Molecule-doped rare gas clusters: structure and stability of $\text{Ar}_n\text{NO}(X^2\Pi_{1/2,3/2})$, $n\leq 25$, from new \textit{ab initio} potential energy surfaces of ArNO

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High level \textit{ab initio} calculations carried out for the $^2A'$ and $^2A''$ states of ArNO($X^2\Pi$) predict a crossing near the T-shape configuration, with the $^2A'$ minimum being slightly deeper. Spin-orbit coupling is included through a model treatment and results in two potential energy surfaces with similar topologies, nearly parallel to each other and close to the averaged non-relativistic surface. These results are used to construct a DIM-like model for Ar$_n$NO clusters. The lowest energy cluster structures are found to resemble those for Ar$_{n+1}$ with NO lying in the surface. The set of major magic numbers (structures of pronounced stability) is also the same as for the Ar$_{n+1}$ clusters, and is emphasized further by the detachment of NO, which requires a larger energy than for detachment of a single Ar atom. The relations of the difference between the two dissociation energies and of the Ar$_n$NO($1/2 \rightarrow 3/2$) excitation energy to the magic numbers are discussed.

1. Introduction

Van der Waals complexes of molecules with rare gas atoms have been studied by both experimentalists and theoreticians for decades. The weak interactions have been characterized in terms of binding energies and equilibrium configurations, scattering cross-sections, microwave and infrared spectra, etc. Related processes and phenomena in bulk matter are represented, e.g., by photoinduced dynamics of molecules embedded in rare gas solid matrices, including dissociation, recombination, transition spectra, etc. The intermediate size range, i.e., clusters, has received less attention.

One such system of interest is the NO molecule in an argon environment. The ArNO complex has been investigated, in particular, by means of photoionization spectroscopy [1], an IR-UV double resonance technique [2], electronic resonance spectroscopy [3], and total integral and differential cross-section scattering [4, 5] (see [2] for a recent review). Also Rydberg excitation of NO has been studied in the Ar solid matrix [6]. Ar$_n$NO clusters have been probed by multiphoton ionization and photodissociation [7].

There are a few ground state Ar–NO potential energy surfaces (PESs) available. The recent \textit{ab initio} PES by Alexander [8] was calculated using the correlated electron pair approximation (CEPA) and was used successfully to describe the experimental differential and integral cross-sections for inelastic scattering and the collisional transfer of rotational energy [2]. The empirical PES of Casavecchia \textit{et al.} [5] was constructed by fitting the experimental scattering data to a two-even-terms Legendre expansion. This PES exhibits significantly stronger binding between Ar and NO in both the linear and T-shape geometries, in accord with the spectroscopic data [9, 10].

The present work investigates the Ar–NO($X^2\Pi$) interaction potential at a higher level of theory to check the empirical predictions. We also investigate Ar$_n$NO clusters for $n \leq 25$ in terms of their structure and stability.

2. Theory

2.1. The model potential

The electronic structure of NO, with its singly occupied molecular $\pi$ orbital, can be interpreted within a valence-bond (VB) framework in terms of a single half-occupied atomic $p$ orbital orthogonal to the molecular axis ($z$). For Ar–NO different orientations of this orbital with respect to the Ar–N–O plane ($xz$) produce two electronic states: $^2A'$ (for $p \parallel p_x$) and $^2A''$ ($p \parallel p_y$). In an Ar$_n$NO cluster, the orientation of this $p$ orbital depends upon the interplay of interactions in all
the ArNO units, and thus on the cluster structure. Hence, each Ar atom is associated with a different mixture of $^2A'$ and $^2A''$ states. Therefore a simple additive form for the Ar$_n$NO potential is, strictly speaking, an oversimplification:

$$V_{\text{Ar,NO}} = \sum_{n}^{n} V_{\text{Ar,NO}} + \sum_{n}^{n} V_{\text{Ar,Ar}}$$  \hspace{1cm} (1)$$

However, the additivity with respect to Ar atoms can be preserved within a matrix formalism similar to the diatomics-in-molecules approach [11] by treating NO as an effective monoatomic species, whose states are determined by the orientation of the half-occupied $p$ orbital. We can represent the Ar$_n$NO potential in the basis set associated with the fixed $p_x$ and $p_y$ orientations:

$$V_{\text{ArNO}} = V_{A'} \cos^2 \phi + V_{A''} \sin^2 \phi \left( V_{A'} - V_{A''} \right) \sin \phi \cos \phi$$

$$= (V_{A'} - V_{A''}) \sin \phi \cos \phi + V_{A''} \sin^2 \phi + V_{A'} \cos^2 \phi,$$  \hspace{1cm} (2)

with $V_{A',A''} = V_{A',A''}(R, \theta)$ being the $^2A'$ and $^2A''$ state potentials for the Ar position relative to the mid-point of the NO bond, determined by spherical coordinates $R, \theta, \phi$. Here we assume the N–O distance to be fixed, e.g., at equilibrium. However, it could be treated as a parameter so long as the interaction with Ar remains weak, so that excited states of NO need not be included.

The total cluster Hamiltonian matrix is then (using the $2 \times 2$ unit matrix $E$)

$$H_{\text{Ar,NO}} = \sum_n^{n} V_{\text{Ar,NO}} + E \sum_n^{n} V_{\text{Ar,Ar}}$$  \hspace{1cm} (3)$$

Here we define the zero of energy for non-interacting Ar atoms and NO. Diagonalization of $H$ yields potential energy surfaces of two electronic states of the system, which therefore can be obtained analytically by solving the quadratic eigenvalue equation.

Even though spin–orbit splitting, $\Lambda$, between the $^2\Sigma_{3/2}$ and $^2\Pi_{1/2}$ states of NO is relatively small (around 120 cm$^{-1}$), it may affect significantly the associated ArNO potentials due to their close non-relativistic energies, which are degenerate for the linear geometry. We use the following model for the relativistic case.

The above splitting is determined mostly by the half-occupied $p$ orbital, as for a system containing a rare gas ion or a halogen atom. The relevant spin–orbit interaction matrix, $H_{\text{SO}}$, which is added to the non-relativistic Hamiltonian matrix within the ‘atoms-in-molecules’ approach [12], couples states corresponding to the $p_x, y$ and $p_z$ orientations (see, e.g., [13, 14]). In our case the $p_z$ orientation means an excited state of NO, and any such state is separated from the ground state by more than 5 eV (at least near the ground state equilibrium geometry). The off-diagonal elements in $H_{\text{SO}}$ due to $p_z$ have values of a fraction of $\Lambda$ and will not affect the relativistic potentials significantly. A similar prediction was confirmed [15] for the analogous Ar–I$^2\Pi_{1/2,3/2}$ interactions, associated with even stronger spin–orbit coupling and smaller gaps between the non-relativistic states. Thus, a suitable approximation is to consider only the part of $H_{\text{SO}}$ associated with $p_{x,y}$, which leads, for a given spin projection (and with $i = \frac{1}{2}$), to

$$H_{\text{SO}} = \begin{pmatrix} 0 & i\delta \\ -i\delta & 0 \end{pmatrix},$$

with $\delta$ being a characteristic parameter of the spin-orbit interaction. To reproduce the splitting for the isolated NO molecule, we have $\delta \equiv \frac{1}{2} \Lambda$. Finally, the relativistic Hamiltonian matrix is obtained, using $H$ of equation (3), as

$$H^{\text{rel}} = H + H_{\text{SO}},$$

and diagonalization produces potentials for the Ar$_n$NO($^2\Sigma_{1/2,3/2}$) clusters. The results are analytical, as before:

$$V_{1/2,3/2} = V_0 \left[ V_{1/2} + V_{3/2} \mp \left( \left( V_{1/2} - V_{3/2} \right)^2 + 4V_{12}^2 + 4\Lambda^2 \right)^{1/2} / 2 \right],$$

$$V_0 = \sum_{n}^{n} V_{\text{Ar,Ar}},$$

$$V_{1/2} = \sum_{i}^{i} \left( V_{A^+} \left( i \right) \cos^2 \phi_i + V_{A^-} \left( i \right) \sin^2 \phi_i \right),$$

$$V_{12} = \sum_{i}^{i} \left( V_{A^+} \left( i \right) - V_{A^-} \left( i \right) \right) \cos \phi_i \sin \phi_i,$$  \hspace{1cm} (6)

and in the case of a single Ar atom reproduce the expressions given previously (see, e.g., [5]). As above, spherical polar coordinates are employed for the Ar atom relative to an origin at the mid-point of the NO bond. Note that in this case $\phi = 0$ or $90^\circ$, depending on which non-relativistic state is lower in energy for a given position of Ar.

Spin–orbit coupling requires a definite value for the total angular momentum projection, which implies mixing of the $p_x$ and $p_y$ based states with equal weights. This effect may therefore lead to averaging the $^2A'$ and $^2A''$ potentials, and it is common to use the mean value (see [8] and references therein). Such averaging has been shown to occur in Ar–I$^2\Pi_{1/2,3/2}$, where spin–orbit terms are much larger [15]. The above formalism allows for a direct check of this approximate treatment in the case of NO and for an investigation of the effect of
the Ar–NO interactions on this mixing. In particular, if the averaged Ar–NO potential is a sufficiently good description, then the equality in expression (1) would be restored and the simple additive representation of \( V_{\text{Ar,NO}} \) would be a valid approximation.

2.2. Global optimization

The same global optimization approach was used as for our previous studies of Ne\(_n\), Ar\(_n\)Cl\(_2\) and Ar\(_n\) clusters using the DIM model [16–18]. In this ‘basin-hopping’ or Monte Carlo minimization [19] technique the potential energy \( E \) is transformed to give a new surface:

\[
E(X) = \min \{ E(X) \},
\]

where \( X \) is the vector of nuclear coordinates and \( \min \) signifies that an energy minimization is performed starting from \( X \).

Canonical Monte Carlo (MC) sampling was used to explore the \( E \) surface. For each cluster size five runs of 5000 MC steps were performed from random starting geometries. The maximum step size for the displacement of any Ar Cartesian coordinate was dynamically adjusted to give an acceptance ratio of 0.5. The runs were conducted at temperatures corresponding to 0.01 \( E_h \) and 0.005 \( E_h \) for the ground state relativistic and non-relativistic potentials, respectively. The coordinates were reset to those of the current minimum in the Markov chain at each step.

No systematic attempt was made to optimize the temperature of the MC sampling, since the lowest minima found in all five runs for each size were usually the same. The lowest minimum was always found by a majority of the runs. The global minima for the ground state relativistic potential were relaxed using the relativistic first excited state; the changes involved are very small and so we did not conduct separate global optimization runs for this state. All the results will be made available from the Cambridge Cluster Database [20].

3. Results and discussion

3.1. ArNO \( \text{ab initio potential energy surfaces} \)

The ArNO\(^{2A', 2A''}\) potential energy surfaces (PES) have been calculated \( \text{ab initio} \) with the open-shell coupled-cluster RCCSD-T method [21, 22] and the spdf (aug-cc-pVTZ) basis set [23, 24] using the Molpro package [25]. The results have been corrected for the basis set superposition error using the standard counterpoise method [26]. The N–O bond length was fixed at the ground state value \( r_0 = 1.154 \) Å [27]. Calculations have been carried out for 9 equidistant polar angles between \( \theta = 0 \) and 180°, the data being listed in table 1.

Figure 1 shows both PESs interpolated radially with cubic splines and angularly with Legendre polynomials. The \(^2A'\) PES exhibits three minima, the lowest for the T-shape configuration (with Ar slightly nearer to the O atom) and two almost equally deep local minima for the two linear configurations, with a slightly stronger binding (larger \( D_e \) and shorter \( R_e \)) for the Ar–ON geometry (table 2). The \(^2A''\) PES has a well only for the distorted T-shape configuration (significantly shifted towards the N end of NO), and saddles for both linear configurations. The \(^2A'\) state is found to be more strongly bound by about 2.4 cm\(^{-1}\), and the two states cross between the linear and T-shaped geometries. These results are consistent with the very close approach of the two PESs predicted in previous calculations [8], although there the \(^2A'\) global minimum was found to lie above that of \(^2A''\) by 1.3 cm\(^{-1}\) and the surfaces did not cross. The present results predict the Ar–NO binding to be generally stronger (by 20–30% in \( D_e \)), with a deeper well for the Ar–ON geometry than for Ar–NO [8, 28].

To improve the accuracy further and check these predictions we have employed ArN and ArO potentials calculated [29, 30] at the same level of theory using spdf and spdfg (aug-cc-pVQZ [23, 24]) basis sets. A correction was applied within the anisotropic atom–atom model [31, 32] assuming a small difference between the perturbations of these pair interactions on formation of the NO molecule, calculated for the different basis sets:

\[
V_{\text{ArNO}} = V_{\text{ArN}}^{\text{eff}} + V_{\text{ArO}}^{\text{eff}}
\]

\[
V_{\text{ArX}}^{\text{eff, new}} = V_{\text{spdfg}}^{\text{ArX}} + (V_{\text{spdfg}}^{\text{ArX}} - V_{\text{spdf}}^{\text{ArX}}).
\]

(7)

where \( V_{\text{ArX}}^{\text{eff, new}} \) (X = N, O) are the effective atom–atom interactions within the ArNO complex. These interactions can be represented in terms of their components parallel and perpendicular to the ArNO axis, similar to the ArN\(_2\) and ArO\(_2\) cases [29, 30]:

\[
V_{\text{ArX}} = V_{||} (R_X) \cos^2 \theta_X + V_{\perp} (R_X) \sin^2 \theta_X,
\]

(8)

with \( R_X \) being the Ar–X distance and \( \theta_X \) the angle between the ArX and NO axes. Such a correction has been shown [33] to reproduce the direct \( \text{ab initio} \) results accurately for the total system, obtained with the larger basis set.

The topologies of both the \(^2A'\) and \(^2A''\) surfaces are unchanged by the above correction, which mainly increases their binding (table 2). The behaviour of the two surfaces near the T-shape configuration is also preserved (figure 2), with the gap between the minima increasing to 5.7 cm\(^{-1}\). The \( D_e \) values increase by 12–18% (twice as much for the T-shape compared with the linear configurations, as expected) and \( R_e \) shortens by 0.06 ± 0.01 Å, with \( \theta_e \) unaffected. The global minima become more stable along the bending coordinate, as does the well near the N end for the \(^2A'\) state, while
the minimum for Ar–ON is slightly more destabilized with respect to bending.

The observed PES topologies can be interpreted, at least in part, using the atom–atom model of equations (6) and (7). For the \( ^2A'' \) state, the Ar–O interaction is isotropic and determined by the \( ^3\Sigma^+ \) state only, and hence there is no minimum for the Ar–ON geometry. For the \( ^2A' \) state, \( V_{ArO} \) is given by equation (8) with \( V = V(\hat{\Sigma} \Pi) \).
and $V_\perp = V'(3\Sigma^-)$ the energy increasing with bending (due to weaker binding for the $3\Sigma^-$ state), leading to a well for the linear Ar—O—N configuration. For unperturbed N the isotropic Ar—N interaction leads to no well near the N end in this model, consistent with the *ab initio* result for the $2A''$ state, but not for the $2A'$ state. The well obtained for Ar—NO in the $2A'$ state can be rationalized in terms of the electron density shift associated with formation of the strong N—O bond. In the VB picture this shift may affect the half-occupied $p_x$ orbital on N facing the doubly occupied $p$ orbital on O more weakly, while pulling the $p_y,z$ orbitals of N towards the centre of NO. Bending in the $xz$ plane would then increase repulsion between Ar and the $p_x$ electron, leading to a well near the N end, unlike bending in the $yz$ plane. The slightly shallower global minimum on the $2A''$ PES is consistent with such a shift, increasing the repulsion of Ar in the T-shape configuration from the electron density of the $p_y$ orbital. The model using unperturbed ArX potentials predicts the $2A''$ state to be more strongly bound due to a larger contribution from the more attractive ArO(3Π) component. Finally, the global minimum for the T-shape configuration on each PES is a consequence of the sum of the two Ar—X interactions rather than (mainly) one for either linear configuration.

As a consequence of the PES crossing, the lowest energy at any given point in the absence of spin—orbit coupling is a function with two minima near the T-shape configuration, separated by a low barrier, and saddles for the linear configurations (figure 3).

Spin—orbit coupling splits the non-relativistic surfaces in the linear geometry and in the crossing region by $\lambda$, and shifts them more weakly in other places. As a result, both relativistic surfaces have wells in the T-geometry which are slightly shallower and less resistant to bending (figure 4). Their well depths are equal within 1% and their positions almost coincide and approach a T-shape configuration with the Ar atom at the mid-point of the N—O bond (table 2). The associated mixing of the original (non-relativistic) PES topologies produces very shallow wells for the linear configurations for the

Figure 1. *Ab initio* Ar—NO PES for the (a) $2A'$ and (b) $2A''$ states. $z$ and $x$ are coordinates of Ar relative to the centre of the NO molecule lying along the $z$ axis. Contours are given in steps of 0.5 meV.
ground $1/2$ state (originally $2\text{A}^/'$), and reduces the corresponding well depths for the excited $3/2$ state (originally $2\text{A}''$). The new surfaces do not cross and lie nearly parallel to each other (figure 2), separated by about $\Delta$. In particular, they are both close to the averaged non-relativistic PES (figure 5), which is the approximate relativistic PES in the limit where the Ar–NO interaction is much weaker than spin–orbit coupling. In particular, the $D_c$ and $\theta_c$ values for the T-well on the averaged PES are between those for the $1/2$ and $3/2$ PES, while $R_c$ is practically the same (figure 2 and table 2). The actual mix for the $1/2$ state in this geometry is $\approx 2\% 2\text{A}' + 48\% 2\text{A}''$.

Comparison with empirical Ar–NO PESs [4, 5, 34] fitted to reproduce measured scattering cross-sections shows that the present ground state surface is closest to the empirical PES [5] with the deepest well for the T-shape configuration (table 2). The slight underestimation of the empirical $D_c$ value is consistent with the further increase in binding expected for still larger basis sets. However, our ab initio PES is significantly deeper for both linear configurations, and this effect is expected to increase with the size of the basis. Hence, the empirical PES may overestimate the anisotropy of the Ar–NO interaction. This situation resembles that found for ArN$_2$ [29]. On the other hand, the 2-even-term Legendre polynomial expansion employed in [5] for $D_c$ and $R_e$ could not reflect differences in their values for $\theta = 0$ and $180^\circ$, as well as deviation of $\theta_c$ from $90^\circ$, thus missing these contributions to the anisotropy.

### 3.2. $Ar_nNO$ cluster structures and stabilities

The above ArNO potentials were used within the model of section 2.1 to describe Ar$_n$NO clusters. We employed the Aziz potential [35] for Ar and included the Axilrod–Teller term to account for three-body non-additivity in Ar$_3$ subsystems.

The predicted global minima for Ar$_n$NO (figure 6) generally are based on the the lowest minima of Ar$_{n+1}$, with NO playing the role of a surface atom. This result is different from, e.g., Ar$_n$Cl$_2$ clusters, where Cl$_2$ is ‘solvated’ by Ar atoms when $n$ is sufficiently large [17], and may be understood in terms of the binding between the molecule in question and Ar relative to that between

![Figure 2](image2.png)

**Figure 2.** Angle dependence of the equilibrium parameters of the non-relativistic mean (dotted), $2\text{A}'$ (solid) and $2\text{A}''$ (dashed) Ar–NO PESs, and of the relativistic PESs for the $1/2$ (bold solid) and $3/2$ (bold dashed) states.

![Figure 3](image3.png)

**Figure 3.** Minimal energy non-relativistic Ar–NO ‘PES’ formed by taking the lowest of the $2\text{A}'$ and $2\text{A}''$ energies at each point from the ab initio data corrected with the more accurate ArN and ArO potentials. Coordinates and contours are as for figure 1.
two Ar atoms. As \( D_e(\text{Ar}_2) = 12.3 \text{meV} \) is only slightly less than the \( D_e(\text{Ar—NO}) \) value for the T-shape configuration, and exceeds the binding energy for the linear configurations (unlike for \( \text{ArCl}_2 \)), the \( \text{Ar}_n \text{NO} \) cluster would gain less binding with NO inside the Ar shell. In other words, the angularly averaged Ar—NO interaction represented by its isotropic component has \( D_e = 9.6 \text{meV} \) and \( 11.0 \text{meV} \) for the \( ^2A' \) and \( ^2A'' \) states, respectively, and therefore is less attractive than the \( \text{Ar}_2 \) potential, the opposite of the Ar—Cl\(_2\) case (see [17]). Spin–orbit coupling appears to have little effect upon the global minima.

Both Ar atoms in \( \text{Ar}_2\text{NO} \) occupy the T-shaped positions relative to NO, and in \( \text{Ar}_3\text{NO} \) the third Ar atom

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**Figure 4.** Relativistic Ar–NO PES for the (a) 1/2 and (b) 3/2 states. Coordinates and contours are as for figure 1.

**Figure 5.** The averaged non-relativistic Ar–NO PES as the mean of the \(^2A'\) and \(^2A''\) surfaces. Coordinates and contours are as for figure 1.
lies closer to the oxygen atom. The same tilt in the orientation of NO with respect to the rest of the cluster holds for most of the larger sizes. The NO molecule lies in the equator of the Ar$_6$NO pentagonal bipyramid, but in an axial site in the Ar$_7$NO capped pentagonal bipyramid. It lies on the principal rotation axis in Ar$_8$NO, Ar$_9$NO and Ar$_{10}$NO, but in Ar$_{11}$NO it lies in the open face. The familiar double, triple and quadruple polyicosahedral motifs appear at Ar$_{18}$NO, Ar$_{22}$NO and Ar$_{25}$NO [20]. The NO molecule never appears as a three-coordinate cap or enclosed in argon atoms, but instead prefers to sit in the surface. Usually it adopts a roughly tangential orientation with respect to the radius vector from the centre of mass.

For the ground state relativistic potential the only deviation in structure from the global minimum of Ar$_{n+1}$ occurs for Ar$_{20}$NO [20], where the double icosahedron is capped differently from Ar$_{21}$.

Only four global minima of the ground state non-relativistic potential are noticeably different from their counterparts with the relativistic potential. Ar$_{18}$NO is still based upon a double icosahedron, but the oxygen atom of NO sticks a little further out of the surface. For Ar$_{21}$NO the unfilled site of the triple icosahedron is different from that obtained with the relativistic potential, while for Ar$_{23}$NO and Ar$_{25}$NO the NO molecule occupies a different site of the same framework.

Table 3 lists the dissociation energies $D_e$ of the global minima for the process Ar$_n$NO $\rightarrow$ $n$Ar + NO along with the atomic binding energies $\Delta D_e = D_e(n) - D_e(n-1)$. The $D_e$ values increase with the cluster size, almost linearly for larger $n$ (figure 7), and the $\Delta D_e$ values exhibit
Table 3. Dissociation energies (in eV) of Ar$_n$NO global minima. The bold values mark the sizes expected to have special stability. SO stands for spin–orbit coupling.

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$^a$ Ar$_n$NO $\rightarrow$ $^{1/2}$Ar $\rightarrow$ NO.

$^b$ Ar$_{n-1}$NO $\rightarrow$ Ar $\rightarrow$ NO.

$^c$ Ar$_n$NO $\rightarrow$ Ar $\rightarrow$ NO.

relatively large peaks at $n \geq 12$, 18, 22 and 25, matching the ‘magic’ numbers of Ar$_{n-1}$, with smaller peaks at $n \geq 6, 9$ and 15, which are associated with weaker features for Ar$_{n-1}$. Here we compare our results with the data for argon clusters obtained with the same Ar$_2$ potential. The predicted magic numbers are unaffected by spin–orbit coupling and are the same for the 1/2 and 3/2 states. Our results are consistent with the magic numbers 12, 18, and 22, obtained in mass spectroscopic experiments [7] on photonization of Ar$_n$NO clusters produced in supersonically expanded Ar $\rightarrow$ NO gas mixtures, while the additional detected magic number 8 deviates from nearest predicted 6 and 9. We assume that the experimental results reflect the relative stabilities of the neutral clusters.

The surface location of NO suggests an alternative dissociation mechanism through detachment of NO. The associated energies $\Delta D_e$(NO) are larger than those for detachment of a single Ar atom (except for $n \geq 6$ and 13), due to $D_e$(Ar–NO) for the T-shape configuration being larger than $D_e$(Ar–Ar) and to the orientation of NO in the cluster. The associated magic numbers coincide with those most pronounced for $\Delta D_e$, i.e., 6, 12, 18, and 22 (table 3), and the weak features at $n \geq 9$ and 15 are missing for $\Delta D_e$(NO) for the 1/2 state. This result supports the above mentioned set of magic numbers observed in experiments [7]. The differences between the two $\Delta D_e$ values increase for sizes between subsequent magic numbers (figure 8).

The above variations in the dissociation energies suggest that the clusters are more likely to be formed through Ar$_n$NO $\rightarrow$ Ar$_{n-1}$NO than through Ar$_{n-1}$NO $\rightarrow$ Ar $\rightarrow$ Ar$_n$NO and are more likely to dissociate through Ar$_n$NO $\rightarrow$ Ar$_{n-1}$NO $\rightarrow$ Ar than through Ar$_n$NO $\rightarrow$ Ar $\rightarrow$ NO. The overall process

Ar$_n$NO $\rightarrow$ Ar$_{n-1}$NO $\rightarrow$ Ar

is exothermic, and the calculated energy release, $\Delta D_e$(NO)–$\Delta D_e$, peaks at $n \geq 11, 17$, and 21 (for the 1/2 state), i.e., one size before the magic numbers
For the 3/2 state, however, the first two peaks are shifted to \( n = 10 \) and 16. Since the global minima for the relativistic 1/2 and 3/2 states appear to be practically identical, the energy difference between these structures at any given size is usually just \( \Delta \), the splitting for free NO. The 1/2 \( \rightarrow \) 3/2 excitation energy \( \Delta = D_e(3/2) - D_e(1/2) \) exhibits peaks at \( n = 10, 16 \), and (more weakly) 20, i.e., two sizes before the magic numbers (figure 8), mainly as a consequence of reduced \( D_e \) values for the 3/2 state.

**4. Conclusion**

An analytical DIM-like model potential including spin–orbit coupling has been developed for Ar\(_n\)NO clusters. It is additive in a matrix rather than scalar fashion. High level \textit{ab initio} potential energy surfaces of the Ar–NO(\( X^2\Pi \)) van der Waals complex have been calculated and found to cross near the T-shape configuration. The \( ^2\text{A}' \) surface has two shallow wells for both linear configurations and, for the equilibrium T-shape geometry, appears to lie slightly below the \( ^2\text{A}'' \) PES, which has only a single well for the distorted T-shape configuration.

Within this model, spin–orbit coupling is shown to couple the two states strongly, producing two relativistic PESs of generally similar topology close to that of the averaged non-relativistic PES. The ground state PES is found to be more attractive than previous empirical surfaces for the linear geometries, suggesting a smaller anisotropy in the Ar–NO interaction.

The lowest energy structures of the Ar\(_n\)NO clusters are found to be affected weakly by spin–orbit coupling and closely resemble those for Ar\(_{n\parallel}\), with NO occupying a position in the surface of the cluster. No low lying local minima with NO fully solvated were found for the range of sizes studied \((n < 25)\). The predicted Ar\(_n\)NO 'magic' numbers \((12, 18, 22\) and 25\) reproduce those for the corresponding Ar\(_{n\parallel}\) clusters and correlate well with those found experimentally for Ar\(_n\)NO\(^+\). The NO detachment channel associated with the surface location of the NO molecule is found to have a larger dissociation energy than for detachment of Ar.

The \( D_e \) values for the two dissociation channels suggest that Ar\(_n\)NO may form by adding NO to Ar\(_n\). Accordingly, Ar\(_n\)NO seem more likely to dissociate through detachment of Ar. The energy change for Ar\(_{n\parallel}\) + NO \( \rightarrow \) Ar\(_{n\parallel}\) NO + Ar is generally negative and
exhibits peaks at the sizes preceding (immediately for the 1/2 state) magic numbers.

The NO(1/2–3/2) excitation energy varies weakly with the cluster size, exhibiting maxima at magic numbers minus two. The cluster stability is affected weakly by this excitation.

As the Ar–NO+ system is predicted [36] to have an order of magnitude larger binding energy than Ar–NO and Ar₂, the ionization of ArₙNO is likely to lead to a significant structural change associated (particularly for larger n) with ‘solvation’ of the molecule in the cluster, in accord with experiments [9].

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Note added in proof
Since this paper was accepted, new work by Alexander [37] on the ArNO(A′,A″) PES has appeared. There, the PES is calculated using the unrestricted coupled-cluster method UCCSD(T) with spd¹ (aug-cc-pVTZ) and spdfg (aug-cc-pVQZ) basis sets and extrapolated to the basis set limit. The resulting surfaces are essentially the same as those reported by us.

Of particular interest is the comparison between our PES, constructed in terms of the more accurate ArN and ArO potentials (for the spdfg basis set), and the PES obtained directly with this basis. Our predictions lead to only slightly deeper (by 2%) wells for both states in the same positions, with the gap between the two minima being somewhat larger (0.70 compared to 0.56 meV). These results confirm the reliability of our procedure. In fact, our surfaces are even closer to the basis set limit results.

In the basis set limit, the global minima for both states are predicted to be deeper by less than 1 meV relative to the spdfg data. When this difference is added the averaged (isotropic) Ar–NO potentials remain bound more weakly than the Ar–Ar potential. This result supports our prediction of surface locations for NO in ArₙNO (n ≤ 25) clusters.

References