ANION PHOTOELECTRON SPECTROSCOPY AND HIGH LEVEL AB INITIO CALCULATIONS OF THE HALIDE-NITRIC OXIDE DIMER COMPLEXES

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ABSTRACT: Anion photoelectron spectra are presented for gas phase complexes formed between halide anions and nitric oxide, $X^{-}\cdots NO$ where $X^{-} = Cl^{-}$, Br^{-}, and I^{-}. Electron binding energies are experimentally determined to be 3.82, 3.51 and 3.17 eV. Results from CCSD(T)/aug-cc-pVTZ calculations are presented for the anion species, whereby a single minimum of C_s symmetry is predicted. Binding energies (D_0) of 15.3, 13.3 and 11.7 kJ mol^{-1} are predicted from complete basis set limit extrapolation, and are found to be in line with previous experimental studies.

DEDICATION: It is with great pleasure that we contribute this paper towards a special edition of The Australian Journal of Chemistry, dedicated to Graham Chandler on the occasion of his 80th birthday. Graham is a wonderful colleague (for one of us listed on this paper, he has been so for over 25 years!). He is a brilliant sounding board for us experimentalists as we undertake ab initio calculations to support our experiments. Over the years, his insights have proved to be invaluable, he always makes time for discussions with both students and colleagues alike, and he has been a formidable Squash opponent! Congratulations, Graham, for this special edition of the journal; it is well deserved.

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1 Introduction

Anion photoelectron spectroscopy has earned its place in the armoury of techniques for characterising neutral gas phase species, and can provide rich information on intermolecular interactions between loosely bound complexes. The major piece of information from the experiment is the electron binding energy of the neutral complex which can be used as a critical test for computational methodologies, however one can also map out the neutral potential energy surface should the spectrum display vibrational resolution. There has been a large volume of work produced in this area, with some recent representative examples provided in references [1–8]. In this contribution, we address the gas phase anion species formed between the halides, Cl^-, Br^-, and I^- and the nitric oxide molecule. There has been quite a deal of work undertaken on the neutral systems, however not the same depth for the analogous anion systems.

The nitrosyl halides, XNO, belong to the C_s symmetry point group, featuring a long separation between the halogen and a slightly perturbed NO molecule. The species are unstable, increasingly so as the halogen increases in size. The neutral FNO, ClNO, BrNO and INO species have been widely studied over the decades using such methods as infrared, Raman and microwave spectroscopy [9–27]. In addition, these species have been investigated using photoelectron spectroscopy, which in turn targets the cation potential energy surface [28–31]. However in order to probe the interaction between the neutral halogens and nitric oxide via photoelectron spectroscopy, one must interrogate the anion. The neutral species photolectron spectroscopy experiments were complemented by ab initio calculations (SCF) on ClNO in 1976 [32], with renewed interest in the 90s in the FNO, ClNO and BrNO species using HF and MP2 with the 6-31G* basis set [33] and SCF and CISD with the DZP basis sets [34]. These three species were further investigated in 2000 using DFT methods (B3LYP/6-31G*) [35]. Abnormally long halogen-nitrogen bond lengths have been noted for these species, compared to mean halogen-nitrogen bond lengths in other organic compounds, suggestive of van der Waals-type structures rather than covalent bonding. The separation between the halogen and nitrogen increases with halogen size, although Cl and Br are quite similar, both in separation and the calculated bond dissociation enthalpies ($165.3\,\mathrm{kJ\,mol^{-1}}$ and $147.3\,\mathrm{kJ\,mol^{-1}}$ respectively [35]). In contrast, the F−N bond (about 0.5 Å shorter than ClNO) stands out by being extremely strong in comparison ($266.9\,\mathrm{kJ\,mol^{-1}}$), indicating covalent and not van der Waals-type bonding [35]. It is reasoned that the difference between the fluorine species, and the other halogen species, is due to the formation of an ionic resonance structure which contributes more strongly for the highly electronegative atom F. This is supported by force constant [36] and bond dissociation energetic data [37].

It is worthwhile mentioning another possible bonding motif for the neutral species, namely the hypohalite isomers, i.e., XON. These species have been approached only from a theoretical perspective, with the first treatment in 1985 on ClON [38] followed by FON in 1990 [39]. This study questioned whether XON is an open-shell species, and it was later determined to be closed-shell and the chlorine and bromine hypohalite isomers proven to exist (theoretically) [34]. No information could be found in the literature for the ION species, however. The XON isomers are far less stable than their XNO counterparts. For example, at the CISD+Q level of theory ClON was determined to lie 131 kJ mol^{-1} higher in energy than ClNO, while BrON was predicted to lie 117.6 kJ mol^{-1} above BrNO [34]. These energy separations were again predicted in a later study [35] from B3LYP/6-31G calculations to be 113.0 kJ mol^{-1} for ClON and 110.0 kJ mol^{-1} for BrON, although the value for fluorine remained significantly large (182.4 kJ mol^{-1}) in agreement with Meredith, Davy, and Schaefer III [39]. Meredith, Quelch, and Schaefer III[34] conducted an SCF and CISD investigation into the barrier for the rearrangement of ClON to ClNO. At the SCF level, the barrier is only 9.6 kJ mol^{-1} however is significantly increased to 41.4 kJ mol^{-1} when CISD+Q calculations were employed. For this reason the authors believed it might be possible to study ClON experimentally and, due to the similarity of BrON to ClON for both to have comparable barrier heights to conversion to the nitrosyl halide form.

In contrast, the anion XNO species have received far less attention, from either theoretical and experimental studies. Thermochemical stabilities of the van der Waals $F^- \cdots (NO)_n$ [40], $Cl^- \cdots (NO)_n$, $Br^- \cdots NO$ and $I^- \cdots (NO)_n$ clusters were determined from pulsed electron-beam high-pressure mass spectrometery experiments with supporting DFT calculations (B3LYP/6-31G*) [41]. The geometries of the anion species predicted from the calculations feature significantly extended halide-nitrogen bond lengths (> 0.4 Å) when compared with the analogous neutral nitrosyl halides. The NO moiety also experiences a slight increase in bond length and the XNO angle is smaller by a few degrees, compared with the neutral counterparts. These data indicate that a progression in the X–N stretching mode may be observable in high resolution anion photoelectron spectra due to the considerable geometry change from anion to neutral. Matsubara and Hirao[42] later determined the structure for $F^- \cdots NO$ using the larger 6-311++G* basis set, and found similar structural parameters: $r_{XN} = 1.963$ Å, $r_{NO} = 1.185$ Å and $\measuredangle_{XNO} = 108.0°$. In addition to calculating the geometries of the complexes Hiraoka et al.[41] also derived the enthalpy of ligand association, $-\Delta H^0_{n=0,1}$, from thermochemical data: 17.2 kJ mol^{-1} for $Cl^- \cdots NO$, 14.2 kJ mol^{-1} for $Br^- \cdots NO$ and 11.3 kJ mol^{-1} for $I^- \cdots NO$.

To the best of our knowledge the anion halide-nitric oxide species have not been the subject of spectroscopic studies to date. We therefore are in a position to perform these experiments, and also address the complexes with high level CCSD(T) ab initio calculations to refine the stationary points on the potential energy surface. We can critically assess the predicted structures and binding energies (D_0) for the anion complexes through comparison with the experimental electron affinities afforded through photoelectron spectroscopy. We note that there has been some work undertaken on NO^- solvated clusters [43], however in these cases photodetachment is from the closed shell NO^- anion and therefore will be very different to the halide-nitric oxide complexes discussed in the current work.

2 Methodology

2.1 Experimental Methods

The apparatus comprises a time of flight mass spectrometer for anion species coupled to a magnetic bottle photoelectron spectrometer. The design of the spectrometer has been described previously [44], and hence only the experimental conditions employed for halide-nitric oxide complexes, or recent modifications to the apparatus, are described here.

The gas phase anion complexes were formed by directing energetic electrons onto a pulsed supersonic expansion of gas into a vacuum chamber. The electron source has been modified from that described in reference [44] and now includes a home built miniature Einzel lens assembly which allows for the focussing of the electrons onto the gas expansion. The composition of the gas mixture is varied to produce the ion clusters of interest. For the halide-nitric oxide complexes, the mixture consisted of a nitric oxide and argon (1:10 ratio) seeded with traces of CH_3I, CH_2Br_2, or CCl_4 (halide anion precursors). The total pressure of the gas mixture was 400 kPa. Nitric oxide was synthesised and purified in house, by reaction of a 1:1 mixture of 70% nitric acid:water with powdered copper, and more details on this procedure can be found in reference [45].

The $X^- \cdots NO$ complexes are selected via mass spectrometry and overlapped with a 5 ns pulse of 266 nm radiation (4.66 eV, 4th harmonic of a Nd:YAG laser, Spectra Physics Quanta Ray Pro). The photoelectrons are detached in the presence of a strongly divergent magnetic field and are guided to a detector at the end of a 1.5 m flight tube by means of a second homogeneous magnetic field subjected to the entire length of the flight tube. The time of flight of the detached photoelectrons is recorded and initially converted to kinetic energy (eKE), and subsequently electron binding energy (eBE). Each individual spectrum was collected over 10 000 laser shots, and averaged over multiple days. Calibration of the spectrometer was achieved by recording spectra of the bare halide anions, and finally the intensities of the spectral features were corrected to account for the conversion from time of flight binning to energy binning of the photoelectrons by application of the Jacobi transform ($dt \rightarrow dE$).

2.2 Computational Methods

The halide-nitric oxide 1:1 anion complexes were investigated by ab initio calculations at the CCSD(T) level of theory with Dunning's triple zeta augmented correlation consistent basis set for nitrogen and oxygen (aug-cc-pVTZ), and for chlorine the aug-cc-pV(T+d)Z basis set with additional d-functions [46–48]. The aug-cc-pVTZ PP basis sets [49, 50] were employed for bromine and iodine, firstly as these basis sets decrease the computational burden as they feature an effective core potential, and secondly account for relativistic effects which are of importance for heavier elements. Henceforth, for the sake of brevity, the basis sets will be referred to as AVXZ with X = T, Q, 5 which signify triple, quadruple, and quintuple zeta. The CCSD(T) calculations were based on a UHF reference wavefunction.

The geometries of the gas phase complexes were determined using standard optimisation routines, with convergence criteria for the gradient being 1×10^{-8} E_h a_0. Vibrational frequency analyses were performed at the located stationary points to determine whether they represented minima, transition states, or high order stationary points on the global potential energy surface. Energies of the bare anions, and the bare nitric oxide molecule were computed to determine the binding energy $\mathrm{D_e}$, and harmonic zero point energies of the complexes and bare nitric oxide were employed to determine $\mathrm{D_0}$. To predict the vertical electron detachment energies of the complexes, single point energy calculations were undertaken at the anion complex geometry, however with charge set to 0 and multiplicity 1. In an effort to improve upon the reliability of the predicted complex binding energies, and vertical detachment energies, we have employed single point energy calculations using up to quintuple-ζ basis sets, and subsequently performed a two point complete basis set limit extrapolation along the lines of W1 and W2 theory [51]. All quantum chemical calculations were performed using the CFOUR package [52].

3 Results & Discussion

3.1 Computational Results

3.1.1 Electrostatic and Induction Modelling

Prior to discussing the results of the ab initio calculations, it is instructive to consider the dominant electrostatic and induction interactions between the negatively charged halide and the nitric oxide molecule.

One can phrase the discussion in terms of the dependence of the interaction energy on angular and radial coordinates. The electrostatic contributions are due to the interplay between the anion charge and the permanent electric moments of the NO molecule, namely the dipole, quadrupole, octopole, and hexadecapole moments. The induction interaction arises from the polarisation of NO by the nearby negatively charged anion, whereby the polarisation parallel and perpendicular to the internuclear axis of NO are considered. The total interaction is given by [53];

$$V_{\text{elec}}(R,\theta) = \frac{q}{4\pi\epsilon_0}\left(\frac{\mu\cos\theta}{R^2} + \frac{\Theta(3\cos^2\theta - 1)}{2R^3} + \frac{\Omega(5\cos^2\theta - 3\cos\theta)}{2R^4} + \frac{\Phi(35\cos^4\theta - 30\cos^2\theta + 3)}{8R^5}\right) \tag{1a}$$

$$V_{\text{ind}}(R,\theta) = -\frac{q^2(\alpha_{\parallel}\cos^2\theta + \alpha_{\perp}\sin^2\theta)}{2(4\pi\epsilon_0)^2R^4} \tag{1b}$$

In the equations above, q is the charge on the anion, R is the distance between the anion and the midpoint of the diatomic NO, and θ the angle between the line defined by R and the NO internuclear axis. μ, Θ, Ω, Φ are the dipole, quadrupole, octopole, and hexadecapole moments of NO respectively. Values for the quadrupole, octopole, and hexadecapole moment were taken from the work of Bruna and Grein ($\Theta = -3.922 \times 10^{-40}\,\mathrm{C\,m^2}$, $\Omega = 2.005 \times 10^{-50}\,\mathrm{C\,m^3}$, $\Phi = 1.3653 \times 10^{-60}\,\mathrm{C\,m^4}$ [54]), while a value of $\mu = -5.25 \times 10^{-31}\,\mathrm{C\,m}$ for the dipole moment was taken from Blumberg and co-workers [55]. Nitric oxide's dipole polarisabilities parallel ($\alpha_{\parallel}$) and perpendicular ($\alpha_{\perp}$) to the internuclear axis were those calculated by Medved et al ($2.079 \times 10^{-40}\,\mathrm{C^2\,m^2\,J^{-1}}$ and $1.624 \times 10^{-40}\,\mathrm{C^2\,m^2\,J^{-1}}$ respectively) [56].

A contour plot illustrating the interaction is presented in Figure 1, produced over the range $3.0 < R < 4.0$ and $0 < \theta < 180$, whereby darker shading indicates lower energy and the contours are separated by $100\,\mathrm{cm^{-1}}$. The major finding from this analysis is that the complex favours neither a linear nor 'tee-shaped' geometry. One might have expected a linear geometry considering the charge-dipole and charge-induced dipole interactions, however, the interaction is clearly dominated by the interaction of the anion charge with the higher order electric moments. This understandably follows from the relatively small dipole moment, compared with the higher order moments, and the dependence of the charge-quadrupole interaction falling off as $1/R^3$ as opposed to $1/R^4$ for the induction interaction.

3.1.2 Ab Inito Calculations

Turning our attention now to the ab initio CCSD(T) calculations, a survey of the ground A'' state potential energy surface revealed a single minimum for the halogen-nitric oxide gas phase complex. This point

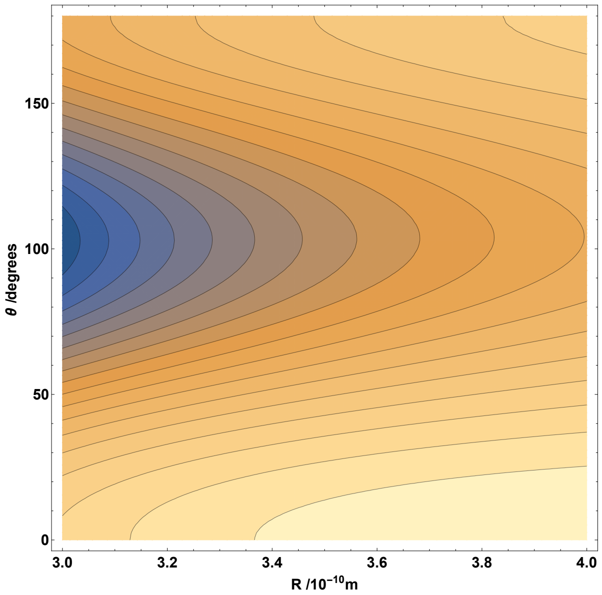

Figure 1: *Contour plot illustrating the intermolecular interaction between a point negative charge, and nitric oxide. R is the distance between the anion and the midpoint of the diatomic NO, and θ the angle between the line defined by R and the NO internuclear axis. Darker shading corresponds to lower energy. Contours are separated by* 100 cm^{-1}.

corresponds to a bent C_S symmetry structure, in agreement with the electrostatic and induction interaction analysis whereby neither a linear nor 'tee-shaped' geometry was preferred. The geometry is in qualitative agreement with the previous findings of Hiraoka et al [41]. The structure of the complex is depicted in Figure 2, and features the nitrogen end of the molecule closer to the halide anion. Structural parameters are provided in Table 1, with additional data for the complexes provided in the supplementary information, including absolute electronic energies, vibrational mode frequencies, and zero point energies. We also provide rotational potential energy curves for both the ground A'' state and an excited A' state. The A' curve suggests a C_S symmetry $X^- \cdots ON$ minimum, however this stationary point lies some 15 kJ mol^{-1} above the ground A'' state, from MP2/AVTZ calculations.

The perturbation of the NO moiety arising from close proximity of the halides is quite small. When the NO bond length of the complex is compared with that of the bare NO molecule (CCSD(T)/AVTZ calculations), the bond length increases marginally from 1.153 Å to 1.159 Å for the chloride and bromide complexes, and

Figure 2: *Predicted geometry of the halide-nitric oxide gas phase complex, with the nitrogen of NO closer to the halide anion. Structural parameters are provided in Table 1.*

to 1.158 Å for the iodide complex. There is an associated decrease in the NO stretching frequency from 2112 cm^{-1} for the bare NO molecule, to 2020, 2035 and 2060 cm^{-1} for the chloride, bromide, and iodide complexes respectively. Comparison between the geometries determined at CCSD(T)/AVTZ and those at B3LYP/6-31G* is also made in Table 1. In the case of both $Cl^{-}\cdots NO$ and $Br^{-}\cdots NO$, the intermolecular bond length is some 0.3 Å to 0.4 Å longer, and the $X^{-}\cdots N{=}O$ angle is decreased by around 10°. Since publication of the B3LYP data [41] it has been shown by Grimmme and Goerigk, however, that B3LYP is not able to properly model loosely bound van der Waals complexes [57], and therefore we feel confident that the current CCSD(T) results are more accurate in terms of the geometries.

Complete basis set limit extrapolated electronic energies were used in the prediction of the binding energies of the complexes, D_e, and estimates for D_0 were subsequently determined using zero point energies calculated at the CCSD(T)/AVTZ level of theory. These data are presented in Table 1, where the obvious trend is a decrease in D_e and D_0 for increasing halide size, where D_0 is predicted to be 15.3, 13.3 and 11.7 kJ mol^{-1} for Cl^-, Br^-, and I^- complexes respectively. The decrease in complex binding energy results from the increased anion radius, which therefore impacts upon the closeness of approach of the anion to the NO molecule. This is in line with the electrostatic and induction modelling shown in Figure 1, where the dependence of the interaction energy on the distance between halide and NO is clearly observed. To better compare with the available experimental data, we have calculated the enthalpy of ligand association

Table 1: *Structural parameters of the C_s halide-nitric oxide anion gas phase complexes predicted from CCSD(T)/AVTZ calculations. D_e and D_0 are predicted using CCSD(T)/CBS results.*

	$r_{X\cdots N}$ Å	$r_{N=O}$ Å	$\angle_{X\cdots N=O}$ °	D_e kJ mol^{-1}	D_0 kJ mol^{-1}	$\Delta H_{0\to1}$ kJ mol^{-1}
Cl···NO	2.982	1.159	102.6	16.4	15.3	-19.1
Lit.*	2.651	1.180	111.6			-17.2 *exp.*
Br···NO	3.149	1.159	103.7	14.3	13.3	-16.9
Lit.*	2.777	1.180	113.5			-14.2 *exp.*
I···NO	3.464	1.158	103.7	12.4	11.7	-14.6
Lit.*						-11.3 *exp.*
NO		1.153				

$*$ B3LYP/6-31+G* values and experimental $\Delta H_{0\to1}$ are taken from reference [41]

using the method of Del Bene et al [58]. These data are provided in Table 1 alongside the experimental values of Hiraoka and co-workers [41]. The agreement between our CCSD(T)/CBS predictions and the experimental results is reasonable, and reflect the trend in the enthalpies correctly.

The Vertical Detachment Energy (VDE) for each complex was predicted by performing single point energy calculations at CCSD(T)/AVQZ and CCSD(T)/AV5Z and subsequent CBS extrapolation, on the neutral potential energy surface at the geometry of the anion complexes. These data are presented in Table 2, alongside the experimental results. The predicted VDEs do not take intially take into account the two spin-orbit states of the neutral halogens, and as such this is accounted for by splitting the predicted VDE using the known spin-orbit coupling constants, producing the $^2P_{3/2} \leftarrow {}^1S_0$ and $^2P_{1/2} \leftarrow {}^1S_0$ transitions [59, 60]. Furthermore, to account for errors introduced by the CCSD(T) level of theory a second correction was applied, determined by the differences in the predicted detachment energy of the bare halogen anions and the known experimental values. The data needed to perform these operations are provided in the supplementary material. The correction decreases upon increased basis set size, and is small when the CBS limit extrapolated single point energies are compared with experiment. For chloride, bromide, and iodide the corrections are -0.014, -0.005 and -0.002 eV.

3.2 Experimental Results

We now present the experimental results of this study, comprising mass and anion photoelectron spectra recorded using the TOF-PES apparatus.

3.2.1 Mass Spectrometry

Representative mass spectra are provided in Figure 3. As described in the methodology section, the anion-molecule complexes were produced from a gas mixture of nitric oxide and argon (1:10 ratio), seeded with halide anion precursor. For all three spectra, the most intense peak is assigned to the bare halide anion, which is clipped on the expanded scale needed to show the less intense anion complexes. The halide-nitric oxide peaks are labelled on the figure, and were produced in sufficient abundance to allow for photoelectron spectroscopy studies. There is evidence for the formation of larger clusters, with more than one nitric oxide coordinating to the anion, for all three halide anions (labelled with an asterisk in Figure 3). Additionally, all three spectra show evidence of the NO_2^- anion, which is presumably formed from reaction of NO and O_2 present as a contaminant. Other peaks present in the spectra are assigned as clusters of the halides with one or more water or argon species, the former appearing due to contamination of the gas mixture, the latter as argon is the major component of the mixture.

3.2.2 Anion Photoelectron Spectroscopy

Anion photoelectron spectra for the halide-nitric oxide complexes are presented in Figure 4, recorded using a photon energy of 4.66 eV. For the chloride and bromide complexes, the ^{35}Cl and ^{79}Br isotopologues were targeted. Due to the low resolution of the spectrometer, the spectra do not show vibrational progressions, however they do reveal a shift in the electron binding energies compared with the bare halide anions. The spectrum of each complex closely resembles the bare anion which is clear evidence for a non-covalent interaction between the halides and NO, with the situation best described as the halide being slightly perturbed by the solvating species NO. The shift to higher energy is a direct result of the stabilisation of the anion afforded through complex formation with the nitric oxide molecule, or more precisely is due to the difference in the dissociation energies of the anion and neutral complexes. If D_0 were the same for both anion and neutral complexes, then the result would be no shift of the photoelectron band compared with the bare X^- anions. As the anion-nitric oxide species are bound by electrostatic and induction forces, the interaction is clearly stronger than for an analogous neutral van der Waals complex which is bound by dispersion interactions.

We are now in a position to compare the predicted and experimentally determined VDE values. While the predicted binding energies and enthalpy of ligand association are in line with previous experimental findings, as shown in Table 1, there appears to be an issue with the predicted VDE. In all cases, the predicted VDE lies below the experimental value, and indeed with reference to the supplementary information,

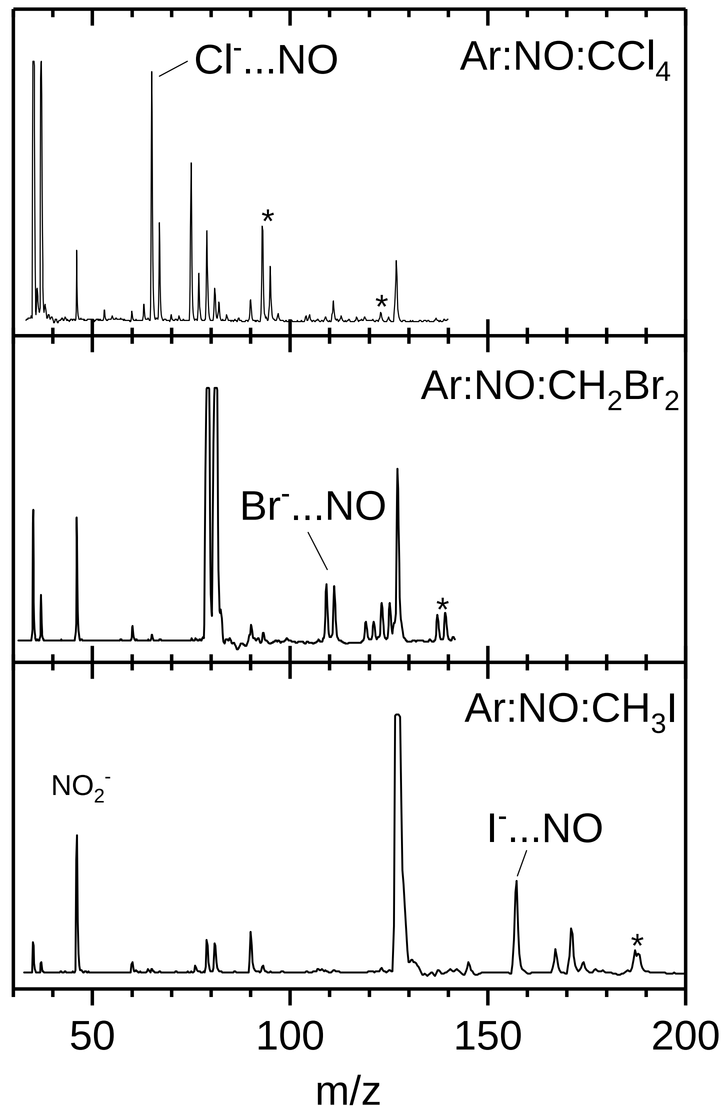

Figure 3: *Representative mass spectra of the halide-nitric oxide anion complexes. Peaks labelled with an * correspond to larger* $X^{-}\cdots(NO)_n$ *clusters*

lie below the predicted detachment energy of the bare anions. When one considers the nature of the complexes, the anion complex possess an unpaired electron due to the solvating species being the radical molecular species NO. The neutral species could have overall singlet or triplet multiplicity, however single point energies on the triplet surface revealed that it lay some $10\,\mathrm{m}E_\mathrm{h}$ above the singlet surface. We have previously shown that the method used for VDE prediction has yielded very good correspondence with experiment [61–63], however in those cases the anion was closed shell, while the neutral surface is of doublet multiplicity, greatly simplifying the calculations. In the case of the halide-nitric oxide complexes,

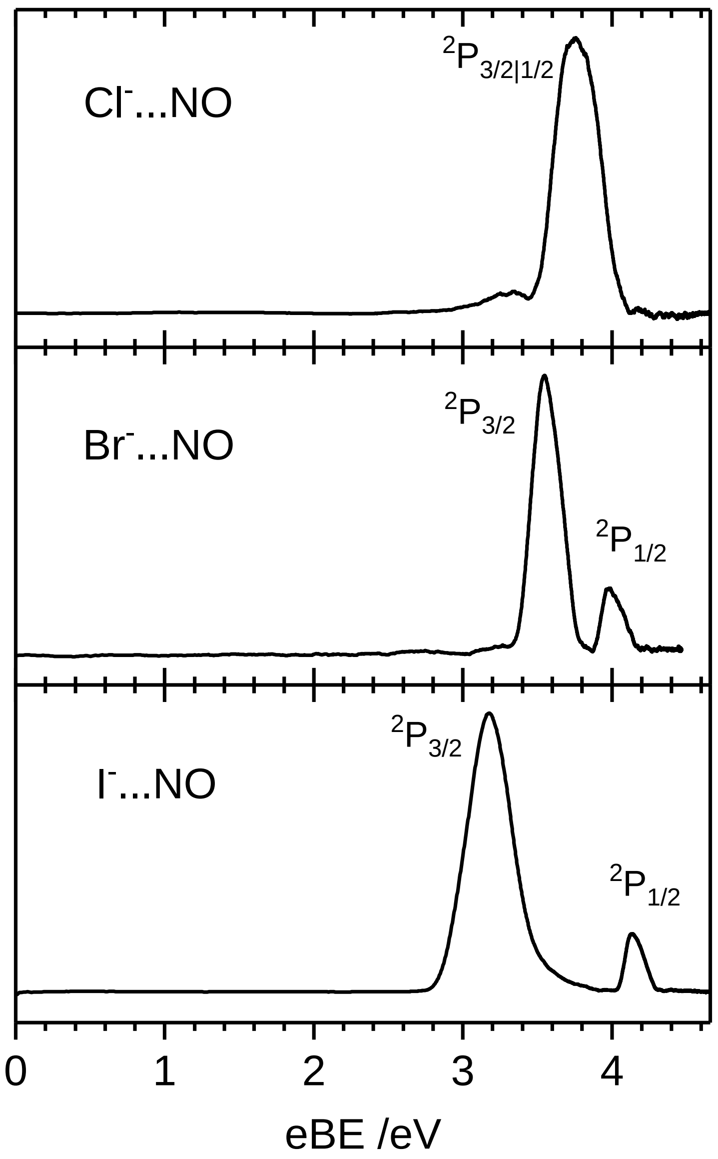

Figure 4: *Anion photoelectron spectra of the* $X^-\cdots NO$ *complexes, where* $X^- = Cl^-$, Br^-, *and* I^-.

it may well be that multi-configuration calculations are necessary due to the open shell nature of the ligand molecule, and therefore warrant further investigation.

3.2.3 Comparison With Other Halide-Molecule Complexes

We conclude this discussion by comparing the electron binding energies of the halide-nitric oxide complexes with similar species. Firstly, we note that the stabilisation energies for 1:1 complexes decrease down the halide series, which is due to the diminution of the dissociation energy upon increased halogen size.

Table 2: *Experimental photoelectron band positions for the halide-nitric oxide complexes, and predictions from CCSD(T)/CBS calculations. Band positions have an error of* ±0.05eV

Species	$^2P_{3/2}$ eV	$^2P_{1/2}$ eV	E_{stab} meV
Cl^-	3.58		
$Cl^- \cdots NO$	3.82		240
CCSD(T)/CBS	*3.51*	*3.62*	
Br^-	3.37	3.82	
$Br^- \cdots NO$	3.51	3.96	140
CCSD(T)/CBS	*3.32*	*3.78*	
I^-	3.05	4.00	
$I^- \cdots NO$	3.17	4.12	120
CCSD(T)/CBS	*3.09*	*4.04*	

Referring to Table 1 the predicted binding energies at the CCSD(T)/CBS limit are 15.3, 13.3 and 11.7 kJ mol^{-1}, while from Table 2 the stabilisation energies are 240, 140 and 120 meV. The stabilisation energy correlates strongly with the dissociation energy (D_0) of the anion-molecule complex due to the fact that D_0 is generally much larger for the anion compared with the neutral.

When compared to other complexes investigated previously by our group, for example the halide-carbon monoxide species, the halide-nitric oxide set display quite similar stabilisation energies, which is to be expected considering that the predicted D_0 values for the carbon monoxide complexes are quite close to those of the nitric oxide complexes. The predicted binding energies are 14.6, 9.9 and 7.3 kJ mol^{-1} for the chloride, bromide, and iodide-carbon monoxide respectively, while the stabilisation energies are 160, 140 and 90 meV [44, 64, 65]. In both cases, the anion is bound via electrostatic and induction interactions, and in both cases the interaction is quite weak due to the small dipole moments for both molecules, and that the interaction is primarily due to the charge-quadrupole interaction.

Finally, it is interesting to compare the stabilisation energies of the halide-nitric oxide complexes with a more strongly bound set, also studied by our group, the halide-acetylene complexes [63]. For these complexes, the dissociation energy is much higher, due to the fact the bonding is best described as hydrogen bonding, with the binding energies predicted to be 43.2, 37.3 and 31.0 kJ mol^{-1} for chloride, bromide, and iodide-acetylene complexes respectively [59]. This is again reflected in quite large experimental stabilisation energies of 500, 410 and 378 meV.

4 Summary

High level CCSD(T) calculations and anion photoelectron spectroscopy have been applied to the halide-nitric oxide 1:1 complexes. A single minimum was predicted from the calculations, corresponding to a bent C_s symmetry geometry. The complex is quite loosely bound, with binding energies less than 20 kJ mol^{-1} for the halide series. Electron detachment energies, predicted from CCSD(T)/CBS calculations, do not line up well against the experimental values which is possibly due to the radical nature of the nitric oxide molecule, and the need for MCSCF calculations. The photoelectron spectral features move to higher electron binding energy when compared with the bare halide anions, resulting from the disparity in cluster binding energies between the anion and analogous neutral complexes. Effectively, the electron is stabilised on the halide when in the complex compared with the bare halide.

5 Acknowledgements

KLM acknowledges the support of an Australian Postgraduate Award (APA). We acknowledge financial support from the Faculty of Science and the School of Chemistry and Biochemistry, and the Australian Research Council is acknowledged for funding under the LIEF scheme (LE110100093).

The authors declare no conflicts of interest.

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