Threshold-Photoelectron Spectroscopic Study of Methyl-Substituted Hydrazine Compounds[†]

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The valence shell electronic structures of methylhydrazine (CH_3NHNH_2), 1,1-dimethylhydrazine (($CH_3)_2$-NNH_2) and tetramethylhydrazine (($CH_3)_4N_2$) have been studied by recording threshold and conventional (kinetic energy resolved) photoelectron spectra. Ab initio calculations have been performed on ammonia and the three methyl substituted hydrazines, with the structures being optimized at the B3-LYP/6-31+G(d) level of theory. The ionization energies of the valence molecular orbitals were calculated using the Green's function method, allowing the photoelectron bands to be assigned to specific molecular orbitals. The ground-state adiabatic and vertical ionization energies, as determined from the threshold photoelectron spectra, were $IE_a = 8.02 \pm 0.16$ eV and $IE_v = 9.36 \pm 0.02$ eV for methylhydrazine, $IE_a = 7.78 \pm 0.16$ eV and $IE_v = 8.86 \pm 0.01$ eV for 1,1-dimethylhydrazine and $IE_a = 7.26 \pm 0.16$ eV and $IE_v = 8.38 \pm 0.01$ eV for tetramethylhydrazine. Due to the large geometry change that occurs upon ionization, these IE_a values are all higher than the true thresholds. New features have been observed in the inner valence region and these have been compared with similar structure in the spectrum of hydrazine. The effect of resonant autoionization on the threshold photoelectron yield is discussed. New heats of formation ($\Delta_f H$) are proposed for the three hydrazines on the basis of G3 calculations: 107, 94, and 95 kJ/mol for methylhydrazine, 1,1-dimethyhydrazine and tetramethylhydrazine, respectively. The previously reported $\Delta_f H$ for tetramethylhydrazine is shown to be erroneous.

Introduction

Photoelectron spectroscopy allows the conformation[1−7] of the molecules and ions such as hydrazine and its derivatives to be probed by measuring the splitting between the ionization energies of the two nitrogen lone pairs. This splitting is dependent upon the interaction between the lone pair electrons which, in turn, is dependent upon the dihedral angle subtended by the lone pair orbital axes. The magnitude of the interaction is affected by both hyperconjugation and induction with neighboring groups.[3] Theoretical studies have confirmed that the binding energies of the two lone pair orbitals are equal in symmetric hydrazine compounds in the absence of lone pair−lone pair mixing, whereas in unsymmetrical hydrazine compounds these lone pair orbitals have different energies even in the absence of this mixing.[5] As the lone pairs usually form the two most weakly bound orbitals, they give rise to the two photoelectron bands with the lowest binding energies and are thus readily studied using He I radiation. Such spectra have enabled the dihedral angle in numerous acyclic and cyclic alkylhydrazines to be deduced from the splitting between the two outermost bands.[1−7]

The ground-state photoelectron bands of ammonia,[8,9] hydrazine[3,4,10,11] and the hydrazine derivatives[1,3,5,12,13] are all fairly broad, with only that associated with ammonia displaying resolved vibrational progressions. Close to threshold, the photoionization yields of these compounds exhibit a gradual rise as a function of energy. Only in the case of ammonia can step structure, corresponding with ionization from successive vibrational levels, be discerned. These experimental observations are typical of those expected for molecules where the geometric configuration in the initial neutral state differs significantly from that in the ionic state. The changes in geometry, which are particularly significant for the tetraalkylhydrazines, result in a large difference in the adiabatic (IE_a) and vertical (IE_v) ionization energies. This difference, sometimes referred to as the relaxation energy,[14,15] represents the change in energy of the ion in adapting from the geometry of the neutral species to that of the ionic state in its equilibrium configuration. For the alkylhydrazines,[15] the relaxation energy reflects mainly the difference between alkyl group steric interactions in the equilibrium geometries of the neutral and ionic forms.

The photoabsorption and photoionization spectra of hydrazine have been measured by Syage et al.[14] in the vicinity of the ionization threshold. The interpretation of their results was consistent with ionization occurring from the C_2 gauche conformer, wherein the interaction between the nitrogen lone pairs is minimized, to an ion having D_{2h} symmetry. The geometric structures of several tetraalkylhydrazines have been studied using high-pressure mass spectrometry[15] and photoelectron[12,16] techniques. The results obtained by Meot-Ner et al.[15] indicate that neutral tetraalkylhydrazines, and their vertical cations, have nearly perpendicular lone pairs and bent nitrogens. In contrast, the relaxed cation (the adiabatic cation) has eclipsed alkyl groups and planar nitrogen atoms.

The goal of this study is to record the full photoelectron spectra of three methyl substituted hydrazines from threshold up to 32 eV to observe and assign the photoelectron bands

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TABLE 1: Comparison of Orbital Energies in Electronvolts for Ammonia

orbital		experiment		theory[c] 6-31+G(d)		theory[c] 6-311+G(d,p)		theory[c] cc-pVTZ	
		$IE_v{}^a$	$IE_v{}^b$	HF	ROVGF	HF	ROVGF	HF	ROVGF
3	1e	16.6		17.19	16.32	17.13	16.36	16.94	16.46
4	1e								
5	$3a_1$	10.93	10.910 ± 0.002	11.55	10.44	11.57	10.60	11.51	10.65

[a] Edvardsson et al.[9] [b] Locht et al.[8] [c] B3-LYP/6-31+G(d) optimized structure, C_{3v} symmetry, $E = -56.5231275$ hartrees.

arising from the inner valence molecular orbitals generated from the overlap of the 2s atomic orbitals.

Experimental Section

Materials. Methylhydrazine, 1,1-dimethylhydrazine and tetramethylhydrazine were commercially available from Aldrich with a purity greater than 97% and were used without further purification. The samples were subjected to three freeze−pump−thaw cycles to remove air before the measurements.

Experimental Overview. The experiments were carried out at the Daresbury Laboratory synchrotron radiation source using a rotatable hemispherical electron energy analyzer and a threshold photoelectron spectrometer. A full description of the experimental apparatus and procedure has been reported previously,[17,18] so only a brief account will be given here.

The complete valence shell photoelectron spectra of methylhydrazine and 1,1-dimethylhydrazine were measured in the binding energy range 7−32 eV using excitation energies of 35 and 80 eV. These spectra were recorded using the rotatable electron energy analyzer[17] attached to a spherical grating monochromator.[19] The spectrometer was set at the so-called magic angle such that the measured intensity was independent of the asymmetry parameter. The raw data have been corrected for the kinetic energy dependent transmission function of the analyzer.[17] The binding energy scale was calibrated by recording a spectrum of a mixture of the sample, together with helium and xenon.

The threshold photoelectron spectra were measured using a threshold photoelectron spectrometer[18] attached to a 5 m normal incidence monochromator.[20] Ionization occurs in a source region across which is applied a small electric field to extract the threshold (zero kinetic energy) electrons. The detection system consists of a lens optimized for high transmission of low energy electrons, followed by a hemispherical electrostatic analyzer. Spectra of methylhydrazine, 1,1-dimethylhydrazine and tetramethylhydrazine were recorded in the photon energy range 7−32 eV using a resolution (fwhm) of 0.1 nm (∼18 meV at $h\nu$ = 15 eV). The binding energy scale was calibrated by measuring the Kr $^2P_{1/2}$ peak using first- and second-order radiation. A lithium fluoride filter could be inserted into the photon beam to suppress higher order radiation. After passing through the interaction region, the incident radiation impinged upon a sodium salicylate screen. The resulting fluorescence was detected with a photomultiplier and the signal was used for normalization purposes.

Calculations. Ab initio molecular orbital calculations were performed using the Gaussian 98[21] suite of programs. For the optimization of the 1,1-dimethylhydrazine structure and the calculation of its vibrational frequencies, three levels of electron correlation were used (HF, MP2 and B3-LYP) with a total of eight different basis sets (from 6-31G(d) to 6-311+G(2df,p)). Of these, the 6-31+G(d) basis set was found to adequately describe the geometries and vibrational frequencies compared to the 6-311+G(2df,p) basis set. The B3-LYP treatment was chosen because it also gave relative energies consistent with

experiment. Results[22] obtained from metastable ion (MI) and collision-induced dissociation (CID) experiments performed on a modified VG ZAB-2HF mass spectrometer[23] showed that metastable ionized 1,1-dimethylhydrazine dissociates by loss of H and CH_3 in a 1:1.7 ratio. MP2 calculations predicted the energy difference between these two channels (44 kJ mol^{-1}) to be too large for them to compete on the microsecond time scale. The structures of the other molecules (ammonia, hydrazine, methylhydrazine and tetramethylhydrazine) were optimized at the B3-LYP/6-31+G(d) level of theory. The optimized structures were used to perform restricted outer valence Green's function (ROVGF)[24] calculations of the molecular orbital ionization energies with three basis sets: 6-31+G(d), 6-311+G(d,p) and cc-pVTZ.[25] The molecular orbital coefficients to assign the atomic orbital overlap were obtained using the keyword "pop=full" in Gaussian. The molecular characters were assigned by considering carefully the MO coefficients and MO pictures for each molecular orbital. G3 calculations,[26,27] based on the optimized B3-LYP/6-31+G(d) geometries and the scaled B3-LYP ZPE, were performed on the neutral and ionic methyl-substituted hydrazines to obtain adiabatic ionization energies and heats of formation for the neutrals and radical cations.

Results and Discussion

Validation of the Theoretical Treatment. Table 1 shows the correlation between the calculated and experimental[8,9] photoelectron spectrum of ammonia. The HF results are included for comparison. The ROVGF calculations were performed using three different basis sets to probe the minimum-reliable basis set requirements. Ammonia was used as a model molecule because it is the simplest compound containing a saturated nitrogen. As expected, the HF orbital IE results are all too high compared to the experimental values and will not be discussed further. With the 6-31+G(d) basis set, the vertical ionization energy of the highest occupied molecular orbital (HOMO) obtained from the third-order perturbation ROVGF treatment is 0.49 eV lower than the experimental value of 10.93 eV. Going to a triple-ζ basis set decreases this difference to 0.33 eV. A triple-ζ basis set that includes core-correlation (cc-pVTZ) gives the best agreement, a difference with experiment of 0.28 eV. Agreement is even better for the doubly degenerate 1e orbital; the cc-pVTZ basis set yielding a value only 0.14 eV lower than experiment. From these observations, cc-pVTZ is the most reliable of the three basis sets. The average deviation of the molecular orbital energy was calculated. With the 6-311+G-(d,p) basis set, the average deviation is 0.45 and 0.47 eV for methylhydrazine and 1,1-dimethylhydrazine, respectively, whereas with the cc-pVTZ basis set, the average deviation is 0.43 and 0.31 eV, respectively. Unfortunately, for tetramethylhydrazine, the cc-pVTZ basis set could not be used because of the large disk space requirements, and so orbital energies were calculated using the 6-311+G(d,p) basis set. Thus errors on the order of 0.3−0.4 eV can be expected for this molecule.

Threshold Photoelectron Spectra. The experimental threshold photoelectron spectrum for methylhydrazine (which has C_1

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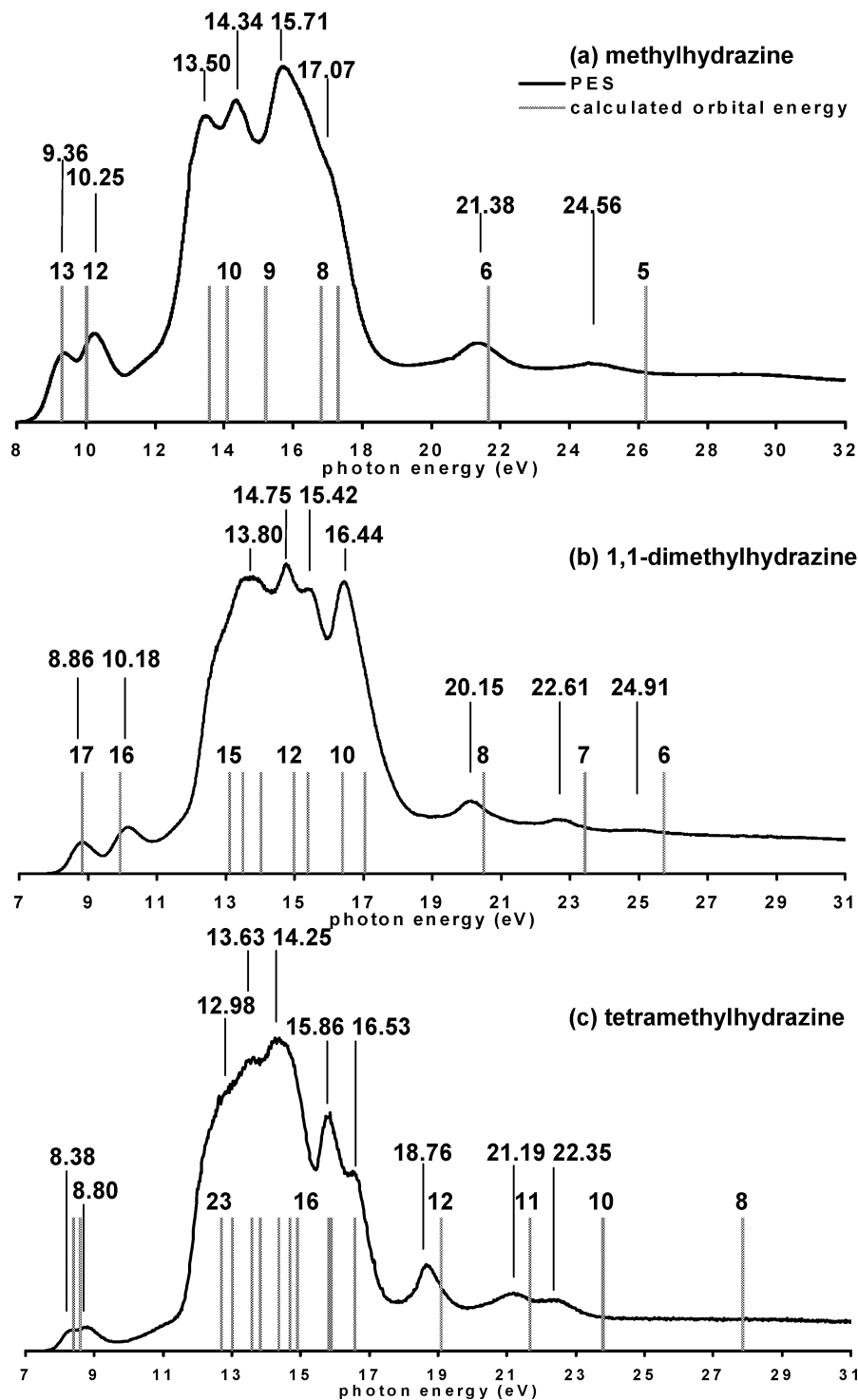*J. Phys. Chem. A, Vol. 110, No. 27, 2006* **8565**

Figure 1. Threshold photoelectron spectra of (a) methylhydrazine, (b) 1,1-dimethylhydrazine and (c) tetramethylhydrazine.

symmetry) is shown in Figure 1a and vertical ionization energies are listed in Table 2. Our experimental results are in accord with those reported by Kimura et al.[10] There is also satisfactory agreement with theory, although as the inner orbitals are probed, the agreement starts to break down as expected. The two highest molecular orbitals, orbitals 12 and 13, correspond to the bonding (n_+) and antibonding (n_-) combinations of the lone pair orbitals on the two nitrogen atoms (n$-$N). The orbital with the lower energy, $IE_v = 9.36$ eV, resides mostly on the methyl-substituted nitrogen atom, whereas the other orbital $(IE_v = 10.25$ eV) is located mostly on the NH_2 group. These experimental values correlate well with the calculated energies of 9.29 and 10.01 eV. The structure of methylhydrazine changes upon photoion-

ization of the highest energy n$-$N orbital (n_-) (Figure 2) in the same way as described by Syage et al.[14] for hydrazine. In the neutral molecule, the two nitrogen p-orbitals are rotated 90° with respect to one another to avoid a destabilizing four electron p$-$p overlap, whereas in the ion, the p-orbitals align to permit a net-stabilizing three electron overlap. In addition, the hydrogen atom on N2 (see Figure 2) lies out of the CNN plane in the neutral molecule and in-plane in the ion. Thus, the neutral ground-state molecule and the ion have different geometries and, as a consequence, the ejection of an electron from the lone pair on N2 results in the formation of an excited ion. Accordingly, Figure 1a shows a significant difference between the ground-state vertical and adiabatic ionization energies. The adiabatic

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TABLE 2: Comparison of Orbital Energies in Electronvolts for Methylhydrazine

		experimental				theoretical[b] ROVGF	
orbital	character	threshold	35 eV	80 eV	He(I)[a]	6-311+G(d,p)	cc-pVTZ
4	σ_{CNN}			29.96 ± 0.07		31.74	31.56
5	σ_{CN}, $\sigma_{NN}*$	24.56 ± 0.05	24.88 ± 0.05	24.96 ± 0.05		26.17	26.20
6	σ_{CH_3}, $\sigma_{NN}*$	21.38 ± 0.04	21.67 ± 0.04	21.57 ± 0.04		21.70	21.64
7	π_{NN}	(17.07 ± 0.03)	16.52 ± 0.03	16.40 ± 0.02	(17.1)	17.37	17.29
8	π_{NH_2}					16.88	16.80
9	$\pi_{NN}*$, $\pi_{CN}*$	15.71 ± 0.02		15.76 ± 0.02	(15.5)	15.10	15.20
10	π_{CH_3}	14.34 ± 0.02	14.35 ± 0.02	14.43 ± 0.02	14.32	14.13	14.09
11	σ_{NN}, π_{CH_3}	13.50 ± 0.02	13.47 ± 0.02	13.47 ± 0.02	13.38	13.60	13.56
12	n_+	10.25 ± 0.02	10.16 ± 0.01	10.26 ± 0.01	10.28	10.03	10.01
13	n_-	9.36 ± 0.02	9.30 ± 0.01	9.35 ± 0.01	9.36	9.30	9.29

[a] Kimura et al.[10] [b] Structure optimized at B3-LYP/6-31+G(d), C_1 symmetry, $E = -151.0996828$ hartrees.
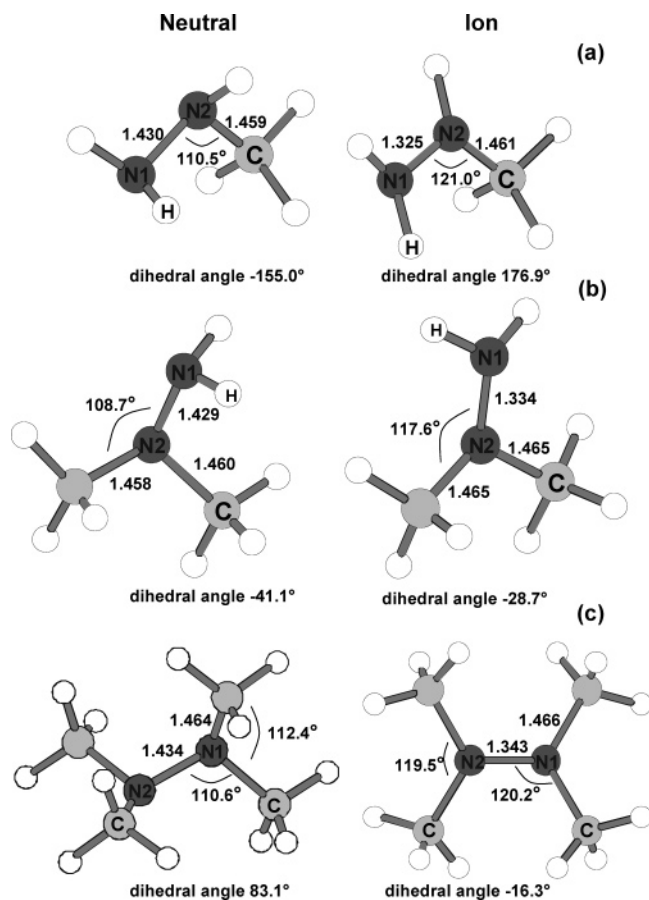

Figure 2. B3-LYP/6-31+G(d) optimized geometries of the neutral (left) and ionic (right) (a) methylhydrazine, (b) 1,1-dimethylhydrazine and (c) tetramethylhydrazine. The nitrogen atoms are dark gray, the carbon atoms are light gray and the hydrogen atoms are white. The dihedral angle is between the atoms identified by a letter (N, C or H).

ionization energy (8.02 ± 0.16 eV) is more than 1.3 eV lower than the vertical IE, a result of the geometric changes that take place upon ionization. As will be seen from calculations, the calculated adiabatic IE is lower than the experimental adiabatic IE by 0.59 eV (see below).

From the calculated orbital energies, it can be deduced that the structured band between 12 and 18 eV in the threshold photoelectron spectrum is due to an overlap of five molecular orbitals (7−11) with the shoulder around 17 eV corresponding to orbital 7.

Orbital 7 has π character located mostly between the nitrogen atoms because the molecular orbital coefficients on the carbon atom are small. Molecular orbital 8 has a shape similar to that of MO 7 and also has π character mostly located on the NH_2

group. Orbital 9 has its largest MO coefficients on the $2p_x$ atomic orbital of N2 and on the $2p_y$ atomic orbital of C and is attributed to a pseudo-$\pi*$ orbital. The next two molecular orbitals (10 and 11) correspond to the overlap of 2p atomic orbitals on the nitrogen and carbon atoms. They both have some π_{CH_3} character. Molecular orbital 11 has in addition some bonding σ character along the NN bond.

We observe two new photoelectron bands with vertical binding energies of 21.38 and 24.56 eV, and the extended outer valence Green's function calculations allow these to be assigned to orbitals 6 and 5, respectively. The calculated IE for orbital 5 is 1.64 eV higher than the experimental value. Such a discrepancy is not unexpected because the ROVGF method is not suitable for the inner valence orbitals where the molecular orbital model of ionization becomes invalid. Orbital 5 has some antibonding character between the nitrogen atoms and some bonding character along the CN bond. Orbital 6 has antibonding character between all backbone atoms and its largest MO coefficients are on the methyl group. This molecular orbital can be viewed as a bonding orbital for the methyl group. These two molecular orbitals are formed by the overlap of 2s atomic orbitals on the nitrogen and carbon atoms.

The MO assignment of methylhydrazine, described above, can be compared with that proposed by Potts et al.[11] for hydrazine (NH_2NH_2). In hydrazine, as in methyl-substituted hydrazine, these are two classes of orbitals called s-type and p-type. These orbitals occur in different energy ranges and are derived from the atomic s and p orbitals, respectively. For hydrazine, the binding energies for the p-type orbitals lie between 10 and 18 eV whereas those for the s-type orbitals occur between 22 and 30 eV. Ionization from the σ_u and σ_g s-type orbitals, which are derived from the N 2s atomic orbitals, results in broad bands with vertical ionization energies of ~24.5 and 30 eV, respectively. The p-type bands involve the N 2p atomic orbitals and give rise to three maxima, at ~10.5, 16 and 17.5 eV. The MOs of methylhydrazine can be classified in a similar manner. The molecular orbitals numbered 7 to 13 involve the nitrogen and carbon 2p atomic orbitals whereas the inner valence orbitals (MO 5 and 6) are formed by the overlap of the N and C 2s atomic orbitals.

The photoelectron spectrum of 1,1-dimethylhydrazine (C_1 symmetry) is shown in Figure 1b, and the orbital energies are listed in Table 3. The HOMO orbital energy ($IE_v = 8.86$ eV) corresponds to the lone pair on the dimethyl-substituted nitrogen atom (N2). As with methylhydrazine, ionization of the HOMO orbital changes the structure of 1,1-dimethylhydrazine. The neutral molecule again adopts a geometry that minimizes the destabilizing four electron p−p overlap between the two n−N orbitals by arranging the two orbitals perpendicular to each other. The ejection of an electron from the lone pair on the substituted

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TABLE 3: Comparison of Orbital Energies in Electronvolts for 1,1-Dimethylhydrazine

orbital	character	experimental				theoretical[b] ROVGF	
		threshold	35 eV	80 eV	He(I)[a]	6-311+G(d,p)	cc-pVTZ
5	σ_{CN}, σ_{NN}			29.86 ± 0.07		32.13	31.90
6	σ_{CN}	24.91 ± 0.05	25.10 ± 0.05	25.11 ± 0.05		26.87	25.67
7	π_{CN}	22.61 ± 0.04	22.84 ± 0.04	22.75 ± 0.04		23.69	23.43
8	σ_{CH_3}	20.15 ± 0.03	20.14 ± 0.03	20.12 ± 0.03		20.53	20.49
9	π					17.09	17.03
10	π_{NNC}	16.44 ± 0.02	16.57 ± 0.03	16.52 ± 0.03	16.35	16.44	16.39
11	σ_{CN}	15.42 ± 0.02	15.53 ± 0.02	15.60 ± 0.02	15.40	15.41	15.39
12	π_{CN}	14.75 ± 0.02	14.75 ± 0.02	14.95 ± 0.02	14.75	15.02	14.99
13	π_{CH_3}	13.80 ± 0.02				14.05	14.03
14	σ_{NN}		13.33 ± 0.02	13.43 ± 0.02	13.50	13.54	13.50
15	σ_{NC}		12.79 ± 0.02	12.92 ± 0.02	(13.0)	13.12	13.10
16	n_+	10.18 ± 0.01	10.01 ± 0.01	10.01 ± 0.01	10.07	9.92	9.92
17	n_-	8.86 ± 0.01	8.80 ± 0.01	8.81 ± 0.01	8.85	8.82	8.82

[a] Kimura et al.[10] [b] Structure optimized at B3-LYP/6-31+G(d), C_1 symmetry, $E = -190.3859277$ hartrees.

nitrogen (N2, Figure 2b) allows the NH_2 group to rotate to accommodate the stabilizing three-electron p−p overlap of the lone pair orbitals. In the ion, the lone pair orbitals are thus parallel and the NH_2 hydrogens lie almost in the CNC plane. As for the methylhydrazine ion, the 1,1-dimethylhydrazine ion is generated vibrationally excited. There is a difference of almost 1.1 eV between the measured HOMO vertical and adiabatic IEs (8.86 ± 0.01 eV vs 7.78 ± 0.16 eV, respectively).

Orbitals 16 and 17 are formed by the overlap of the 2p atomic orbitals of the nitrogen. For orbital 16, the MO coefficients are much larger on N1 than on any other atoms whereas for orbital 17, the MO coefficient is largest on N2.

The broad photoelectron band with a maximum at 13.80 eV is due to the ionization of three molecular orbitals (15, 14 and 13). Orbital 13 is assigned π character on both methyl groups because no electron density is found on the nitrogen atoms. Orbital 14 has a positive interaction of the $2p_y$ orbitals on the backbone atoms and therefore has bonding π character. As for orbital 15, there is essentially no electron density on the terminal nitrogen. It has a positive overlap of the $2p_x$ orbitals on N2 and the carbon atoms whereas the $2p_y$ orbitals on each carbon are out-of-phase. From considerations of MO coefficients and MO pictures, orbital 15 is assigned a σ_{NC} character.

The molecular orbitals 10, 11 and 12 may be associated with the three maxima observed in the photoelectron spectrum at 16.44, 15.42, and 14.75 eV, respectively. Orbital 10 was assigned a pseudo-π character between the two nitrogen atoms and the left carbon atom. MO 11 has some positive overlap between the two $2p_x$ atomic orbitals on N2 and C (the right carbon) and was given a σ_{NC} character. MO 12 has a positive overlap between N2 and both methyl groups and was assigned a π_{CN} character.

Distinct structure due to ionization from orbital 9 cannot be identified in the threshold photoelectron spectrum. The calculated IE_v of this orbital is 17.03 eV. Thus it may be contributing to the shoulder on the high binding energy side of the band centered at 16.44 eV. Orbital 9 is formed from the constructive overlap of the $2p_z$ atomic orbitals on the carbon and nitrogen atoms and thus is a pseudo-π orbital. Three new molecular orbitals, at higher energies, were identified in the photoelectron spectrum. The band at 20.15 eV can be assigned to orbital 8, that at 22.61 eV to orbital 7 and the third band observed slightly below 25 eV is assigned to orbital 6. These three molecular orbitals all have 2s as well as some 2p atomic orbital character involved. Orbital 6, which involves only the 2s atomic orbitals, is bonding between both methyl groups and N2 and has no bond between the two nitrogen atoms. Orbital 7 was assigned with π

TABLE 4: Comparison of Orbital Energies in Electronvolts for Tetramethylhydrazine

orbital	symmetry	character	experiment threshold	theory[a] ROVGF/6-311+G(d,p)
8	4b	σ_{NN}*, σ_{NC}		27.85
10	5a	σ_{CH_3}		23.79
9	5b	π_{CH_3}	22.35 ± 0.04	23.77
11	6a	σ_{CH_3}	21.19 ± 0.04	21.66
12	6b	σ_{NN}*, σ_{CH_3}	18.76 ± 0.03	19.07
13	7a	σ_{NN}, σ_{CH_3}	16.53 ± 0.03	16.58
14	7b	π_{NN}, σ_{CH_3}	15.86 ± 0.02	15.87
15	8a	σ_{NN}, σ_{CN}		15.80
16	8b	π_{CH_3}		14.90
17	9a	σ_{CH_3}		14.68
18	9b	π_{CH_3}	14.25 ± 0.02	14.36
19	10a	σ_{CH_3}		13.80
20	10b	π_{CH_3}	13.63 ± 0.02	13.56
21	11a	σ_{CH_3}		13.00
22	11b	π_{CH_3}	12.98 ± 0.02	12.99
23	12a	π_{NN}		12.67
24	13a	n_+	8.80 ± 0.01	8.58
25	12b	n_-	8.38 ± 0.01	8.38

[a] B3-LYP/6-31+G(d) optimized structure, C_2 symmetry, $E = -268.9475449$ hartrees.

character and has no electron density on N1. In orbital 8, there is no bonding between the methyl groups and the 2s atomic orbital of N2. Orbital 8 was therefore assigned with a σ_{CH_3} character.

Tetramethylhydrazine belongs to the C_2 point group. Many groups have reported the IE of the two nitrogen lone pairs as well as some higher ionization energies.[2,5,12,13,15,16,28] We report the full photoelectron spectrum of tetramethylhydrazine, shown in Figure 1c. The photoelectron spectrum is complicated and exhibits extensive overlap of many photoelectron bands. Ionization from the two nitrogen lone pairs gives rise to the doublet observed around 8.5 eV. Ionization of tetramethylhydrazine changes the nitrogen atoms from pyramidal in the neutral molecule to planar in the ion (Figure 2c), the ionic tetramethylhydrazine having C_1 symmetry. The change in geometry results in a measured difference of 1.12 ± 0.16 eV between the ground-state vertical and adiabatic IE values (Tables 4 and 5). Calculations of the orbital energies for tetramethylhydrazine were performed at the ROVGF/6-311+G(d,p) level of theory (Table 4). The ROVGF calculations for tetramethylhydrazine could not be carried out with the cc-pVTZ basis set because of the large size of the molecule. Nevertheless, there is good agreement between the calculated IEs and the photoelectron bands. Assignment of the molecular orbitals was thus possible.

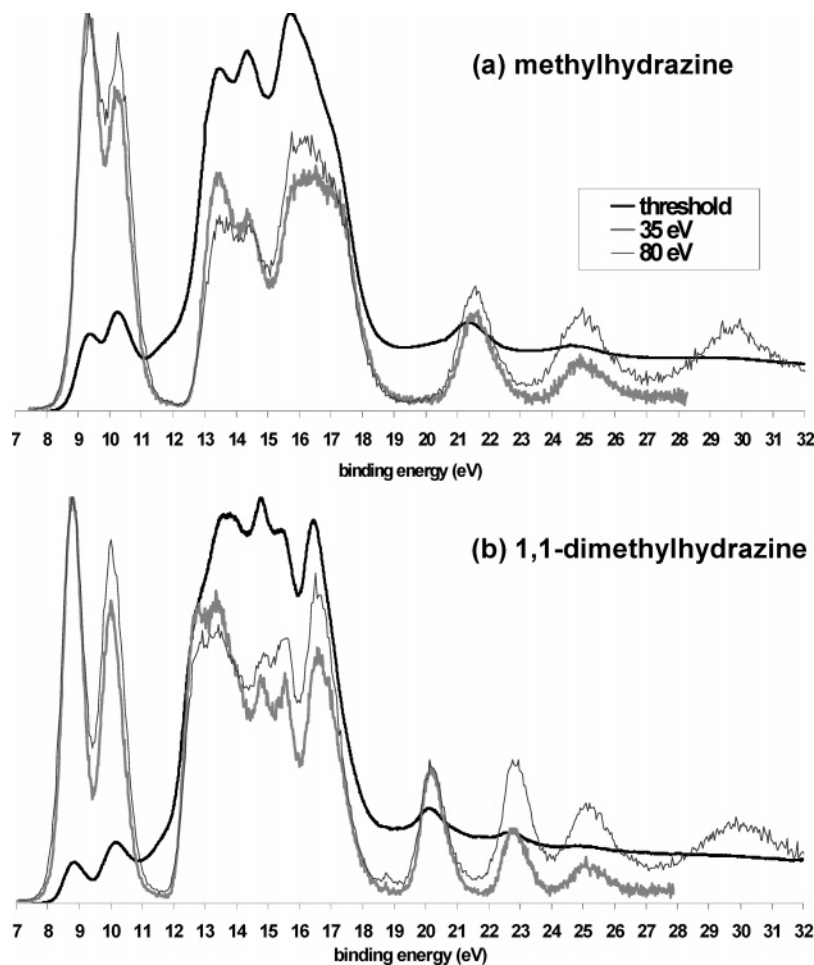The complex structure observed between ~11 and 18 eV in the threshold photoelectron spectrum may be attributed to

Figure 3. Comparison of the photoelectron spectra of (a) methylhydrazine and (b) 1,1-dimethylhydrazine at threshold, 35 and 80 eV.

overlapping bands associated with eleven molecular orbitals (23−13). This large structure has three distinct maxima at 14.25, 15.86 and 16.53 eV and two shoulders at 12.98 and 13.63 eV. From the ROVGF calculations, the first part of the structure seems to correspond to the overlap of MO 23 to 16. The second maximum at 15.86 eV appears to be due to the overlap of two MOs (15 and 14) whereas the maximum at 16.53 eV may arise from MO 13. All the molecular orbitals involved in these overlapping photoelectron bands are formed by the combination of the carbon and nitrogen 2p atomic orbitals.

Tetramethylhydrazine, a symmetric molecule, belongs to the C_2 point group unlike methylhydrazine and 1,1-dimethylhydrazine which belong to the C_1 point group. Hence, its molecular orbitals also have a symmetry identified by the letter a or b, which is related to the symmetry or antisymmetry with respect to the principal axis of symmetry, C_2. The three bands observed at binding energies greater than 18 eV correspond to ionization from molecular orbitals 9−12. A point of interest is that the calculated energy of orbital 5a (MO 10) is lower than that of orbital 5b (MO 9) by 0.02 eV. These are the only two orbitals calculated in this study for which the energy is actually inverted (relative to their HF ordering) with the use of Green's function. From the extended ROVGF calculations, we were able to calculate the inner valence orbital energy for MO 8. However, a peak due to ionization from this orbital is not discernible in our threshold photoelectron spectrum due to the low photoionization partial cross section. Orbital 8 is antibonding for the NN bond and orbital 9 pseudo π_{CH_3} character.

It is also important to mention that the calculated IEs for the molecular orbitals of methylhydrazine and 1,1-dimethylhydra-

zine also agree with the conventional photoelectron spectra obtained at 35 and 80 eV.

Comparison Between the Threshold and the Conventional Photoelectron Spectra. Figure 3 shows the threshold photoelectron spectra and the conventional photoelectron spectra, recorded at excitation energies of 35 and 80 eV, of methylhydrazine and 1,1-dimethylhydrazine. The threshold photoelectron spectra differ significantly from the conventional electron energy resolved spectra because resonant autoionization strongly affects the threshold photoelectron yield, particularly in the outer valence shell energy region. In conventional photoelectron spectra, the relative band intensities are determined by the energy dependent photoionization partial cross sections, and the profile of a specific band is governed by the Franck−Condon factor connecting the initial neutral ground state with the ionic state. Structure attributable to individual vibrational excitations is rarely observed in molecules the size of the methyl-substituted hydrazines. Thus, in the absence of autoionization, the band profile is independent of the excitation energy.

In contrast to conventional photoelectron spectra that are dominated by direct photoionization, threshold photoelectron spectra are strongly influenced by resonant autoionization.[29] This indirect, two step, process can affect both the band profile and the relative intensity. Thus the vertical ionization energy measured in a threshold photoelectron spectrum may differ from that determined in a conventional photoelectron spectrum.

The differences evident in the conventional and threshold photoelectron spectra of methylhydrazine and 1,1-dimethylhydrazine, are typical of those observed in small polyatomic molecules. Experimentally, it has been found that the relative
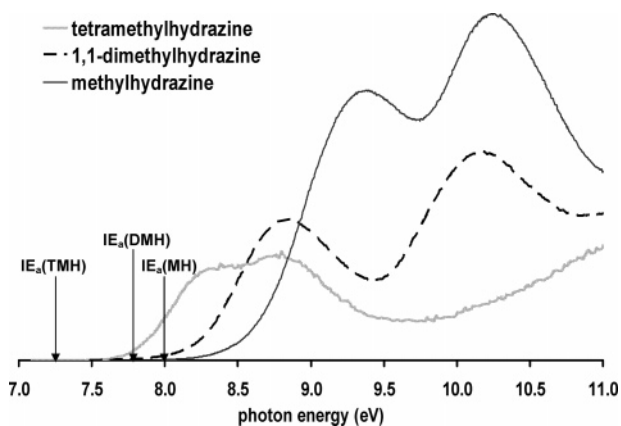
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Figure 4. Comparison of the first photoelectron band in the threshold photoelectron spectra of the three methyl-substituted hydrazines.

intensities of photoelectron bands associated with weakly bound orbitals tend to be greater in conventional spectra than in threshold spectra, whereas the converse holds for the more tightly bound orbitals. For both methylhydrazine and 1,1-dimethylhydrazine the two bands due to ionization from the nitrogen lone pair orbitals are more prominent in the conventional photoelectron spectra. Conversely, the overlapping bands due to orbitals with binding energies in the ~12−18 eV range are much more intense in the threshold photoelectron spectra. The enhancement in the latter bands can be attributed to resonant autoionization from numerous superexcited (Rydberg or valence) states lying in this region.

The photoelectron bands occurring in the inner valence region may be associated with the carbon and nitrogen atomic 2s orbitals. The inner valence photoelectron spectrum of hydrazine[11] exhibits two broad bands, derived from the N 2s orbitals, at binding energies of ~24.5 and 30 eV. The greater complexity of the structure observed in the inner valence region of methylhydrazine and 1,1-dimethylhydrazine can be attributed to the additional contributions from the C 2s orbitals. A direct correspondence between the experimental peaks and ionization from specific molecular orbitals cannot be expected in this energy region because the molecular orbital model of ionization is invalid.[30]

Effect of Methyl Substitution on the Ionization Energies of the Nitrogen Lone Pair Orbitals. Figure 4 shows an enlargement of the first two threshold photoelectron bands (corresponding to the nitrogen lone-pair orbitals) for the three molecules studied. Comparing methylhydrazine and 1,1-dimethylhydrazine, in which a hydrogen atom is substituted by a second methyl group, the IE_v of the substituted orbital is lowered whereas that of the orbital on the NH_2 group is unchanged. This shift to lower energy is due to the hyperconjugative overlap of the nitrogen atom lone pair with the pseudo-π^* orbital on the methyl groups. Double substitution of the amino group hydrogen atoms with methyl groups in tetramethylhydrazine lowers the energy of that orbital while leaving the original $N(CH_3)_2$ lone pair at the same energy. Tetramethylhydrazine, as mentioned previously, is a symmetric molecule. The energies of its two nitrogen lone pairs, however, are not equal because they have different symmetries (orbital 25 has a "b" symmetry whereas orbital 24 has an "a" symmetry). The orbital shifts due to methyl substitution are fairly additive. The calculated values for the two lone pairs are: hydrazine (9.97, 10.23 eV), methylhydrazine (9.29, 10.01 eV), 1,1-dimethylhydrazine (8.82, 9.92 eV), 1,2-dimethylhydrazine (8.93, 9.25 eV) and tetramethylhydrazine (8.38, 8.58 eV). Single methyl substitution lowers the first orbital ionization energy by ~0.68 eV whereas double substitution

TABLE 5: Comparison of the Present Experimental Adiabatic and Vertical Ionization Energies with Previously Reported Values and Calculated G3 Adiabatic Ionization Energies

molecule	IE_a (eV)	IE_v (eV)	$G3^a$ (eV)
methylhydrazine	8.02 ± 0.16^a	9.36 ± 0.02^a	7.44
	7.7 ± 0.15^b	9.32^i	
	7.67 ± 0.02^c	8.67^j	
	8.05^d	9.30^e	
	8.40^e	9.36^k	
	8.63 ± 0.1^f		
	7.67 ± 0.02^g		
	8.00 ± 0.06^g		
1,1-dimethylhydrazine	7.78 ± 0.16^a	8.86 ± 0.01^a	7.36
	7.29 ± 0.04^b	8.88^l	
	7.28 ± 0.04^c	8.88^i	
	7.87^d	8.28^j	
	8.05^e	8.80^e	
	8.12 ± 0.1^f	8.85^k	
	7.46 ± 0.02^g		
	7.67 ± 0.05^g		
tetramethylhydrazine	7.26 ± 0.16^a	8.38 ± 0.01^a	7.02
	6.78 ± 0.04^b	8.43^m	
	6.87^c	8.27^i	
	7.76 ± 0.05^f	8.26^h	
	6.87 ± 0.03^h	7.93^j	
		8.38^n	
		8.27^o	

^{a} Present work. ^{b} Meot-Ner.[15] ^{c} Lias.[35] ^{d} Syage.[14] ^{e} Vovna.[3] ^{f} Dibeler.[33] ^{g} Akopyan.[38] ^{h} Nelsen.[13] ^{i} Nelsen.[5] ^{j} Bodor.[28] ^{k} Kimura.[10] ^{l} Nelsen.[6] ^{m} Nelsen.[12] ^{n} Rademacher.[2] ^{o} Nelsen.[16]

TABLE 6: Comparison of the Calculated 298 K Heats of Formation of the Neutral and Ion Compounds with Reported Values

molecule	$\Delta_f H°$ (neutral) (kJ mol^{-1})		$\Delta_f H°$ (ion) (kJ mol^{-1})	
	lit.	G3	lit.^{d}	G3
methylhydrazine	$94.6 \pm 0.6,^a 81,^b 96^b$	107	835	825
1,1-dimethylhydrazine	$83.9 \pm 3.2,^a 77^b$	94	786	804
tetramethylhydrazine	69.5^c	95	732	772

^{a} Pedley et al.[32] ^{b} Bohn.[36] ^{c} Dibeler et al.[33] ^{d} Lias.[35]

results in an orbital IE ~ 1.10 eV lower than that in hydrazine. The calculated orbital energies assignments for hydrazine and 1,2-dimethylhydrazine can be found in supplementary information.

Hydrazine Ion Thermochemistry. Ground-state adiabatic and vertical ionization energies were determined from the threshold photoelectron spectra (Figure 4) and the results are summarized in Table 5. The present vertical ionization energies are in reasonable agreement with previous values but, as expected, the adiabatic ionization energies are somewhat higher than those measured by Meot-Ner et al.[15] using high pressure mass spectrometry. Because the geometric configurations of methylhydrazine, 1,1-dimethylhydrazine and tetramethylhydrazine change significantly upon ionization, the true adiabatic ionization thresholds are unlikely to be measured using photoelectron spectroscopy. For example, the adiabatic ionization energy of tetramethylhydrazine obtained by Meot-Ner et al.[15] is 0.48 eV lower than the present value.

Table 6 compares the heats of formation at 298 K for the neutral and ionic compounds. The heats of formation of the ions were calculated using the following relation (employing the stationary electron hypothesis):[31]

$$\Delta_f H(\text{ion}) = \Delta_f H(\text{neutral}) + IE_a \qquad (1)$$

The problem one encounters is the uncertainty in the three

neutral molecule $\Delta_f H$ values. The values reported by Bodor et al.,[28] 87, 129 and 249 kJ mol^{-1}, suggest an unreasonably large destabilizing methyl substitution effect and so will not be used further. The values for methylhydrazine and 1,1-dimethylhydrazine reported by Pedley et al.[32] are 94.6 ± 0.6 and 83.9 ± 3.2 kJ mol^{-1} respectively. These values indicate a methyl-substitution effect of 11 kJ mol^{-1}, which is roughly half that observed for methyl substitution on ethane (∼20 kJ mol^{-1}). The heat of formation of tetramethylhydrazine reported by Dibeler et al.[33] (69.5 kJ mol^{-1}) was obtained by group additivity. They used the heats of formation of hydrazine and 1,1-dimethylhydrazine given by Harshman[34] to estimate the value of the H_2N- and $(CH_3)_2N-$ additivity groups. This group additivity approach assumes that there are no interactions in the tetramethyl substituted molecule that are not equally present in the dimethyl substituted species. This is an erroneous assumption in this case. For example, the $\Delta_f H$ for the analogous molecule 2,2,3,3-tetramethylbutane can be estimated on the basis of doubling the additivity term for the *tert*-butyl group. If we obtain this term using the $\Delta_f H$ values for ethane (to get $-CH_3$) and neopentane (to then extract the *tert*-butyl group), the resulting $\Delta_f H$ for 2,2,3,3-tetramethylbutane is -252 kJ mol^{-1} compared to the experimental value of -226 kJ mol^{-1}.[35] Bohn and Klapötke[36] have calculated the heats of formation for methyl-hydrazine and 1,1-dimethylhydrazine using DFT and G2MP2. Their values, listed in Table 6, are lower than the reported values from Pedley et al.[32] except for the G2MP2 $\Delta_f H$ for methylhy-drazine. We performed G3 calculations on these molecules and the $\Delta_f H$ values obtained for the neutral and ionic species are $10-26$ kJ mol^{-1} higher than the reported values (Table 6). For the neutral compounds, the $\Delta_f H$ values do not decrease uniformly with increasing methyl substitution as expected from additivity. This can be explained by the fact that tetramethyl-hydrazine is more hindered due to the four methyl groups and that the stabilization obtained from the substitution is not large enough to compensate for the steric hindrance around the two nitrogen atoms. Nevertheless, the ionization energies derived from the G3 heats of formation are in rough agreement with those listed by Lias et al.[35] For 1,1-dimethylhydrazine and tetramethylhydrazine the calculated energies are 0.08 and 0.15 eV lower than those given by Lias et al., whereas that for methylhydrazine is 0.23 eV higher.

The ionization energies of homologous compounds have been shown to follow a linear relationship with $1/n$, where n is the number of atoms in the molecule.[31,37] Figure 5 shows the linear relationship between ionization energies and $1/n$ for the hydra-zines. Although previously deduced for adiabatic ionization energies, the present data indicate that this relationship also holds for the lowest vertical ionization energy. However, as can be observed from the graph, the energies of the orbitals identified as HOMO−1 to HOMO−3 inclusively (for example, HOMO−1 is orbital 24 in the case of tetramethylhydrazine) do not follow the linear trend. This can be explained by the fact that as one goes from hydrazine through to tetramethylhydrazine, the HOMO and HOMO−4 MOs involve the same atomic orbitals, whereas for HOMO−1 through HOMO−3, different atomic orbitals participate in the MOs for each compound. For example, HOMO−1 corresponds to the lone pair on the unsubstituted nitrogen atom in methylhydrazine and 1,1-dimethylhydrazine whereas in tetramethylhydrazine and hydrazine, this lone pair is delocalized on both nitrogen atoms. In Figure 5, Meot-Ner IE$_a$[15] values and our G3 IE$_a$ values have also been plotted and show linear relationships with respect to $1/n$.
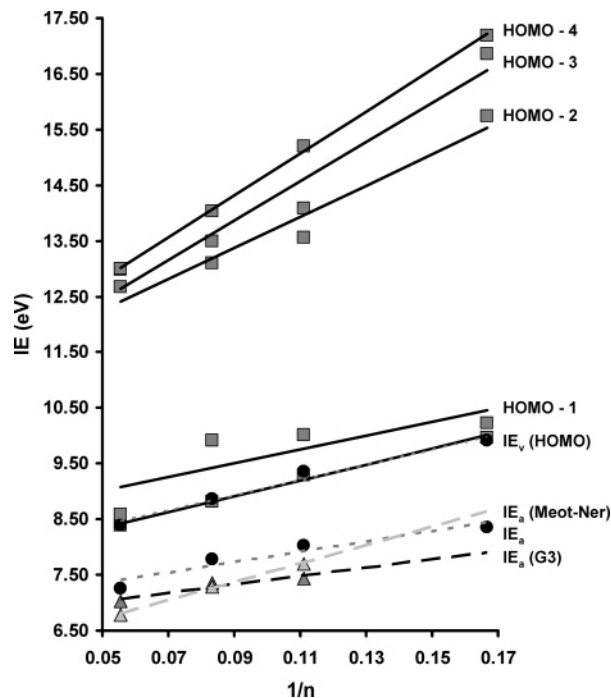

Figure 5. Plot of the experimental ionization energies as a function of the inverse of the size ($1/n$) of the molecule, including the ionization energies of hydrazine (IE$_v$ = 9.91 eV [10,14] and IE$_a$ = 8.36 eV[14]) as well as the calculated ROVGF energies of the first five highest occupied molecular orbitals (HOMO). The experimental data are shown in (●), the theoretical results for the HOMO are shown in (■) and the G3 and Meot-Ner[15] IEs are shown in (▲).

Summary

The valence shell electronic structures of methylhydrazine, 1,1-dimethylhydrazine and tetramethylhydrazine have been studied by recording threshold photoelectron spectra in the binding energy range $7-32$ eV. In addition, conventional photoelectron spectra have been measured at excitation energies of 35 and 80 eV. A comparison between the threshold and conventional photoelectron spectra has enabled the effect of resonant autoionization on the threshold photoelectron yield to be assessed. New features have been observed in the inner valence region and these have been compared with similar structure in the spectrum of hydrazine. The ionization energies of the valence molecular orbitals have been calculated using the Green's function method, thereby allowing the photoelectron bands to be assigned. Methyl substitution on the hydrazine backbone has the effect of lowering the ionization energy. A linear relationship between the ionization energy of a specific orbital and the inverse of the size of the molecule has been demonstrated. Neutral and ion heats of formation for methyl-hydrazine, 1,1-dimethylhydrazine and tetramethylhydrazine have been obtained from G3 calculations.

Supporting Information Available: Calculated orbital energies assignments for hydrazine and 1,2-dimethylhydrazine

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(Tables 1S and 2S). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Rademacher, P. *Tetrahedron Lett.* **1974**, *1*, 83.

(2) Rademacher, P. *Angew. Chem. Int. Ed.* **1973**, *12*, 408.

(3) Vovna, V. I.; Vilesov, F. I.; Lopatin, S. N. *Opt. Spectrosc.* **1975**, *38*, 143.

(4) Osafune, K.; Katsumata, S.; Kimura, K. *Chem. Phys. Lett.* **1973**, *19*, 369.

(5) Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 2392.

(6) Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6982.

(7) Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6987.

(8) Locht, R.; Leyh, B.; Hottmann, K.; Baumgärtel, H. *Chem. Phys.* **1998**, *233*, 145.

(9) Edvardsson, D.; Baltzer, P.; Karlsson, L.; Wannberg, B.; Holland, D. M. P.; Shaw, D. A.; Rennie, E. E. *J. Phys. B: At. Mol. Opt. Phys.* **1999**, *32*, 2583.

(10) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*; Japan Scientific Societies Press: Tokyo, 1981.

(11) Potts, A. W.; Williams, T. A.; Price, W. C. *Faraday Discuss.* **1972**, *54*, 104.

(12) Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 2011.

(13) Nelsen, S. F.; Rumack, D. T.; Meot-Ner, M. *J. Am. Chem. Soc.* **1988**, *110*, 7945.

(14) Syage, J. A.; Cohen, R. B.; Steadman, J. *J. Chem. Phys.* **1992**, *97*, 6072.

(15) Meot-Ner, M.; Nelsen, S. F.; Willi, M. R.; Frigo, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 7384.

(16) Nelsen, S. F.; Peacock, V.; Weisman, G. R. *J. Am. Chem. Soc.* **1976**, *98*, 5269.

(17) Holland, D. M. P.; MacDonald, M. A.; Hayes, M. A.; Baltzer, P.; Karlsson, L.; Lundqvist, M.; Wannberg, B.; von Niessen, W. *Chem. Phys.* **1994**, *188*, 317.

(18) Holland, D. M. P.; Shaw, D. A.; Sumner, I.; Hayes, M. A.; Mackie, R. A.; Wannberg, B.; Shpinkova, L. G.; Rennie, E. E.; Cooper, L.; Johnson, C. A. F.; Parker, J. E. *Nucl. Instrum. Methods Phys. Res. B* **2001**, *179*, 436.

(19) Finetti, P.; Holland, D. M. P.; Latimer, C. J.; Binns, C.; Quinn, F. M.; Bowler, M. A.; Grant, A. F.; Mythen, C. S. *Nucl. Instrum. Methods* **2001**, *B184*, 627.

(20) Holland, D. M. P. *Nucl. Instrum. Methods Phys. Res. B* **1989**, *44*, 233.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; J. Tomasi; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98,* revision A.6; Gaussian Inc.: Pittsburgh, PA, 1998.

(22) Subject of a future publication.

(23) Holmes, J. L.; Mayer, P. M. *J. Phys. Chem. A* **1995**, *99*, 1366.

(24) Cederbaum, L. S. *J. Phys. B* **1975**, *8*, 290.

(25) Dunning Jr, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(26) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

(27) Nicolaides, A.; Rauk, A.; Glukhovtsev, M. N.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 17460.

(28) Bodor, N.; Dewar, M. J. S.; Jennings, W. B.; Worley, S. D. *Tetrahedron* **1970**, *26*, 4109.

(29) Stockbauer, R. *Adv. Mass Spectrom.* **1980**, *A8*, 79.

(30) Cederbaum, L. S.; Domcke, W.; Shirmer, J.; von Niessen, W. *Adv. Chem. Phys.* **1986**, *65*, 115.

(31) Aubry, C.; Holmes, J. L. *Int. J. Mass Spectrom.* **2000**, *200*, 277.

(32) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: New York, 1986.

(33) Dibeler, V. H.; Franklin, J. L.; Reese, R. M. *J. Am. Chem. Soc.* **1959**, *81*, 68.

(34) Harshman, R. C. *Jet Propulsion* **1957**, *27*, 398.

(35) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*.

(36) Bohn, M. A.; Klapötke, T. M. *Z. Naturforsch.* **2004**, *59b*, 148.

(37) Holmes, J. L. *Int. J. of Mass Spectrom. Ion Processes* **1992**, *118/119*, 381.

(38) Akopyan, M. E.; Vilesov, F. I.; Terenin, A. N. *Bull. Acad. Sci. USSR Phys. Ser.* **1963**, *27*, 1054.