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# Vacuum Ultraviolet Photoelectron Spectroscopic Study of the $NH_2O$ and HNO molecules

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UV photoelectron spectra have been recorded for the F + $NH_2OH$ reaction at different reaction times. At short reaction times three bands associated with $NH_2O$ were observed, whereas at longer reaction times one band associated with NHO was seen.

The $NH_2O$ bands were assigned with the aid of *ab initio* molecular orbital calculations which used an essentially planar equilibrium geometry for the neutral ground state. The HNO band showed resolved vibrational structure which was analysed in terms of excitation of the N—O stretching and HNO deformation modes in $HNO^+(\tilde{X}\ ^2A')$. The first adiabatic and vertical ionization energies of $HNO(\tilde{X}\ ^1A')$ were measured as 10.18 ± 0.01 and 10.56 ± 0.01 eV, respectively. Assignment of the vibrational structure was confirmed by recording the first photoelectron band of DNO, prepared from the F + $ND_2OD$ reaction.

The molecules $NH_2O$ and HNO, their isomers HNOH and NOH, as well as their low-lying ionic states are thought to play important chemical roles in a number of environments. For example, it has been suggested the $NH_2O$ may be involved in the catalytic destruction of ozone in the stratosphere[1] and combustion studies of $NH_3$, NO and $O_2$ mixtures[2] indicate that HNO is an important intermediate in such systems. Also, the reactions

$$H_3^+ + NO \rightarrow HNO^+ + H_2 \quad (1)$$

$$H_3^+ + NO \rightarrow NOH^+ + H_2 \quad (2)$$

$$H_3^+ + NO \rightarrow NH_2O^+ + H \quad (3)$$

$$H_3^+ + NO \rightarrow HNOH^+ + H \quad (4)$$

have been postulated as ways in which the NO concentration can be reduced in dense interstellar clouds.[3] These reactions were proposed because NO has not yet been detected in these clouds despite predictions which indicate that $H_3^+$ and NO should be present as major constituents. This proposal is supported by the detection of radiofrequency emission from HNO in interstellar clouds,[4] an observation which represented the first identification of a molecule containing an NO bond in interstellar space.

In the laboratory, the first gas-phase observation of $NH_2O$ was achieved approximately six years ago by Davies *et al.*[5] using far-infrared laser magnetic resonance spectroscopy. In this work, $NH_2O$ was produced by both the F + $NH_2OH$ and $NH_2 + O_3$ reactions. The F + $NH_2OH$ reaction gave the most intense spectra, which were associated with a planar $C_{2v}$ structure for the radical. The isomer HNOH has yet to be observed spectroscopically in the gas phase, although *ab initio* calculations indicate it to be a stable molecule *ca.* 26 kJ $mol^{-1}$ higher in energy than $NH_2O$.[6–11] These expectations are supported by a neutralisation reionisation mass-spectrometric study of $NH_2O$ and HNOH which clearly indicate that both molecules are stable gas-phase species, with $NH_2O$ being the more stable.[8] The equilibrium geometry of HNOH in its ground state has been computed in a number of separate theoretical investigations to be a *trans* planar structure.[6,9] There is, however, some uncertainty concerning the equilibrium geometry of the ground state of $NH_2O$ as planar and non-planar minimum energy structures have been calculated,[6,10–12] although the more recent *ab initio* calculations[11–13] indicate that if $NH_2O$ is non-planar the zero-point energy is greater than the barrier to planarity.

HNO was first observed in the gas phase by electronic absorption spectroscopy by Dalby in 1958.[14] Since then there have been numerous spectroscopic studies on this molecule including microwave,[15,16] infrared[17–19] and electronic absorption and emission investigations.[20–23] The isomer HON does not appear to have been observed in the gas phase, although *ab initio* calculations indicate it to be a minimum on the HNO potential surface, *ca.* 100 kJ $mol^{-1}$ higher than the HNO minimum.[24–26]

The purpose of this present study is to record the UV photoelectron spectra of the primary and secondary reaction products of the gas-phase reaction F + $NH_2OH$. For each reaction intermediate observed, the photoelectron spectrum should yield the relative position of the ionic states accessible by one-electron ionization from the neutral molecule and the structure within a band should allow estimates to be made of the vibrational constants in the corresponding ionic state.

In the reaction of fluorine atoms with hydroxylamine two primary hydrogen-abstraction routes are possible:

$$F + NH_2OH \rightarrow NH_2O + HF \quad (5)$$

$$F + NH_2OH \rightarrow HNOH + HF \quad (6)$$

Because the enthalpies of formation ($\Delta H_f^{\ominus}$) of $NH_2O$ and HNOH are not available, it is not possible to calculate the enthalpies of reactions 5 and 6. However, it is clear from the neutralisation reionisation mass-spectrometric work of ref. 8 and previous *ab initio* calculations of the relative stabilities of $NH_2O$ and HNOH[6,7] that reaction 5 is more exothermic than reaction 6 by *ca.* 26 kJ $mol^{-1}$. HNO could be obtained in a secondary step by hydrogen abstraction from $NH_2O$, and HNO and NOH could be obtained from hydrogen abstraction from HNOH.

Although no direct measurements have been made of the first ionization energies of $NH_2O$ or HNOH, the first adiabatic ionization energy of DNO has been determined by electron-impact mass spectrometry as 10.29 ± 0.14 eV.[27] This value has been corrected to yield a value for the first adiabatic ionization energy of HNO of 10.23 ± 0.14 eV, using zero-point energies derived from *ab initio* calculations.[28] Similarly, although no calculations of the $NH_2O$ and HNOH valence ionization energies appear to have been carried out, the valence ionization energies of $HNO(\tilde{X}\ ^1A')$ and $HON(\tilde{X}\ ^3A'')$ have been computed in a number of separate studies.[24,29] In a series of *ab initio* MRD-CI calculations on HNO and $HNO^+$, the first vertical ionization energy of

HNO was computed as 10.05 eV (computed adiabatic value 9.75 eV) and the second and third vertical ionization energies were computed as 15.85 and 17.15 eV,[24] respectively. Similar calculations for NOH gave the first four vertical ionization energies as 10.08, 11.34, 14.40 and 16.00 eV with the first two adiabatic ionization energies being computed as 9.53 and 10.45 ± 0.15 eV.[24]

Obviously, $NH_2O$, NHOH, HNO and HON are all possible products of the $F + NH_2OH$ reaction. Hence to assist the assignment of the experimental photoelectron spectra, *ab initio* molecular orbital calculations were performed in this work on the ground electronic states of $H_2NO$, HNOH, and HNO as well as their low-lying ionic states. Use was also made of the results of existing calculations on NOH and $NOH^+$.[24,25,28,30,31]

## Experimental

The nitroxyl radical ($NH_2O$) and nitrosyl hydride (HNO) were prepared in this work *via* the rapid gas-phase reaction of fluorine atoms with hydroxylamine.

Fluorine atoms were generated by a microwave discharge (2.45 GHz) of a mixture of fluorine in helium (5%; BOC Ltd.). Helium was added to this mixture for further dilution as required. Hydroxylamine was obtained in the gas phase by thermal decomposition of solid hydroxylamine phosphoric acid, $(NH_2OH)_3 \cdot H_3PO_4$ (Fluka, *ca.* 97% purity),[32] which was heated to *ca.* 80 °C on the inlet system of the spectrometer. Apart from a small contribution from water which was present in the solid sample, the photoelectron spectra obtained in this way were consistent with pure $NH_2OH$.[33]

Deuterated hydroxylamine phosphoric acid was prepared using the method of Nightingale and Wagner.[32] This involved dissolving $(NH_2OH)_3 \cdot H_3PO_4$ in an excess of $D_2O$ and heating the solution to *ca.* 90 °C under reduced pressure to remove the solvent. This exchange procedure was repeated three times and resulted in a solid sample which was found by mass spectrometry to be at least 97% deuterated.

Most photoelectron spectra were recorded using a single-detector photoelectron spectrometer that had been specifically designed for the study of short-lived species in the gas phase,[34] although some experiments were also performed using a multidetector instrument.[35] In order to observe the products of the $F + NH_2OH$ reaction at different reaction times, spectra were recorded at reagent mixing distances above the photon beam in the range 0–9 cm.

All spectra were recorded with He Iα (21.22 eV) radiation and calibrated using the first photoelectron bands of NO[36] and $H_2O$ (or $D_2O$).[37] Nitric oxide was a reaction product, whereas water was present as a minor contaminant of the hydroxylamine phosphoric acid salt. Typical resolution under normal operating conditions was 25–30 meV (FWHM) as measured for argon with He Iα radiation.

## Computational Details

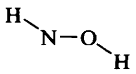
Initially, minimum-energy geometries were computed at the SCF level for $NH_2O$ and NHOH in their ground electronic states. Vertical ionization energies, which include the effects of electron correlation, were then computed by performing single-point calculations on the neutral and low-lying ionic states, obtained by one-electron ionization from the neutral molecule, at the computed SCF neutral molecule geometry. Geometry optimizations were also performed on the low-lying states of $NH_2O^+$ and $HNOH^+$.

Calculations were carried out using the quantum chemistry programs CADPAC[38] and ATMOL.[39] The basis set used, which was of triple-zeta valence plus polarization quality, consisted of the contracted Gaussian basis set of Dunning[40] ([5s3p] for nitrogen and oxygen and [3s] for hydrogen) augmented by polarization functions [these were Nd (exp. 0.98), Od (exp. 1.28) and Hp (exp. 1.00)].[41] All SCF calculations were of the restricted Hartree–Fock type. The optimized geometries and computed total energies obtained from these calculations are shown in Table 1.

As can be seen from Table 1, the computed minimum-energy geometry of HNOH ($\tilde{X}$ $^2A''$) is a *trans* planar geometry, in agreement with the results of earlier *ab initio* calculations.[6,9] The minimum-energy geometry of $NH_2O$ is computed to be a pyramidal $C_s$ geometry with an out-of-plane angle of 30.2° at the SCF level. As expected, however, the computed barrier to planarity (0.02 eV) is small compared with the zero-point vibrational energy (estimated from frequencies calculated with an SCF potential as 0.79 eV). In agreement with the results of previous calculations[6,7] at the SCF level, $NH_2O(\tilde{X}\ ^2A')$ is computed to be lower in energy than $NHOH(\tilde{X}\ ^2A'')$ by 22 kJ $mol^{-1}$, where both molecules are at their SCF minimum-energy geometries. When configuration interaction calculations are performed with allowance for Davidson's correction this difference increases to 37 kJ $mol^{-1}$.

**Table 1** Minimum-energy SCF geometries of the ground electronic states of HNOH and $NH_2O$ and some low-lying cationic states calculated using a TZP Gaussian basis set[a]

| | point group | r(N—H)/Å | r(N—O)/Å | r(O—H)/Å | ∠HNO/° | ∠NOH/° | out-of-plane angle, α/° |
|---|---|---|---|---|---|---|---|
| $NHOH(\tilde{X}\ ^2A'')$ | $C_s$[b,c] | 1.007 | 1.346 | 0.942 | 102.3 | 106.1 | 0.0 |
| $NHOH^+(\tilde{X}\ ^1A')$ | $C_s$[b] | 1.026 | 1.191 | 0.972 | 107.5 | 111.9 | 0.0 |
| $NHOH^+(\tilde{a}\ ^3A'')$ | $C_s$[b] | 1.022 | 1.242 | 0.965 | 127.2 | 113.5 | 0.0 |
| $NH_2O(\tilde{X}\ ^2A')$ | $C_s$[c] | 0.996 | 1.272 | — | 116.4 | — | 30.2 |
| $NH_2O(\tilde{X}\ ^2B_1)$[d] | $C_{2v}$ | 0.993 | 1.261 | — | 119.2 | — | 0.0 |
| $NH_2O^+(\tilde{X}\ ^1A_1)$ | $C_{2v}$ | 1.024 | 1.140 | — | 120.0 | — | 0.0 |
| $NH_2O^+(\tilde{a}\ ^3A_2)$ | $C_{2v}$ | 1.014 | 1.253 | — | 117.3 | — | 0.0 |
| $NH_2O^+(\tilde{A}\ ^1A_2)$ | $C_{2v}$ | 1.016 | 1.290 | — | 117.4 | — | 0.0 |

[a] See text for details of the calculations. [b] Both $NHOH(\tilde{X}\ ^2A'')$ and the $NHOH^+$ states considered, have computed *trans* planar  equilibrium geometries. [c] The SCF computed total energies for $NHOH(\tilde{X}\ ^2A'')$ and $H_2NO(\tilde{X}\ ^2A')$ at their minimum-energy geometries are −130.429856 and −130.438078 hartree, respectively. [d] At the SCF level the planar $C_{2v}$ structure for $NH_2O$ is a saddle point on the ground-state potential surface. [e] The minimum-energy geometry for $NH_2O$ computed at the UHF/MP2 level is a planr $C_{2v}$ structure with r(N—O) = 1.264 Å, r(N—H) = −1.010 Å, ∠HNO = 120.1°. [$NH_2O(\tilde{X}\ ^2B_1)$].

The electronic configurations of $NH_2O(\tilde{X}\ ^2A')$ and $HNOH(\tilde{X}\ ^2A'')$ at their optimized SCF geometries are

$$\ldots(5a')^2(6a')^2(2a'')^2(7a')^1 \quad NH_2O(\tilde{X}\ ^2A')$$

$$\ldots(6a')^2(1a'')^2(7a')^2(2a'')^1 \quad HNOH(\tilde{X}\ ^2A'')$$

For $NH_2O(\tilde{X}\ ^2A')$, ionization from the 7a′ level will give a $^1A'$ state whereas ionization from the 2a″ or 6a′ levels gives $^3A''$ and $^1A''$, or $^3A'$ and $^1A'$ states, respectively. Similarly, for $HNOH(\tilde{X}\ ^2A'')$, ionization from the 2a″ level gives a $^1A'$ state, whereas ionization from the 7a′ or 1a″ levels gives $^3A'$ and $^1A'$, or $^3A''$ and $^1A''$ states, respectively. By carrying out SCF calculations on these states as well as on the neutral ground state at the computed neutral molecule geometry, ΔSCF vertical ionization energies were obtained (see Tables 2 and 3). The computed total energies for each state were then corrected for the effects of electron correlation *via* configuration interaction calculations. The SCF calculations were performed using the ATMOL3 suite of programs[39] and the configuration interaction calculations used the ATMOL Direct CI method.[42] All configurations generated by single and double excitations with respect to the reference configuration were considered in the configuration interaction procedure. In each case it was found that the reference configuration was the main contributor to the wavefunction of the state in question, with a coefficient greater than 0.95. Quadruple excitations were allowed for by applying Davidson's correction.[43] Adiabatic ionization energies were derived from similar calculations performed at the computed equilibrium geometries for both the neutral and cationic states of NHOH and $NH_2O$. The results of these calculations are presented in Tables 2 and 3.

**Table 2** Computed vertical ionization energies for $NHOH(\tilde{X}\ ^2A'')$ in eV[a]

| orbital ionized | ionic state | ΔSCF[b] | ΔSCF + CI + Q[b] |
|---|---|---|---|
| 2a″ | $^1A'$ | 10.46 (9.15) | 9.58 (9.24) |
| 7a′ | $^3A''$ | 10.44 (9.67) | 11.48 (10.41) |
| 7a′ | $^1A''$ | 12.55 — | 13.16 — |
| 1a″ | $^3A'$ | 12.17 — | 13.63 — |
| 1a″ | $^1A'$ | 12.30 — | — — |

[a] See text for details of calculations. All calculations were performed at the minimum-energy SCF geometry of $NHOH(\tilde{X}\ ^2A'')$ computed in this work and shown in Table 1. The SCF + CI + Q total energy obtained for $NHOH(\tilde{X}\ ^2A'')$ is −130.843 384 hartree. [b] Adiabatic ionization energies are shown in brackets. They were calculated from the minimum-energy geometries found for $NHOH^+(^1A')$ and $NHOH^+(^3A'')$ with SCF + CI + Q total energies of −130.503 766 and −130.460 762 hartree, respectively.

**Table 3** Computed vertical ionization energies for $NH_2O(\tilde{X}\ ^2A')$ in eV[a]

| orbital ionized | ionic state | ΔSCF[b] | ΔSCF + CI + Q[b] | experimental values[c] |
|---|---|---|---|---|
| 7a′ | $^1A'$ | 9.80 (8.71) | 9.26 (8.71) | 9.48 ± 0.02 |
| 2a″ | $^3A''$ | 9.50 (9.20) | 10.92 (10.25) | 10.77 ± 0.01 |
| 2a″ | $^1A''$ | 10.01 (9.70) | 11.48 (10.95) | 11.46 ± 0.01 |
| 6a′ | $^3A'$ | 11.38 — | 13.03 — | |
| 6a′ | $^1A'$ | 11.55 — | — — | |

[a] See text for details of calculations. All calculations were performed at the minimum-energy SCF geometry of $NH_2O(\tilde{X}\ ^2A')$ computed in this work and shown in Table 1. The SCF + CI + Q total energy obtained for $NH_2O(\tilde{X}\ ^2A')$ is −130.853 617 hartree. [b] Adiabatic ionization energies are shown in brackets. They were calculated from the minimum-energy SCF geometries for $NH_2O^+(\tilde{X}\ ^1A_1)$, $NH_2O^+(\tilde{a}\ ^3A_2)$ and $NH_2O^+(\tilde{A}\ ^1A_2)$ with SCF + CI + Q total energies of −130.533 526, −130.477 001 and −130.451 118 hartree respectively. [c] This work.

Analogous calculations were also performed for HNO and the results are presented in Table 4.

As the equilibrium out-of-plane angle of $H_2NO$ in its ground electronic state is one of the central issues of this present study, it was decided to perform further calculations, which include the effects of electron correlation, to provide a more reliable estimate of the equilibrium geometry of this molecule.

$NH_2O$ and $H_2CF$ are isoelectronic radicals with 13 valence electrons. They are both expected to be non-planar on the basis of Walsh's rules.[44] Although gas-phase microwave[45,46] and far infrared LMR[5,47] studies indicate that both these molecules are effectively planar, the possibility of a small inversion barrier in these radicals cannot be excluded.

Initially, configuration interaction calculations were performed for $NH_2O$ at both the non-planar SCF minimum-energy geometry and for a planar geometry with all other parameters held at their SCF minimum-energy values. These calculations indicated that the planar $NH_2O$ structure was lower in energy than the pyramidal geometry. The geometry of the ground state of $NH_2O$ was then optimized at the UHF-MP2 level with the triple-zeta valence plus polarization basis set described earlier. The equilibrium geometry of $NH_2O$ in its ground state was computed to be planar at this level of theory with the other geometrical parameters being very similar to those obtained at the SCF level (see Table 1).

For planar $NH_2O$, the electronic ground state configuration is

$$\ldots(5a_1)^2(1b_1)^2(2b_2)^2(2b_1)^1,\ NH_2O(\tilde{X}\ ^2B_1)$$

Ionization from the $2b_1$ level gives a $^1A_1$ state whereas ionization from the $2b_2$ or $1b_1$ levels gives $^3A_2$ and $^1A_2$, or $^3A_1$ and $^1A_1$ states.

## Results and Discussion

Spectra of the F + $NH_2OH$ reaction were recorded at a range of mixing distances above the photon beam in the region 0–9 cm, at fixed reagent partial pressures. At long

**Table 4** Computed vertical ionization energies (eV) for $HNO(\tilde{X}\ ^1A')$[a]

| ionization | ionic state | Koopmans' theorem value | ΔSCF | | ΔSCF + CI | | ΔSCF + CI + Q | |
|---|---|---|---|---|---|---|---|---|
| | | | $I_v$, | $I_a$ | $I_v$, | $I_a$ | $I_v$, | $I_a$ |
| $(7a')^{-1}$ | $\tilde{X}\ ^2A'$ | 11.34 | 9.84 | 9.46 | 10.07 | 9.75 | 9.95 | 9.81[b] |
| $(1a'')^{-1}$ | $^2A''$ | 16.71 | 14.83 | 14.02 | 16.39 | 15.31 | 16.63 | 15.44 |
| $(6a')^{-1}$ | $^2A'$ | 18.41 | —(c) | 16.30 | — | | — | |
| $(5a')^{-1}$ | $^2A'$ | 20.72 | — | | — | | — | |

[a] See text for details of these calculations, which were all performed using geometries optimized at the SCF level. The electronic configuration of $HNO(\tilde{X}\ ^1A')$ is … $(5a')^2(6a')^2(1a'')^2(7a')^2$. [b] The experimental first adiabatic and vertical ionization energies of $HNO(\tilde{X}\ ^1A')$ measured in this work are 10.18 ± 0.01 and 10.55 ± 0.01 eV, respectively. [c] Convergence problems were encountered with this state at the neutral molecule geometry.

mixing distances (>6 cm), bands due to NO[36] and HF[48] were observed as the only reaction products. At shorter mixing distances two different types of spectra were obtained. Examples of these spectra are shown in Fig. 1 and 2. Fig. 1 was recorded at 1.5 cm above the photon beam and shows the ionization energy range 8.5–13.5 eV. A number of bands can be readily assigned in this spectrum. First, the first band of NO[36] (a reaction product) and the first two bands of the unreacted parent $NH_2OH$[33] can be identified. The first band of water[37] was also observed. Water was present in all spectra as it arose as an impurity in the solid hydroxylamine phosphoric acid used and was evolved with $NH_2OH$ on heating. This proved useful because, as the first bands of $H_2O$ and NO were present in all spectra and as their band positions are accurately known, these features could be used to calibrate the spectra obtained. HF, first vertical ionization energy 16.04 eV,[48] was also observed even at the shortest mixing distances. It arose as a primary reaction product at these reaction times. The only other known major feature to be seen at short reaction times was the first band of atomic fluorine (first ionization energy 17.42 eV[49]). However, as shown in Fig. 1, in the ionization energy region 12.5–13.5 eV weak contributions arising from HOF, a known product of the F + $H_2O$ reaction,[50] were also observed. The remaining features in Fig. 1 cannot be assigned to the reagents or any known stable product of the F + $NH_2OH$ reaction. The two sharp bands (labelled $NH_2O$ in Fig. 1 and 2) at 10.77 ± 0.01 and 11.46 ± 0.01 eV were found to be proportional in intensity to each other over a range of reagent partial pressures and mixing distances. Their experimental relative intensity, corrected for the transmission function of the analyser, was measured from a large number of expanded spectra as $(2.9 \pm 0.1):1$ with the band at 10.77 eV ionization energy being the more intense. A broad band (labelled as $NH_2O$ in Fig. 1) was also seen underneath the first band of NO. Although it was heavily overlapped by the first band of NO, some vibrational structure could be resolved associated with this feature. The vertical component was measured as 9.48 ± 0.01 eV and the average vibrational separation over four components was measured as $1640 \pm 40$ cm$^{-1}$. This band was proportional in intensity to the bands at 10.77 and 11.46 eV over the range of experimental conditions used. Also, the observed components cannot be attributed to ionization of vibrationally excited NO, as they were not in the correct positions as calculated from the first adiabatic ionization energy of NO($\tilde{X}\ ^2\Pi$) and known spectroscopic constants of NO($\tilde{X}\ ^2\Pi$) and NO$^+$($\tilde{X}\ ^1\Sigma^+$).[36]

Some features seen in Fig. 1 (*e.g.* the structured band labelled as HNO) were also observed in Fig. 2. This spectrum was recorded at the same reagent partial pressures as used for Fig. 1, but at a longer mixing distance above the photon beam (3.5 cm). On inspection of Fig 1 and 2, it can be seen that when the mixing distance is increased from 1.5 to 3.5 cm the bands labelled as $NH_2OH$ and $NH_2O$ decrease whereas the first band of NO increases and the band labelled as HNO stays approximately constant. The band labelled as HNO in these figures has adiabatic and vertical ionization energies of 10.18 ± 0.01 and 10.56 ± 0.01 eV, respectively. It exhibits two distinct vibrational series with average separations of $1960 \pm 30$ and $1090 \pm 40$ cm$^{-1}$. The observed intensity changes, as a function of mixing distance at constant reagent partial pressures, of the bands associated with $NH_2OH$, NO, HNO, $NH_2O$ and HF are shown in Fig. 3. Under the conditions used, $NH_2O$ maximises at *ca.* 1 cm mixing distance whereas at longer reaction times it decreases to be replaced by HNO, which in turn is subsequently converted into NO.

Inspection of spectra in the ionization energy region 12.0–21.0 eV gave no evidence of any bands which chould be associated with the bands labelled as $NH_2O$ and HNO in the lower ionization energy region (9.0–12.0 eV). This is almost certainly because higher bands associated with these molecules are masked by more intense bands arising from HF, NO, $NH_2OH$, HOF and $H_2O$.

The F + $ND_2OD$ reaction was also investigated as a function of mixing distance above the photon beam. The spectra obtained were very similar to those obtained for the F + $NH_2OH$ reaction and showed very similar behaviour with mixing distance to that shown in Fig. 3. For spectra of the

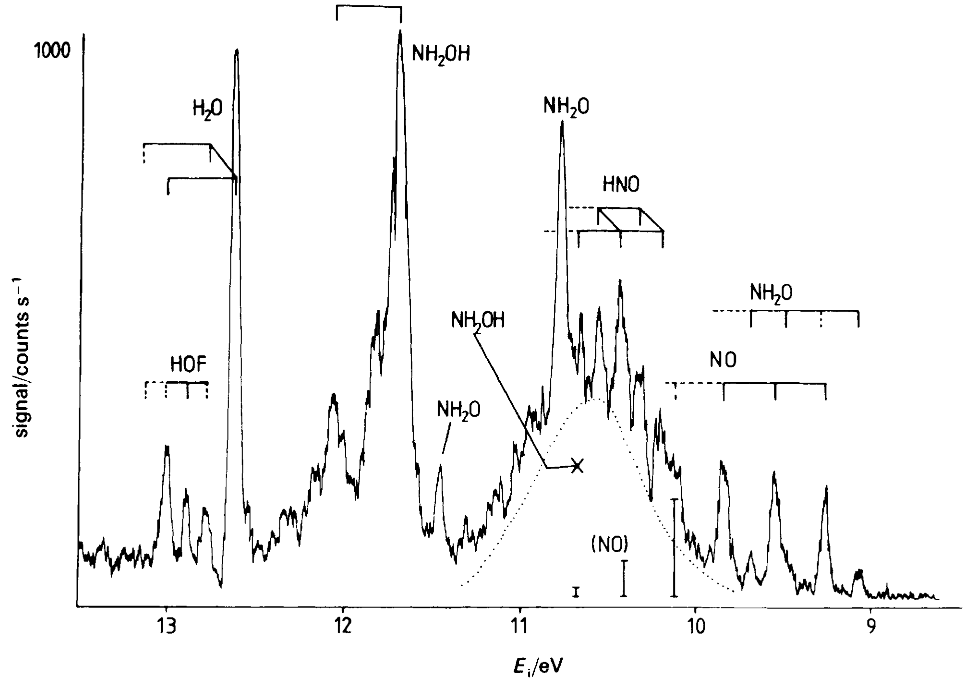


**Fig. 1** He I photoelectron spectrum recorded for the F + $NH_2OH$ reaction over the ionization energy range 8.5–13.5 eV at a reagent mixing distance of 1.5 cm above the photon beam

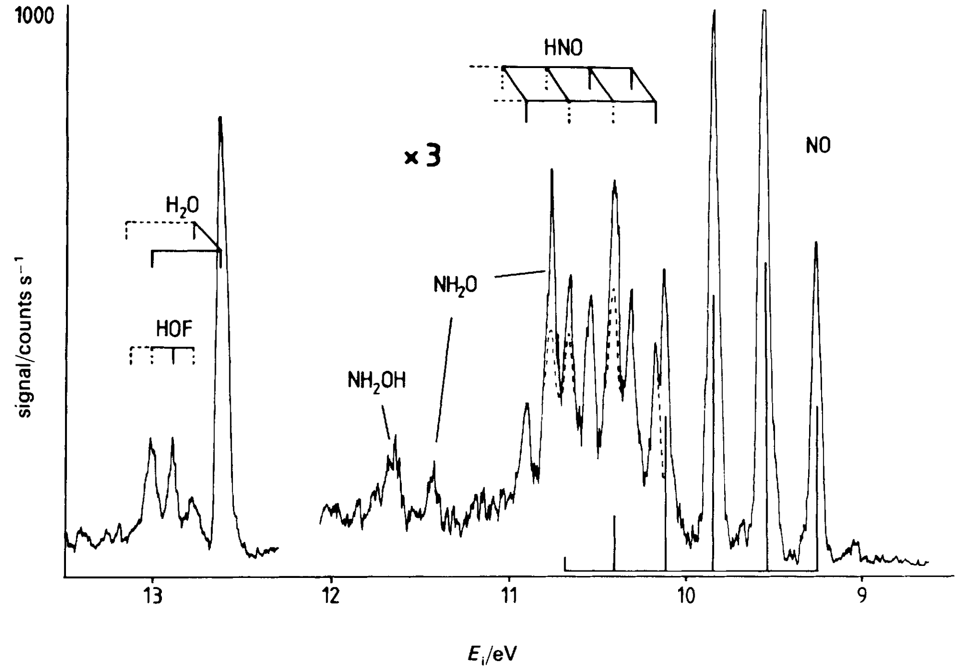


**Fig. 2** He I photoelectron spectrum recorded for the F + $NH_2OH$ reaction over the ionization energy range 8.5–13.5 eV at a reagent mixing distance of 3.5 cm above the photon beam. The initial reagent partial pressures used were the same as that used to obtain Fig. 1

type shown in Fig. 1, three bands assigned to $ND_2O$ were observed (see Fig. 4) and their measured vertical ionization energies are presented in Table 5. The first band assigned to $ND_2O$ also showed slightly increased vibrational separations from those measured for $NH_2O$ and an average vibrational separation over four components of $1710 \pm 60$ cm$^{-1}$ was obtained. The vibrational separations in the first band of DNO (Fig. 4) were also slightly different from those in the first band of HNO and the average vibrational separations measured for the two resolved series are presented in Table 5.

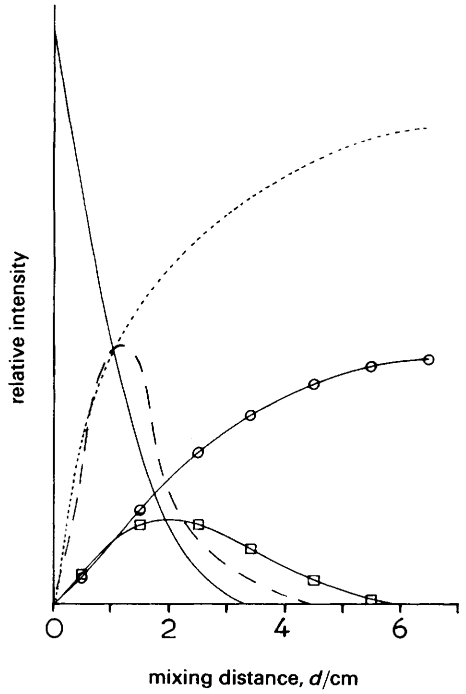


**Fig. 3** Variation of observed band intensities as a function of mixing distance above the photon beam at constant initial reagent partial pressures. (——) $NH_2OH$, (-------) HF, (– – –) $NH_2O$, (□—□) HNO, (○—○) NO

Assignment of the structured band at $10.56 \pm 0.01$ eV in Fig. 2 to HNO was achieved on the basis of the following evidence.

(i) As can be seen from Fig. 3, the band labelled as HNO in Fig. 1 and 2 maximizes at a larger mixing distance than the bands labelled $NH_2O$. It is clear therefore that the 10.56 eV band arises from a secondary reaction product, which subsequently reacts with fluorine atoms to produce NO.

(ii) The experimental adiabatic ionization energy obtained from the F + $ND_2OD$ reaction ($10.20 \pm 0.01$ eV) is in good agreement with the first adiabatic ionization energy of DNO of $10.29 \pm 0.14$ eV measured in an electron-impact mass-spectrometric study.[27] The observed HNO photoelectron band is also similar to that obtained in a lower resolution PE spectrum recorded for the products of heated sodium *N*-hydroxybenzene sulphonamide,[51] a compound which is known to give HNO on pyrolysis.[52] In these pyrolysis experiments,[51] an unstructured broad band was recorded with adiabatic and vertical ionization energies of $10.1 \pm 0.1$ and $10.6 \pm 0.1$ eV, in good agreement with the corresponding values obtained in this work for the band at 10.56 eV (see Table 5).

(iii) Other molecules were also considered as candidates for assignment of the 10.56 eV band. These include $NF_2$,[53] $NF_2H$,[54,55] $H_2NF$,[55] FNO[56] and $NF_3$.[55,57] The UV photoelectron spectra of all these molecules are known and they can be eliminated as being associated with the band at 10.56 eV, as they each have a first vertical ionization energy greater than 11.5 eV. FON was also considered, but was eliminated as the measured vibrational separations are different between the F + $NH_2OH$ and F + $ND_2OD$ preparative routes (see Table 5).

NOH was also considered as being associated with the band at 10.56 eV. This molecule has been shown in a series of *ab initio* MRD-CI calculations to have an open-shell ground state corresponding to the configuration $(6a')^2$ $(7a')^1$ $(2a'')^1$ ($\tilde{X}$ $^3A''$).[24] The two ionizations corresponding to the $(7a')^{-1}$

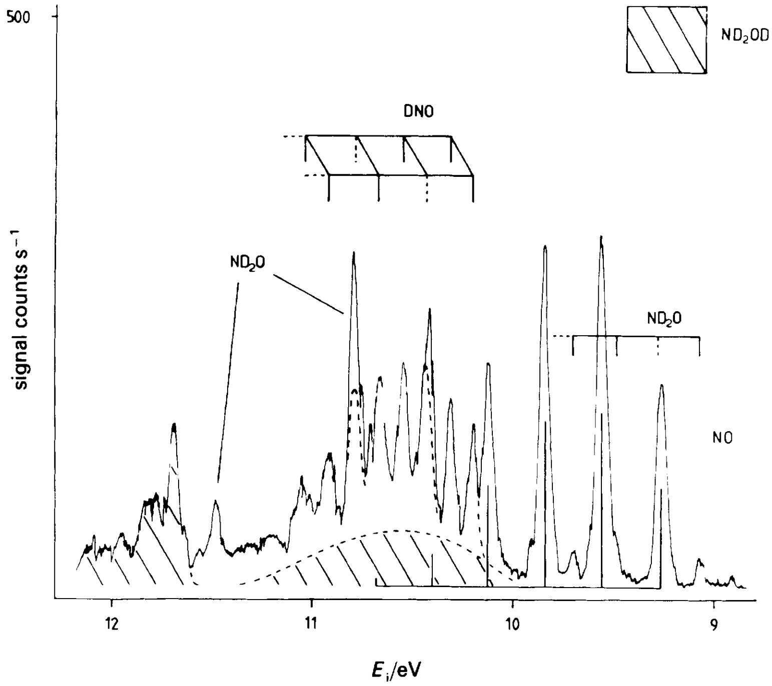


**Fig. 4** He I photoelectron spectrum recorded for the F + $ND_2OD$ reaction over the ionization energy range 9.0–12.0 eV at a reagent mixing distance of 2.5 cm above the photon beam

and $(2a'')^{-1}$ processes are expected to give broad bands with vertical and adiabatic ionization energies of 10.08 and 9.53 eV $(7a')^{-1}$, and 11.34 and 10.45 ± 0.15 eV $(2a'')^{-1}$, respectively.[24] Equivalent calculations for the ground state of HNO [$\ldots (6a')^2 (1a'')^2 (7a')^2$, $\tilde{X}\ ^1A'$] place the first ionization, corresponding to the $(7a')^{-1}$ process, at a vertical ionization energy of 10.05 eV, adiabatic value 9.75 eV, in reasonably good agreement with the experimental values of 10.56 ± 0.01 and 10.18 ± 0.01 eV for the band labelled HNO in Fig 1 and 2.

The second ionization energy, corresponding to the $(6a')^{-1}$ ionization,[29] is placed at 15.85 eV[24] (see also Table 4 for the values computed in this work). This would be consistent with the experimental spectra because, although the ionization energy region 12.5–15.0 eV is not heavily masked by bands from reagents or stable reaction products, the region above 15.0 eV is heavily overlapped by intense bands arising from NO and HF.

(iv) If the band at 10.56 eV is assigned to the first ionization of HNO, vibrational structure is anticipated in both the N—O stretching mode and the HNO deformation mode of $HNO^+(\tilde{X}\ ^2A')$ because the main change in equilibrium geometry on ionization is expected to be a shortening of the N—O bond and an increase in the HNO angle.[28,31] As shown in Fig. 2, the observed vibrational separations in the 10.56 eV band can be analysed in terms of excitation of two vibrational modes. Two series were observed with average separations of 1960 ± 30 and 1090 ± 40 cm$^{-1}$ and they can be assigned to excitation of the N—O stretching mode and the HNO deformation mode in $HNO^+(\tilde{X}\ ^2A')$. The highest occupied molecular orbital in $HNO(\tilde{X}\ ^1A')$, the 7a′ molecular orbital, is N—O antibonding in character being mainly composed of N $2p_\pi$ and O $2p_\pi$ in-plane atomic orbitals. It is therefore expected that the N—O stretching mode ($\nu_2$) in $HNO(\tilde{X}\ ^1A')$ would increase on going to $HNO^+(\tilde{X}\ ^2A')$. The N—O stretching mode ($\nu_2$) in the ground state of the neutral molecule has been accurately determined as 1565.3 cm$^{-1}$ in a gas-phase study of the infrared spectrum of HNO.[19] In the

**Table 5** Experimental measurements made from the observed HNO and $NH_2O$ photoelectron bands[a]

| molecule | band no. | vertical ionization energy/eV | adiabatic ionization energy/eV | average vibrational separation/cm$^{-1}$ | |
|---|---|---|---|---|---|
| $NH_2O$ | 1 | 9.48 ± 0.02 | 9.07 ± 0.01 | 1640 ± 40 | |
| | | (9.48 ± 0.02) | (9.06 ± 0.01) | (1710 ± 60) | |
| | 2[b] | 10.77 ± 0.01 | 10.77 ± 0.01 | | |
| | | (10.78 ± 0.01) | (10.78 ± 0.01) | | |
| | 3[b] | 11.46 ± 0.01 | 11.46 ± 0.01 | | |
| | | (11.47 ± 0.01) | (11.47 ± 0.01) | | |
| | | | | series 1 | series 2 |
| HNO | 1 | 10.56 ± 0.01 | 10.18 ± 0.01 | 1960 ± 30 | 1090 ± 40 |
| | | (10.55 ± 0.01) | (10.20 ± 0.01) | (1920 ± 40) | (870 ± 40) |

[a] All values refer to measurements made from the F + $NH_2OH$ reaction, except the values in brackets which refer to measurements made from the F + $ND_2OD$ reaction. [b] For $NH_2O$ (and $ND_2O$) bands 2 and 3 had an experimental relative intensity ratio of (2.9 ± 0.1) : 1, after correction for analyser transmission function.

same study the HNO deformation mode ($\nu_3$) was determined as 1500.8 $cm^{-1}$.[19] Therefore, as expected, for the ionization $HNO^+(\tilde{X}\ ^2A') \leftarrow HNO(\tilde{X}\ ^1A')$ the N—O frequency increases and the HNO deformation frequency decreases. Upon deuteriation, the N—O stretching mode in $HNO^+(\tilde{X}\ ^2A')$ reduces slightly to 1920 ± 40 $cm^{-1}$ whereas the deformation mode shows a larger change, as expected, to 870 ± 40 $cm^{-1}$ (see Table 5).

The vibrational separations measured in this work can be compared with the results of a series of *ab initio* SCF calculations with configuration interaction on $HNO^+(\tilde{X}\ ^2A')$ which gave $\nu_1 = 2880$ $cm^{-1}$, $\nu_2 = 2180$ $cm^{-1}$, and $\nu_3 = 890$ $cm^{-1}$.[28] The computed $\nu_2$(N—O) value is in reasonable agreement with the average of the $\nu_2$ separations measured in this work of 1960 ± 40 $cm^{-1}$. In contrast, the computed $\nu_3$ value in ref. 23 is lower than the measured average $\nu_3$ separation of 1090 ± 40 $cm^{-1}$. However, in a later study[58] using a potential generated with the same procedure used in ref. 28, the separations of some of the lower vibrational levels in $\nu_3$ in $HNO^+(\tilde{X}\ ^2A')$ have been computed as larger than the $\nu_3$ value of 890 $cm^{-1}$ quoted in ref. 28. The reasons for these differences are presented in ref. 58 as numerical inaccuracies in the fit performed in ref. 28 and neglect of interaction between the bending and stretching vibrations in ref. 58. The $\nu_3$ separations computed in ref. 58 were 1038 $cm^{-1}$ ($v'' = 3$–$v'' = 4$), 948 $cm^{-1}$ ($v'' = 4$–$v'' = 5$), and 799 $cm^{-1}$ ($v'' = 5$–$v'' = 6$). Inspection of these values indicates that the average separation of the first four vibrational levels in $\nu_3$ in $HNO^+(\tilde{X}\ ^2A')$ measured in this work of 1090 ± 40 $cm^{-1}$ seems reasonable in view of the computed separations quoted in ref. 58.

Having attributed the band at 10.56 eV to ionization of HNO, the bands at 9.48, 10.77 and 11.46 eV shown in Fig. 1 must now be assigned. As indicated earlier, all three bands arise from ionization of the same molecule. This is produced as a primary product of the $F + NH_2OH$ reaction which reacts in a secondary step with fluorine atoms to give HNO. This evidence is consistent with the observed features being associated with ionization of $HN_2O$ or NHOH. Assignment of these bands to $NH_2O$, the more stable isomer,[6–8] was achieved using the computed vertical ionization energies shown in Tables 2 and 3, as the experimental vertical ionization energies of 9.48, 10.77 and 11.46 eV are in much better agreement with the computed vertical ionization energies at the $\Delta SCF + CI + Q$ level for $NH_2O$ of 9.26, 10.92 and 11.48 eV (see Table 3) than the corresponding values computed for NHOH of 9.58, 11.48 and 13.16 eV (see Table 2). It should also be noted that the experimental intensity ratio of the bands at 10.77 and 11.46 eV is (2.9 ± 0.1) : 1, and this is consistent with the expected relative intensity of 3 : 1 for the two bands arising from the $NH_2O(2a'')^{-1}$ ionization, corresponding to the $NH_2O^+(\tilde{a}\ ^3A'') \leftarrow NH_2O(\tilde{X}\ ^2A')$ and $NH_2O^+(\tilde{A}\ ^1A'') \leftarrow NH_2O(\tilde{X}\ ^2A')$ processes. This experimental intensity ratio would also be consistent with the expected relative intensity of the bands produced by the $NHOH(7a')^{-1}$ ionization. However, the computed vertical ionization energies for these processes are in poor agreement with the experimental values.

There is, however, one problem in assigning the three bands to $NH_2O$. This concerns the difference between the computed adiabatic and vertical ionization energies for each band and the corresponding experimental values. As expected from the computed equilibrium geometries shown in Table 1, for the first $NH_2O$ band corresponding to the $(7a')^{-1}$ ionization, the computed adiabatic and vertical ionization energies indicate that a broad band should be observed and this is indeed the case experimentally. In contrast, as can be seen from Fig. 1, the second and third bands are sharp with their adiabatic and vertical ionization energies equal. This indicates little change in equilibrium geometry on ionization. However, the computed difference in the adiabatic and vertical ionization energies at the $\Delta SCF + CI + Q$ level for the $NH_2O$ second and third bands is 0.67 and 0.53 eV, respectively (see Table 3). These values were obtained because a non-planar geometry of $NH_2O$, the SCF minimum-energy geometry, was used in the calculations. As has already been described, at the UHF/MP2 level $NH_2O$ is computed to have a planar $C_{2v}$ equilibrium geometry whereas at the SCF level $NH_2O$ is computed to have a non-planar $C_s$ geometry with a barrier to planarity which is small with respect to the zero-point energy. $NH_2O$ is therefore effectively planar in its ground state. In order to estimate the valence ionization energies of planar $NH_2O$, the calculations described earlier were repeated using the planar $NH_2O(\tilde{X}\ ^2B_1)$ geometry obtained as a saddle point on the $NH_2O(\tilde{X}\ ^2A')$ SCF surface. The computed vertical ionization energies (in eV) (at the $\Delta SCF + CI + Q$ level), with adiabatic values in brackets for the first three bands of $NH_2O$ were 8.94 (8.71)$(2b_1)^{-1}$, 10.29(10.25)$(2b_2)^{-1}$ and 11.04(10.96)$(2b_2)^{-1}$. The corresponding experimental values are 9.48(9.07), 10.77(10.77) and 11.46(11.46) eV. These computed values support the observation that the first $NH_2O$ band is broad and also indicate that the separation of the adiabatic and vertical ionization energies for the second and third $NH_2O$ bands is a lot smaller than indicated by the computed values shown in Table 3. They therefore support assignment of the bands at 9.48, 10.77 and 11.46 eV to ionization of $NH_2O$.

The first band of $NH_2O$ is the only band for which vibrational structure was observed and, although only three components of this band were seen, the average vibrational separation was found to show a small but reproducible increase on deuteriation. This structure was assigned to excitation of the N—O stretching mode in the ion, increased over that in the neutral molecule, as the orbital from which ionization occurs, the 7a′ orbital, is essentially a N $2p_\pi$–O $2p_\pi$ antibonding orbital. The average separation measured for $NH_2O$ was 1640 ± 40 $cm^{-1}$ whereas that measured for $ND_2O$ was 1710 ± 60 $cm^{-1}$. Similar increases on deuteriation have also been observed in the first photoelectron bands of the isoelectronic radicals $CH_2OH$,[59] $CH_2F$[60] and $HO_2$,[61] which show structure in the C—O, C—F and O—O stretching modes , respectively. Second-derivative calculations performed on the ground state of $NH_2O^+$, at the SCF/MP2 level with the triple-zeta valence plus polarization basis set described earlier, indicate that in this state the $NH_2$ deformation mode and the N—O stretching modes are heavily mixed with the N—O stretch being reduced as a result of this mixing from its unperturbed value. The computed values are 1758 and 1632 $cm^{-1}$ for the two mixed modes, with the first mode being approximately described as the $NH_2$ bend and the second mode corresponding approximately to the N—O stretch. In the ground state of $ND_2O^+$, the $ND_2$ deformation mode is lot lower in energy than the N—O stretch and, as a result, the N—O stretching mode retains its unperturbed value. The computed values at the SCF/MP2 level are 1644 $cm^{-1}$ (N—O stretch) and 1245 $cm^{-1}$ ($ND_2$ bend). Hence mixing of the $NH_2$ deformation mode and the N—O stretching mode in $NH_2O^+(\tilde{X}\ ^1A_1)$ is almost certainly the cause of the positive deuterium shift observed in the first photoelectron band of $NH_2O$.

In this work the first adiabatic ionization energy of $NH_2O$ has been measured directly for the first time and an improved value for the first adiabatic ionization energy of HNO has been determined. In principle, for each molecule, the first adiabatic ionization energy can be used to determine the enthalpy of formation of the ion, if the enthalpy of formation of the neutral molecule is available. This is the case for HNO, where the enthalpy of formation ($\Delta H^{\ominus}_{f(298)}$) of the neutral molecule is well established as $1.156 \pm 0.003$ eV from the experimentally determined dissociation energy of HNO [$D$(H—NO)] of $2.039 \pm 0.001$ eV,[21,23] and the known enthalpies of formation of $H(^2S)$ and NO(X $^2\Pi$).[62] $\Delta H^{\ominus}_f$(HNO) when combined with the first adiabatic ionization energy of HNO measured in this work, leads to $\Delta H^{\ominus}_f(HNO^+)$ as $11.34 \pm 0.01$ eV. This compares favourably with determinations of $\Delta H^{\ominus}_f(HNO^+)$ of $11.29 \pm 0.04$ eV derived from measurement of the proton affinity of NO,[63] $11.38 \pm 0.14$ eV derived from the first ionization energy of DNO measured by electron-impact mass spectrometry[27,28] and $11.14 \pm 0.06$ eV determined from the observed threshold for production of $HNO^+$ from $NH_2OH$ as measured by photoionization mass spectrometry.[64] The dissociation energy ($D^0_0$) of $HNO^+(\tilde{X}\ ^1A')$ to give $NO^+(X\ ^1\Sigma^+)$ and $H(^2S)$ can also be calculated from the adiabatic ionization energy of HNO, the known dissociation energy of HNO[23] and the first adiabatic ionization energy of NO.[36] The value of $D_0(HNO^+)$ obtained in this way is $1.126 \pm 0.013$ eV. This compares with $1.08 \pm 0.14$ eV obtained using the first adiabatic ionization energy of DNO determined by electron-impact mass spectrometry,[27] corrected with calculated zero-point energy contributions, to give an HNO first ionization energy of $10.23 \pm 0.14$ eV.[28]

Similar calculations cannot be carried out for $H_2NO$ as the enthalpy of formation of this molecule is not known. However, in a photoionization mass-spectrometric study[64] the onset of $NH_2O^+$ production from $NH_2OH$ has been determined and this has led to an enthalpy of formation of $NH_2O^+$, $\Delta H^{\ominus}_{f(298)}$, of $9.73 \pm 0.01$ eV. This can be combined with the first adiabatic ionization energy of $NH_2O$ determined in this work of $9.07 \pm 0.01$ eV to yield $\Delta H^{\ominus}_{f(298)}(NH_2O)$ as $0.66 \pm 0.02$ eV.

Apart from the measurements made on $HNO^+(\tilde{X}\ ^2A')$ and the three lowest states of $NH_2O^+$, this study has demonstrated that the major pathway in the F + $NH_2OH$ reaction scheme is reaction 5 followed by reaction of $NH_2O$ with fluorine atoms to give HNO. No experimental evidence has been obtained for production of NHOH *via* reaction 6 or for production of HON *via* F + NHOH. It appears therefore, that for both the primary and secondary steps in the F + $NH_2OH$ reaction, only the most stable isomer is produced in each case. The F + $NH_2OH$ and F + $ND_2OD$ reactions would therefore be a useful source of $NH_2O$ and $ND_2O$ for future spectroscopic measurements on these radicals.

It is interesting to compare the exothermicities of the two possible primary channels in the F + $NH_2OH$ and F + $CH_3OH$ reactions. Using $\Delta H^{\ominus}_f(NH_2O)$ obtained in this work, and an estimate of $\Delta H^{\ominus}_f$(NHOH) based on the assumption that NHOH is *ca.* 26 kJ mol$^{-1}$ higher in energy than $NH_2O$,[6–11] the following reaction enthalpies can be calculated

$$F + NH_2OH \rightarrow NH_2O + HF;\ \Delta H_5 = -2.56\ \text{eV} \quad (5)$$

$$F + NH_2OH \rightarrow HNOH + HF;\ \Delta H_6 = -2.29\ \text{eV} \quad (6)$$

In the F + $CH_3OH$ case the corresponding reactions with their reaction enthalpies are:[59]

$$F + CH_3OH \rightarrow CH_3O + HF;\ \Delta H_7 = -1.48\ \text{eV} \quad (7)$$

$$F + CH_3OH \rightarrow CH_2OH + HF;\ \Delta H_8 = -1.69\ \text{eV} \quad (8)$$

and $CH_2OH$ is clearly seen in UV photoelectron spectra recorded for the F + $CH_3OH$ reaction.[59] However, $\Delta H_5$ and $\Delta H_6$ have previously been quoted as −2.11 and −2.89 eV.[5] These reaction enthalpies are clearly incorrect as they were calculated on the assumption that $D(NH_2O—H) = D(HO_2—H)$ and $D(H—NHOH) = D(H—NHNH_2)$. These relative values for $\Delta H_5$ and $\Delta H_6$ were the source of problems experienced initially in assigning the spectra recorded in the present work.

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