85	11.85	9a″	11.13
13.45	9a′	12.76	12.40	11a′	11.87
15.70	8a′	14.61	12.40	8a″	11.99
17.11	2a″	17.93	14.40	10a′	14.77
			16.17	7a″	15.01
			17.32	9a′	17.59

[a] Accuracies vary between ±0.02 eV and ±0.10 eV. [b] For the STO-3G minimum basis.

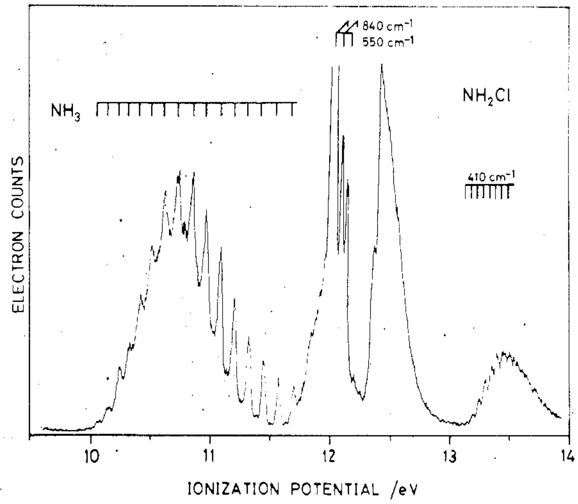

Figure 3. Vibrational assignment of the low ionization potential region of the He I photoelectron spectrum of one of the NH_3/Cl_2 reaction mixtures.

accurate spectrum-stripping results from the use of two experimental spectra which differ less markedly. Consequently, when varying proportions of spectrum 1b are stripped from spectrum 1a, to reduce the Cl_2 first band to the point of disappearance, the resulting spectrum is that shown in Figure 2b, which is assigned to "pure" $NHCl_2$.

When varying proportions of spectrum 1d are stripped from spectrum 1c, until the NH_3 first band is extinguished, the resulting spectrum with the prominent sharp band at 12.0 eV also contains some $NHCl_2$ as represented by the band at 12.4 eV. When spectrum 2b is suitably stripped from this intermediate mixed spectrum, the final spectrum, that of "pure" NH_2Cl, is as shown in Figure 2a. Because each of the four measured spectra of Figure 1 have contributed to the spectrum in Figure 2a, the result is a relatively noisy spectrum, and the apparent fine structure is mostly attributable to inadequacies in the stripping procedure.

Expectations from molecular orbital (MO) theory suggest that NH_2Cl should show a total of five p-based bands below about 18 eV and that $NHCl_2$ should show seven bands. Despite some overlapping of bands in the higher IP regions, Figures 2a and 2b show these expected band totals provided that, in the case of $NHCl_2$, the intense band at 12.4 eV is assigned to two ionizations. This is confirmed by the results of GAUSSIAN 70 ab initio calculations, based on the geometries suggested by the IR spectroscopic analysis.[2] The observed vertical IPs are compared with the calculated eigenvalues in Table I. The calculated assignments are consistent with the observed spectra.

For NH_2Cl, only the second and third bands show obvious fine structure, which is indicated in the high-resolution single-sweep spectrum in Figure 3. The first band of NH_2Cl shows some indications of vibrational structure but this is largely obliterated by the structure of the NH_3 first band.

The second band of NH_2Cl consists of a strong adiabatic peak at 11.95 eV followed by weaker peaks indicating two excited ion vibrations of 840 ± 50 and 550 ± 50 cm^{-1}, respectively. Since this band is assigned to ionization from a nonbonding chlorine orbital, these ion vibrations should be similar to the related symmetric vibrations of the neutral molecule. The IR assignment of Moore and Badger[2] shows frequencies of 1032 cm^{-1} (H_2N–Cl bend) and 686 cm^{-1} (N–Cl stretch), and it is reasonable to assign the measured NH_2Cl^+ ion vibrations accordingly. Hence both the 840 cm^{-1} (H_2N–Cl bend) and 550 cm^{-1} (N–Cl stretch) show small decreases from the molecular values.

Table II. Experimental and Calculated Relative Photoelectron Band Intensities and Ratios for NH_2Cl and $NHCl_2$

NH_2Cl

	Exptl			Calcd (A)			Calcd (PW)		
	Areas[a]			Areas[a]			Areas[a]		
Band	He I	He II	Ratio He I/He II	He I[b]	He II[b]	Ratio He I/He II	He I[c]	He II[c]	Ratio He I/He II
1	1.31	1.88	0.70	0.73	1.15	0.64	1.26	1.29	0.97
2	0.72	0.10	7.20	1.01	0.78	1.29	0.85	0.56	1.51
3	0.97	1.02	0.95	1.26	1.08	1.17	0.90	1.15	0.78

$NHCl_2$

	Exptl			Calcd (A)			Calcd (PW)		
	Areas[d]			Areas[d]			Areas[d]		
Band	He I	He II	Ratio He I/He II	He I[e]	He II[e]	Ratio He I/He II	He I[f]	He II[f]	Ratio He I/He II
1	0.88	2.20	0.40	0.65	1.46	0.44	1.05	1.68	0.62
2	1.29	0.58	2.22	0.76	0.89	0.86	0.90	0.69	1.31
3, 4	2.01	1.02	1.97	1.99	1.46	1.37	1.73	1.46	1.18
5	0.83	1.20	0.69	1.60	1.19	1.34	1.32	1.16	1.13

[a] Normalized to total intensity of 3.0. [b] Calculated total cross sections: He I, 42.3 Mb; He II, 8.53 Mb. [c] Calculated total cross sections: He I, 0.539 Mb; He II, 0.441 Mb. [d] Normalized to total intensity of 5.0. [e] Calculated total cross sections: He I, 87.7 Mb; He II, 11.3 Mb. [f] Calculated total cross sections: He I, 0.716 Mb; He II, 0.602 Mb.

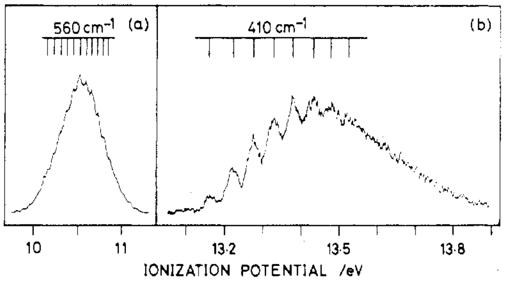

Figure 4. High-resolution He I photoelectron spectra of (a) the first band of $NHCl_2$ and (b) the third band of NH_2Cl.

The third band of NH_2Cl which is shown in an expanded form in Figure 4b has an onset at 13.16 eV and a regular vibrational progression of about eight members with a mean spacing of 410 ± 50 cm^{-1}. Just beyond the band maximum, at about the eighth vibrational peak, at 13.54 eV, the structure is lost and the band descends smoothly to a minimum beyond 14 eV. The 410-cm^{-1} vibrational frequency is clearly that of the N–Cl stretching mode in the ion, reduced from the molecular value of 686 cm^{-1}. The reduction is sufficient to indicate a weakened N–Cl bond in the ion, leading to the onset of ion fragmentation at 13.54 eV, as evidenced by the loss in vibrational structure. The third band of NH_2Cl is then associated with a N–Cl bonding MO.

Assuming that 13.54 eV represents the appearance potential for the NH_2^+ ion from NH_2Cl allows the calculation of some thermodynamic data. On the basis of tabulated heats of formation for NH_2^+[12] and Cl,[13] the $\Delta H_f{}^\circ{}_{298}$ for NH_2Cl is calculated at 16 kcal mol^{-1}. This compares favorably with the approximate value of 12 kcal mol^{-1} obtained using standard bond energy data.[14] Assuming that the N–H bond energy in NH_2Cl and NH_2Cl^+ is the same as that in NH_3 leads to N–Cl bond energies of 43 kcal mol^{-1} in NH_2Cl and 79 kcal mol^{-1} in NH_2Cl^+. The latter value is based on the NH_2Cl^+ appearance potential of 10.10 eV represented by the onset of the first PE band of NH_2Cl. These results suggest that ionization of NH_2Cl involves removal of an electron which is of N–Cl antibonding character.

For $NHCl_2$ only the first band shows identifiable fine structure, as indicated in the high-resolution single-sweep spectrum shown in Figure 4a. A regular vibrational progression of about nine peaks having a mean spacing of 560 ± 50 cm^{-1} is obtained. Moore and Badger[2] assign the 687 cm^{-1} neutral molecule vibration to symmetric N–Cl stretching and suggest that the NCl_2 symmetric bending vibration is not observed in their measurements because it is below 400 cm^{-1}. Since the GAUSSIAN 70 ab initio calculation on $NHCl_2$ shows the associated 12a′ MO to be considerably N–Cl antibonding, the symmetric N–Cl stretching frequency in the ion would be expected to be increased over that in the molecule, to say 750 cm^{-1}. Accordingly, we favor the assignment of the 560-cm^{-1} vibration in $NHCl_2^+$ to the NCl_2 symmetric bending vibration.

To assist in the assignment of the low IP bands of NH_2Cl and $NHCl_2$, single-sweep He II spectra were obtained. Gaseous NH_3/Cl_2 mixtures were used in which the amount of each chloramine was maximized in turn, and the spectra shown in Figure 5 were measured. Each is compared with a He I spectrum obtained under the same conditions. The attenuation expected for the bands of Cl character, as observed previously,[15,16] is obvious in changing from He I to He II radiation. Whereas the spectra in Figures 5c and 5d can be regarded as of pure $NHCl_2$, the spectra of Figures 5a and 5b are of a mixture of NH_2Cl and $NHCl_2$ as well as some NH_3, and the band areas obtained for NH_2Cl by correction for the $NHCl_2$ present can only be regarded as approximate. From the band area measurements, the relative attenuation experienced by the first three bands of NH_2Cl and the first five bands of $NHCl_2$ can be gauged.

The band intensity data are listed in Table II, together with the results of two sets of theoretical cross-section calculations. For each molecule and each wavelength the band intensities are normalized to the total number of bands included. The He I/He II ratios calculated from these normalized relative intensities will be high if the ionized electron is associated with considerable chlorine character and low if N, H character is dominant.

On the basis of the experimental intensity data it is then clear that the second band (11.95 eV) in NH_2Cl and the second (11.85 eV), third and fourth (12.40 eV) bands in $NHCl_2$ are virtually exclusively of Cl character and consistent with the narrow width of each band as observed in the He I spectra.

The first band in both molecules, on the other hand, has considerably less chlorine character and is probably of mainly nitrogen lone-pair character and related to the first band of NH_3. However, the fact that the vertical IPs (10.60 eV and 10.52 eV, respectively) are close to that of NH_3 (10.80 eV) despite the replacement of H by the more electronegative Cl suggests that the corresponding MO includes antibonding Cl character, as represented by the designation $n_N - n_{Cl}$. Similarly

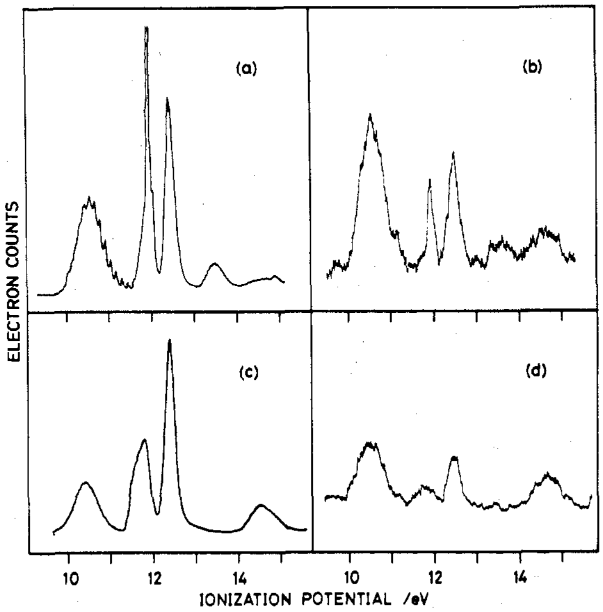

Figure 5. Comparison of the He I and He II photoelectron spectra in the low ionization potential region for NH_3/Cl_2 reaction mixtures. (a) is the He I spectrum and (b) the He II spectrum of a mixture with maximized NH_2Cl concentration. (c) is the He I spectrum and (d) the He II spectrum of a mixture containing mainly $NHCl_2$.

the third band of NH_2Cl (13.45 eV) and the fifth band of $NHCl_2$ (14.40 eV) are of mixed N, Cl character, as represented in the bonding MO designated by $n_{Cl} + n_N$.

Calculations and Discussion

The approximate molecular geometry of NH_2Cl obtained by Moore and Badger[2] does not differ greatly from the more accurate microwave geometry determined by Cazzoli et al.[3] The calculated eigenvalues listed in Table I are based on the Moore and Badger geometries of NH_2Cl and $NHCl_2$ and were determined using the STO-3G minimum basis of the GAUSSIAN 70 ab initio program.[17] For the accurate geometry of NH_2Cl there are only slight changes in the calculated properties.

In agreement with general experience for minimum bases, the theoretical IPs based on the Koopmans approximation are mostly lower, by up to 1 eV, than the experimental values. For small molecules such as these, the inaccuracies in the Koopmans approximation are not expected to cause errors in the order of MOs. The distribution of calculated IPs agrees well with the observed values, so the order of IPs representing the p-based MOs of each molecule are assigned as

NH_2Cl: 10a′ < 3a″ < 9a′ < 8a′ < 2a″
$NHCl_2$: 12a′ < 9a″ < 11a′ ~ 8a″ < 10a′ < 7a″ < 9a′

Analysis of the orbital composition and bonding properties of the calculated MOs, as given in Table III, shows good correlation with details in the PE spectra of both molecules. The bonding coefficient $\rho^i{}_{AB}$ of the ith MO for any pair of atoms A–B is given by the formula

$$\rho^i{}_{AB} = 1000 \sum_{\mu}^{A} \sum_{\nu}^{B} c_{i\mu} c_{i\nu} S_{\mu\nu}$$

in terms of MO coefficients c and AO overlaps S, as part of the population analysis in the GAUSSIAN 70 calculation.

The GAUSSIAN 70 MOs have been used, within the plane-wave (PW) approximation as developed by Ellison,[18] to give theoretical He I and He II cross sections. As well, the simple atomic formula (A) described by Gelius and Siegbahn[19] and based on the accurate theoretical atomic cross-section data of Manson[20] gives a second set of MO cross sections. The theoretical relative cross sections for the first three bands of NH_2Cl and the first five bands of $NHCl_2$ are given in Table II. There is reasonable agreement between the observed and theoretical relative He I/He II cross sections. For both molecules the A method gives the same order of bands in terms of increasing ratios and is marginally better than the PW method in this respect.

Table III. Molecular Orbital Compositions and Bonding Properties by GAUSSIAN 70[a] Calculations on NH_2Cl and $NHCl_2$

NH_2Cl

	% atomic compn			Bonding coeff ρ^b			
MO	N	H	Cl	NH	NCl	HH	HCl
10a′	38	2	60	−9	−46	3	−3
3a″	2	4	94	16	−15	−4	−14
9a′	39	0	61	1	38	0	−1
8a′	46	9	45	4	62	9	−9
2a″	50	44	6	164	11	−33	8

$NHCl_2$

	% atomic compn			Bonding coeff ρ^b			
MO	N	H	Cl	NH	NCl	ClCl	HCl
12a′	37	2	61	−5	−67	4	−1
9a″	1	0	99	0	0	−28	0
11a′	4	3	93	15	−13	7	−20
8a″	0	0	100	0	0	−6	0
10a′	38	0	62	0	46	10	0
7a″	29	0	71	0	73	−3	0
9a′	51	16	33	32	45	1	4

[a] For the STO-3G minimum basis. [b] Using the population analysis formula; see text.

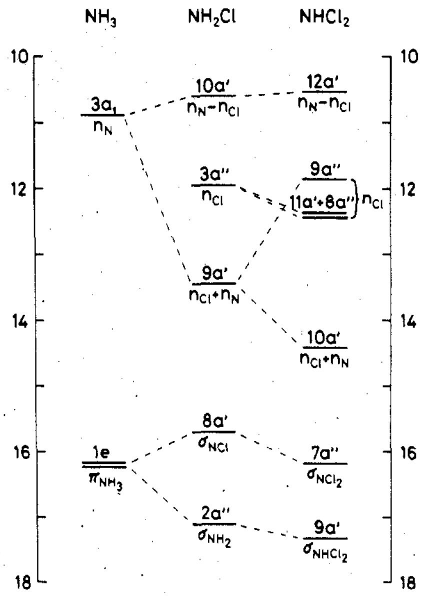

Figure 6. Correlation diagram for the experimental ionization potentials (in eV) of NH_3, NH_2Cl, and $NHCl_2$.

It is also useful to compare the PE spectra of NH_2Cl and $NHCl_2$ with that of ammonia, NH_3. Based on our assignments for the chloramines, a correlation diagram relating the observed IPs is shown in Figure 6.

For NH_2Cl, a major point of interest in the interpretation of the spectrum involves the first and third bands, as to which contains most of the nitrogen lone-pair character. The GAUSSIAN 70 molecular orbital compositions relating to these bands are very similar and show an excess of chlorine character. On the basis of these compositions the A cross section method gives good agreement with the observed He I/He II intensity ratios, though a simple intensity argument would lean toward more nitrogen character contributing to the first band.

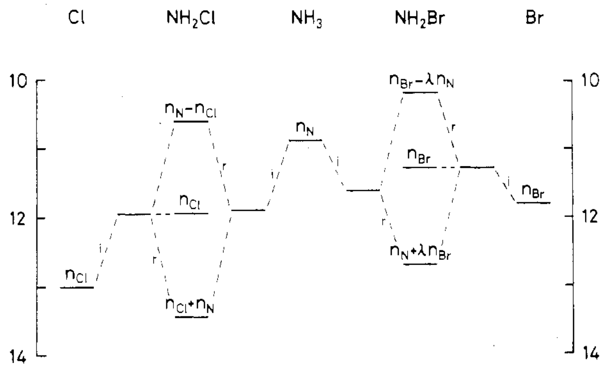

Figure 7. Comparison of the ionization potential correlations for NH_2Cl with NH_3/Cl and NH_2Br with NH_3/Br. In each case the inductive shifts shown as i are followed by resonance interactions r which result in upper MOs of different compositions for NH_2Cl and NH_2Br. IPs are in eV.

Clearly, the balance of n_N and n_{Cl} contributions in these related bands is rather sensitive as the n_N/n_{Cl} interaction is considerable. This means that the first band can be designated as $n_N - n_{Cl}$ which indicates the antibonding nature of the interaction, whereas the third band can be represented as $n_{Cl} + n_N$ which is the corresponding bonding combination.

It is interesting to note that our assignment here differs from the comparable assignment for NH_2Br,[11] where the first band is represented by $n_{Br} - \lambda n_N$ and the third band by $n_N + \lambda n_{Br}$. This difference between NH_2Cl and NH_2Br is due to the different electronegativities of Cl and Br. As illustrated in Figure 7, the interaction of n_N with n_{Cl} and n_{Br} involves different inductive shifts, which in terms of IPs place $n_N \simeq n_{Cl}$ but $n_N > n_{Br}$. Consequently, in NH_2Cl the resonance interaction gives resulting states $n_N - n_{Cl} < n_{Cl} + n_N$ with roughly equal N and Cl contributions, but in NH_2Br the resonance interaction gives resulting states $n_{Br} - \lambda n_N$ of mainly Br character and $n_N + \lambda n_{Br}$ of mainly N character.

The second band of NH_2Cl is clearly of n_{Cl} nonbonding character, and the fourth and fifth bands as illustrated in Figure 6 correlate with the 1e band of NH_3, with the σ_{NCl} band of lower IP than the σ_{NH_2} band.

For $NHCl_2$ the first five bands involve the nitrogen lone pair and chlorine nonbonding orbitals. On the basis of simple overlap considerations the interaction of the four Cl lone pair 3p orbitals would result in MOs ordered by IP as a″ < a″ ≈ a′ < a′ in C_s symmetry with the central pair associated with the most nonbonding overlaps. The observed bandwidths of the overlapped third and fourth bands in the He I spectrum correlate with this expectation for the central pair of MOs a′ ≈ a′. The second, third, and fourth bands are indicated by the He I/He II band intensity ratios to be of mainly chlorine character which is confirmed by the GAUSSIAN 70 calculations for the 9a″, 11a′, and 8a″ MOs.

The nitrogen lone pair is of a′ symmetry and its interaction with the Cl 3p orbitals produces two MOs, 12a′ and 10a′, which according to the calculations are similar balanced mixtures of n_N and n_{Cl} character, being antibonding in one case and bonding in the other. The He I/He II band intensity ratios agree with this result, though suggesting that the higher MO is of greater nitrogen character than the lower MO. Consequently, 12a′ can be represented as $n_N - n_{Cl}$ and 10a′ as $n_{Cl} + n_N$.

The remaining two bands of $NHCl_2$ can be seen from the correlation diagram in Figure 6 to relate directly to the 1e ammonia band. The calculations indicate that the 7a″ MO can be represented approximately as σ_{NCl_2} and the 9a′ MO as σ_{NHCl_2}.

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