Interaction of NO($A^2\Sigma^+$) with rare gas atoms: Potential energy surfaces and spectroscopy

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(Received 3 September 2008; accepted 6 November 2008; published online 24 December 2008)

We present the results of an ab initio study of the interaction of electronically excited NO($A^2\Sigma^+$) with rare gas (Rg) atoms. The bond states of each NO(A)–Rg species are determined from potential energy surfaces calculated at the RCCSD(T) level of theory. Making use of the NO(X$^2\Pi$)–Rg vibrational wavefunctions, we then simulate electronic spectra. For NO–Kr and NO–Xe we obtain good qualitative agreement with the previously published experimental spectra. For NO–Ar, the shallowness of the surface gives rise to agreement that is less satisfactory, but a global scaling provides better qualitative agreement. The assignment of the spectra is far from straightforward and is only possible with guidance from the calculated energies and wavefunctions of the energy levels of the complex. Previous assignments are discussed in the light of this conclusion. © 2008 American Institute of Physics. [DOI: 10.1063/1.3040074]

I. INTRODUCTION

There have been a number of studies of the electronic spectroscopy of complexes between rare gases (Rg) and the NO molecule. The review by Kim and Meyer summarizes the work up to 2001.1 In 2000, well-resolved spectra of the $\tilde{A} \rightarrow \tilde{X}$ transition in NO–Kr and NO–Xe (improving on earlier studies2,4) were reported,4 as well as resonance-enhanced multiphoton ionization (REMPI) spectra for NO–Ar.3 Similar spectra of NO–Ne have not been obtained, consistent with the failures reported by Miller and Cheng5 as well as Carrasquillo et al.7 [using REMPI and Carrasquillo et al.7 [using laser-induced fluorescence (LIF)], although subsequent studies have reported electronic spectra of NO–Ne for different excited electronic states.8,9 In Ref. 4, the lack of an $\tilde{A}$ state spectrum for NO–Ne was attributed to the repulsion between the Ne atom and the NO 3s Rydberg electron. We recently confirmed this conclusion,10 making use of a potential energy surface (PES) calculated by Pajón-Suarez et al.11 No spectra attributable to the NO–He complex have been reported.

The $\tilde{A} \rightarrow \tilde{X}$ spectrum of the NO–Kr complex has never been fully assigned. Only a general interpretation has been presented,2,4 in which a progression of the intermolecular stretch, with a gradual increase in structure caused by the progressive “unlocking” of the hindered internal rotation of NO, was suggested. The complex was hypothesized to be linear close to its equilibrium geometry. The interpretation suggests that as the NO–Kr distance increases the anisotropy in the PES decreases, so that the averaged geometry tends toward a skewed T shape in higher NO–Kr vibrational levels.

Even this kind of broad interpretation has not been possible for NO–Xe,3,4 where no obvious progressions are seen.

In contrast, there have been a number of attempts to obtain and assign the spectra of the NO–Ar complex. A LIF spectrum of NO–Ar was reported by Levy and co-workers7,12 but appeared to consist only of bound-free transitions. The first evidence that the $\tilde{A}$ state had bound levels was provided by Miller,13 when he observed REMPI spectra, monitoring the NO$^+$–Ar mass channel. The spectrum was broad and the apparent structure was tentatively assigned to the NO–Ar stretching vibration.

The first detailed spectrum of the $\tilde{A} \rightarrow \tilde{X}$ transition for NO–Ar was reported by McQuaid et al. in 1994.14 Clear structure was evident to the blue of the corresponding NO transition which revealed that the $\tilde{A}$ state was less strongly bound than the $\tilde{X}$ state. The spectrum displayed a strong transition at ~44 240 cm$^{-1}$, a region where there were no obvious features, followed by a series of reasonably intense features whose intensities decreased at higher wavenumber. It was suggested that the first feature was the origin, the next strong feature was the intermolecular stretch, with the next two features representing bend-stretch combinations.

Since the bonding is so weak, the bending mode $v_b$ is actually a hindered rotation of the NO moiety. As such, there is angular momentum associated with the motion, and this is projected onto the intermolecular axis. Hence $v_b = 1$ can give rise to projections of $K = 0$ or 1, and both of these transitions were assigned. One debatable aspect of this assignment was the attribution of a van der Waals stretch vibration of ~30 cm$^{-1}$, which is an extremely large proportion of the...
binding energy, estimated by McQuaid et al.\textsuperscript{14} to be 
\( \leq 43 \text{ cm}^{-1} \). In addition, some features at higher energy were not assigned.

Tsuji et al.\textsuperscript{15} also reported a similar assignment for their REMPI spectra of NO–Ar. Here, too, the anomalous magnitude of the stretch frequency when compared to the dissociation energy was noted. These authors attributed this to a strong repulsive interaction at short intermolecular separations. In 1998, Bush et al.\textsuperscript{16} reported REMPI spectra of NO–Ar (as well as zero-kinetic energy spectra). Using a very similar assignment to that reported by McQuaid et al.,\textsuperscript{14} these authors reported an apparently successful simulation of the spectrum, making use of the semirigid model of Mills et al.\textsuperscript{17} and Fawzy and Hougen,\textsuperscript{18} which does not allow wide-amplitude bending motion.

The simulation of Bush et al.\textsuperscript{16} took into account only T-shaped geometries, where the rotation of the complex around the \( a \) inertial axis is essentially rotation of NO. In addition, only the high energy end of the spectrum was simulated. The lack of structure at the origin was attributed to the linearity of the complex in its lowest stretching level. Skewed T-shaped geometries were assumed to be accessed only when the intermolecular stretch is excited, increasing the intermolecular distance, and hence decreasing the anisotropy. In addition,\textsuperscript{16} the more comprehensive model of Dubernet et al.,\textsuperscript{19} which considers the evolution of NO rotational motion as the anisotropy of the intermolecular potential increases, was employed to gain insight into the energy levels. Overall, an assignment\textsuperscript{16} relatively consistent with that of McQuaid et al.\textsuperscript{14} was achieved.

Slightly later in 1998 Shafizadeh et al.\textsuperscript{20} reported the results of a LIF study of the NO–Ar complex, in the first observation with this technique of bound-bound transitions. Overall, a spectrum quite similar to that of the REMPI studies was obtained. These authors attempted to simulate the spectrum by first generating the \( \tilde{A} \) state PES. To do so, they combined NO\textsuperscript{+} orbitals with orthogonalized Rydberg orbitals. Separately, a PES of NO\textsuperscript{+}–Ar was then combined with the NO Rydberg orbitals obtained in the previous step. The NO\textsuperscript{+}–Ar PES employed was that of Robbe et al.,\textsuperscript{21} in which the Ar atom was localized at the O atom of NO\textsuperscript{+}. However, more recent work\textsuperscript{22–25} indicates that the Ar atom is localized at the N atom in the NO\textsuperscript{2+}–Ar system. Additionally, we find (see below) that for the NO(A)–Rg complexes (Rg=Ar–Xe), the minimum corresponds to the Rg atom located on the N side of the molecule. Thus, the model used in Ref. 20 needs to be treated with caution. That said, their simulations did lead to qualitative agreement with their experimental \( \tilde{A} \leftarrow \tilde{X} \) spectrum, but the detailed structure was not correct.

The most recent experimental study on the NO–Ar complex was reported in 2000,\textsuperscript{5} where REMPI spectroscopy was employed. The published spectrum appears to have the best signal-to-noise ratio of the spectra so far reported. This allowed the first unambiguous observation of weak features between the origin and the previously assigned stretch vibration; in addition, spectra were recorded for NO–\( ^{36}\text{Ar} \), but no spectral shift was discernible. Again, simulations employing the model of Fawzy and Hougen\textsuperscript{18} were consistent with the observed spectrum in the high energy region. However, simulations were unsuccessful in explaining the weak structure seen just above the origin. Simulations using the more general model of Dubernet et al.\textsuperscript{19} were therefore attempted. Good agreement in both energy and intensity was again obtained for the features at higher wavenumbers, with assignments being given to most of the bands, largely in agreement with previous work.\textsuperscript{5,14,15} The region close to the origin proved problematic, however. The line positions were more or less well reproduced, but the predicted intensities were far from satisfactory.

In summary, all of the previous assignments of the \( \tilde{A} \leftarrow \tilde{X} \) spectrum of NO–Ar have been based on the appearance of the spectrum, with attempts to use available models to rationalize the assignment. However, the apparently normally high frequency of the intermolecular stretch and the assignment of the weak structure at low energies are still unresolved issues.

The poor fits of the available NO(A 2Σ\textsuperscript{+})–Rg spectra led us to seek additional insight by means of high-level bound state calculations based on \textit{ab initio} PESs.

The importance of determining accurate intermolecular potentials for the NO–Rg systems extends to the condensed phase.\textsuperscript{26} In particular, structural relaxation upon impulsive Rydberg excitation of NO-doped Rg matrices has been studied by femtosecond spectroscopy\textsuperscript{27} and associated molecular dynamics (MD) simulations.\textsuperscript{28,29} Most of these simulations have assumed empirical pair potentials to represent the NO–Rg interaction, neglecting completely the anisotropic and/or open-shell character of the interaction.

Although this might seem a reasonable first approximation, given the 3s Rydberg character of the excited state, the present calculations will show that for Rg=Ar, Kr, and Xe, the anisotropic terms are as important as the isotropic terms in the region of the NO–Rg minima. The development of more accurate potentials for these simulations, on the basis of highly accurate \textit{ab initio} calculations, was one of the motivations for a recent study on the NO–Ne system.\textsuperscript{11}

\section{II. COMPUTATIONAL DETAILS}

The electronically excited \( A 2Σ\textsuperscript{+} \) state of NO lies \( \sim 44 \text{ 200 cm}^{-1} \) above the \( \chi \text{ 2II} \) ground state, which has the electron occupancy \( \cdots 2σ^2 2p_π^2 \). Multireference configuration interaction studies by de Vivie and Peyerimhoff\textsuperscript{30} have shown that over the range of NO bond lengths considered here, the first excited state of NO corresponds to a single excitation from the \( 2pπ^* \) orbital to the \( 3sσ \) Rydberg orbital.

To investigate the interaction of this state of NO with Rg atoms, we employed single-reference Hartree–Fock calculations followed by the partially spin-restricted coupled-cluster method with single, double, and perturbative triple excitations, RCCSD(T). For all NO–Rg complexes the \( T_1 \) diagnostic was 0.017, low enough to suggest minimal multireference character. Upon approach of the Rg in nonlinear geometries, the symmetry of the ground \( \chi \text{ 2II} \) state is lowered, so that the \( A 2Σ\textsuperscript{+} \) state is no longer the lowest electronic state of \( A' \).
TABLE I. Dependence of the binding energies $D_e$ (cm$^{-1}$) of NO($^2\Sigma^+$)–Rg complexes with basis set.

<table>
<thead>
<tr>
<th></th>
<th>d-aug-cc-pVQZ</th>
<th>d-aug-cc-pV5Z</th>
<th>d-aug-cc-pV5Z+bf</th>
<th>aug-cc-pVTZ+bf</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO–He</td>
<td>0.83</td>
<td>0.85</td>
<td>0.87</td>
<td>0.81</td>
</tr>
<tr>
<td>NO–Ne</td>
<td>3.87</td>
<td>3.97</td>
<td>4.08</td>
<td>3.75</td>
</tr>
<tr>
<td>NO–Ar</td>
<td>71.7</td>
<td>73.4</td>
<td>75.2</td>
<td>76.1</td>
</tr>
<tr>
<td>NO–Kr</td>
<td>118.0</td>
<td>122.0</td>
<td>126.4</td>
<td>137.8</td>
</tr>
<tr>
<td>NO–Xe</td>
<td>123.6</td>
<td>127.0</td>
<td>130.6</td>
<td></td>
</tr>
</tbody>
</table>

$^a$All-electron calculations; see text.
$^b$Scaled PES; see text.
$^c$ECP; see text.

symmetry. However, because the relatively weak interaction does not break the orthogonality of the diatomic orbitals significantly, it is possible to converge RCCSD(T) calculations of the NO($^2\Sigma^+$)–Rg system without variational collapse to the ground state. This is extremely advantageous, as the RCCSD(T) method is expected to recover more dynamic correlation energy than would a CASSCF+MRCI approach and is, in addition, size consistent.

To generate the NO($A^1\Sigma^+$)–Rg PESs we fixed the NO bond length at the equilibrium distance of the $A^1\Sigma^+$ state, $r_e=1.064\,\text{Å}$.\textsuperscript{31} To improve the description of the Rydberg character of the $A^1\Sigma^+$ state, we added diffuse $s$ and $p$ basis functions on the N and O atoms with exponents equal to 0.02. Unless otherwise noted, we use the standard aug-cc-pVTZ basis set for all atoms.\textsuperscript{32} For Rg=Kr, we include scalar relativistic effects in our all-electron calculations by inclusion of the Douglas–Kroll integrals. For Rg=Xe, we used the ECP28MDF relativistic effective core potential (ECP) developed by Peterson et al., with the associated aug-cc-pVTZ valence basis set.\textsuperscript{33} In all cases, a set of 3s3p2d2f/1g1h valence functions (bfs) located at the midpoint of the NO–Rg Jacobi vector, $R$, was employed to improve the description of the weak intermolecular forces.\textsuperscript{34}

As a test of the quality of our calculations, we also performed calculations without bfs but employing larger, purely atom-centered basis sets. To this end, single-point RCCSD(T) calculations were performed with d-aug-cc-pVQZ and d-aug-cc-pV5Z basis sets, where for Xe, the ECP28MDF ECPs were employed, together with the aug-cc-pVQZ-PP and aug-cc-pV5Z-PP valence basis sets; for all other atoms, standard aug-cc-pVQZ and aug-cc-pV5Z basis sets were employed. In the case of Kr two types of calculations were considered: inclusion of scalar relativistic effects through Douglas–Kroll integrals and the use of the ECP10MDF ECP with its associated valence basis set.\textsuperscript{35} Test calculations were performed at the calculated minimum energy geometry of the RCCSD(T)/aug-cc-pVTZ+bf calculations. For all atoms, we extended the basis sets by one set of basis functions of each angular momentum type in an even-tempered way, with the ratio obtained from the least diffuse orbitals in the standard basis sets. We then calculated the dissociation energy $D_e$ for each of the basis sets and extrapolated these to the complete basis set (CBS) limit using the two-point extrapolation formula of Halkier et al.\textsuperscript{35,36}

III. RESULTS AND DISCUSSION

A. Extrapolated $D_e$ results

In Table I we present the $D_e$ values obtained from the d-aug-cc-pVQZ ($X=Q,5$) calculations, the values extrapolated to the complete basis set limit as described above (denoted by d-aug-cc-pV5Z), and the results from the aug-cc-pVTZ+bf calculations. As is clear, for He, Ne, and Ar the agreement between the d-aug-cc-pVQZ ($X=Q,5$) and the d-aug-cc-pV5Z results is very good, which suggests that the atom-centered d-aug-cc-pV5Z basis set is close to saturation for these species. Furthermore, the aug-cc-pVTZ+bf results are in very good agreement with the d-aug-cc-pV5Z extrapolated values, which suggests that the aug-cc-pVTZ+bf PES is likely to be reliable in the region close to the minimum. Thus, we argue that the TZ+bf basis sets are a more cost-effective way of describing these complexes.

In the case of Kr, two types of calculations were done: an all-electron basis set including the Douglas–Kroll integrals and a basis set incorporating an ECP. The ECP $D_e$ values are slightly larger but similar to the all-electron calculations. This gives us confidence in the reliability of the ECP calculations for the NO($A^1\Sigma^+$)–Xe complex. For both Kr and Xe, the agreement is still good between the d-aug-cc-pVQZ ($X=Q,5$) and the d-aug-cc-pV5Z extrapolated value, but the degree of convergence suggests that the atom-centered basis sets are a little less complete than for the three lighter Rg atoms. This possible lack of convergence is also suggested by the fact that the aug-cc-pVTZ+bf calculations yield slightly larger dissociation energies for Kr and Xe. The differences seen between the purely atom-centered results and those obtained with the inclusion of bfs suggest, conservatively, that the precision of our calculated dissociation energies of the Kr and Xe complexes is of the order of $\pm 10\%$. 

FIG. 1. (Color online) Contour plot of the RCCSD(T)/aug-cc-pVTZ+bf NO($^2\Sigma^+$)–He PES. Contour values are given in cm$^{-1}$, relative to the dissociation asymptote.
B. NO(A $^2\Sigma^+$)–Rg PESs

We initially provide a brief description of the PESs. These will be referred to later when discussing the bound states.

The contour plot of the PES for Rg=He is shown in Fig. 1. The PES is fairly isotropic and largely repulsive. The attractive part of the interaction energy starts at around $R=13\alpha_0$, with the global minimum being a collinear arrangement, with He on the O side ($\theta=180^\circ$) of the NO; for $\theta=0^\circ$, there is a saddle point at an energy of $-0.671$ cm$^{-1}$ at $R=14.7\alpha_0$.

For completeness, we also include in Fig. 2 a contour plot of the PES for Rg=Ne, calculated in Ref. 11 and used in Ref. 10 to calculate bound states. The PES has a global minimum of 3.75 cm$^{-1}$ at $\theta\approx 140^\circ$ and $R=12.6\alpha_0$. The PES is still largely isotropic but approximately five times more attractive than that for Rg=He, allowing it to support some bound states.$^{10}$

The NO–Ar PES has a global minimum at $\theta=0^\circ$, collinear ArNO, at $R=7.75\alpha_0$, with a depth of 76.14 cm$^{-1}$; a second, shallower minimum is located at the ArON collinear geometry, with $R=10.7\alpha_0$ with a depth of 33.04 cm$^{-1}$. The surface is fairly anisotropic, especially close to the global minimum, and despite the larger size of Ar, the global minimum is $\sim 5\alpha_0$ closer than for Rg=He.

As will be discussed below, the calculated dissociation energy of NO(\textit{A})–Ar is $\sim 25\%$ lower than the experimentally determined value.$^{15}$ To correct for this significant underestimation of the well depth, we carried out a global scaling of the PES, in which we multiplied the RCCSD(T) PES by a constant factor of 1.23. Figure 3 shows this scaled NO–Ar PES in panel (b) and the unscaled PES in panel (a).

For Rg=Kr, the contour plot of the PES is shown in Fig. 4. The PES resembles the Rg=Ar surface but has a well twice as large with increased anisotropy. Again, the global minimum is located at the $\theta=0^\circ$ collinear geometry; it is 137.8 cm$^{-1}$ deep and is located at $R=8.0\alpha_0$. There is another local minimum at the other collinear geometry, with a well depth of 63.0 cm$^{-1}$ and $R=9.8\alpha_0$.

For Rg=Xe, the contour plot of the PES is shown in Fig. 5. Again, the global minimum occurs at a collinear RgN with a collinear global minimum at $\theta=0^\circ$; the depth is 174.4 cm$^{-1}$ and $R=8.45\alpha_0$. The second local minimum at $\theta=180^\circ$ is at $R=9.9\alpha_0$ and is 97.4 cm$^{-1}$ deep.

As noted in Sec. I, there are very few calculated PESs for the interaction of NO(A) with Rgs. Outside of those for NO–Ne (Ref. 11) and NO–Ar,$^{20}$ which we mentioned earlier, the only other one the authors are aware of is the NO(A $^2\Sigma^+$)–Kr PES, reported recently by Castro-Palacios et al.,$^{17}$ which was used in MD simulations of the structural relaxation of a krypton matrix upon photoexcitation of the NO molecule to the $\textit{A}$ state. This CASSCF+MRCI PES is mainly repulsive, with a global minimum at $\theta=180^\circ$ and $R=11.3\alpha_0$, a very different topology to the PES obtained here. Further, the predicted dissociation energy ($\sim 14$ cm$^{-1}$) was far lower than the experimentally deter-
mined value (104 cm\(^{-1}\))\(^{4}\) in contrast, our treatment gives rise to a dissociation energy in much better agreement (see below).

**C. Bound state calculations**

Because the spin splitting in the \(A^2\Sigma^+\) state of NO is below the experimental resolution in the NO–Rg spectra discussed here, we will neglect it in the qualitative discussion of the bound levels of these complexes. In this “pseudo-closed-shell” approximation the states of the complex are labeled by \(J\) (the total angular momentum) and its projection \(K\) along the NO–Rg intermolecular axis (the vector which joins the center of mass of the NO molecule with the Rg). To assign the \(K\) quantum number we observe whether a particular bound state appears first for the \(J=0, 1,\) or 2 calculations. Furthermore, contour plots of the eigenfunctions also allow the assignment of the additional quantum numbers \(\nu_s\) to the NO–Rg stretch and \(n\) to the rotational angular momentum of the NO moiety. The projection of \(n\) along the NO–Rg axis is identical to \(K\).

When the vector \(\mathbf{R}\) lies in the plane of rotation of the NO, \(K=0\). This is referred to as \(\Sigma\) bending.\(^{38,39}\) States with \(K=1\) are referred to as \(\Pi\) bending states. When the angular anisotropy is high, then \(K\) becomes the quantum number of the intermolecular bending mode. At higher energies, the bending and van der Waals stretching motion become progressively mixed, so that it becomes difficult, if not impossible, to assign the \(\nu_s\) and \(n\) quantum numbers.

We employed the HIBRIDON program suite\(^{40}\) for the calculation of the bound state energy levels that included the open-shell character of the NO(A) molecule.\(^{41}\) The wavefunctions for all of the NO(A)–Rg bound states were obtained in the pseudo-closed-shell approximation using the collocation method\(^{42}\) on a grid of 100 radial and 30 angular points. The wavefunctions of the ground states of NO(X)–Rg complexes were obtained from HIBRIDON using (in the case of Ar) the PESs of Alexander.\(^{43}\) For Kr and Xe we used potentials developed by Kłos and co-workers.\(^{44}\) For the calculations of the ground Rg–NO(X) wavefunctions we did not use the closed-shell approximation. The bound state calculations of the Rg–NO(X) systems were performed within a coupled-state approximation of the close-coupling equations. The spin-orbit coupling was taken into account together with \(\Lambda\)-doublet splitting of the NO(X) rotational levels. The wavefunction for each Rg–NO(X) system was represented on the numerical grid to use in subsequent integrations together with the Rg–NO(A) wavefunctions to obtain Franck–Condon factors.

We present the values of the bound state energies as supplementary material in Tables S1–S3.\(^{45}\) obtained from full quantum close-coupling calculations with the retention of the open-shell nature of the complex, together with expectation values for the value of the NO–Rg Jacobi coordinates \(R\) and \(\theta\); for NO(A)–Ar, we present the values for the scaled potential, since the agreement with the experimental spectrum is so much better. We employ the bound state wavefunctions, calculated within the pseudo-closed-shell approximation for the Rg–NO(A) systems, to calculate Franck–Condon factors, and hence to simulate the electronic absorption spectrum.

Table II lists the zero-point corrected dissociation energies and compares these with experiment. A comparison of

### Table II. Comparison of experimental and theoretical dissociation energies (cm\(^{-1}\)) of the NO(A \(^2\Sigma^+)\)–Rg complexes.

<table>
<thead>
<tr>
<th>Rg</th>
<th>Theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0(^\text{a})</td>
<td>... (^\text{b})</td>
</tr>
<tr>
<td>Ne</td>
<td>2(^\text{a})</td>
<td>b(^\text{b})</td>
</tr>
<tr>
<td>Ar</td>
<td>32.0(^\text{a})</td>
<td>44(^\text{c})</td>
</tr>
<tr>
<td>Kr(^\text{f})</td>
<td>96.2(^\text{a})</td>
<td>103.7(^\text{a})</td>
</tr>
<tr>
<td>Xe</td>
<td>144.5(^\text{a})</td>
<td>157.6(^\text{a})</td>
</tr>
</tbody>
</table>

\(^{\text{a}}\text{This work.}\)  \(^{\text{b}}\text{Reference 4.}\)  \(^{\text{c}}\text{Scaled PES, see text.}\)  \(^{\text{d}}\text{All-electron calculations; see text.}\)
TABLE III. Equilibrium geometries ($R$, $\Theta$), binding energies ($D_b$), and comparison of experimental and theoretical dissociation energies ($D_0$) (in cm$^{-1}$) for the NO($X\tilde{\Sigma}^+$)–Rg complexes.

<table>
<thead>
<tr>
<th>Rg</th>
<th>$R_g$ (a$_0$)</th>
<th>$\Theta$ (deg)</th>
<th>$D_b$ ($D_0$) (theory)</th>
<th>$D_b$ (experiment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>6.1$^e$</td>
<td>97$^a$</td>
<td>7 (29)$^a$</td>
<td>...$^b$</td>
</tr>
<tr>
<td>Ne</td>
<td>6.2$^e$</td>
<td>96$^b$</td>
<td>35 (60)$^c$</td>
<td>...$^b$</td>
</tr>
<tr>
<td>Ar</td>
<td>6.8$^d$</td>
<td>95$^d$</td>
<td>83 (116)$^d$</td>
<td>88$^d$</td>
</tr>
<tr>
<td>Kr</td>
<td>7.0$^f$</td>
<td>93$^f$</td>
<td>112 (147)$^f$</td>
<td>105–110$^f$</td>
</tr>
<tr>
<td>Xe</td>
<td>7.5$^h$</td>
<td>94$^h$</td>
<td>117 (149)$^h$</td>
<td>121$^h$</td>
</tr>
</tbody>
</table>

$^a$Reference 54.  
$^b$Not determined experimentally.  
$^c$Reference 35.  
$^d$Reference 44(a).  
$^e$Reference 4.  
$^f$Reference 44(b).  
$^g$Reference 4.

Tables I and II shows that the zero-point correction for the NO($A\tilde{\Delta}$–Ar) system is relatively large, especially in comparison to the complex with Kr and Xe. This may be explained by looking at the contour plots of the PESs. In the case of NO($A\tilde{\Delta}$–Ar), the linear minimum is quite narrow, extending only 30$^\circ$–35$^\circ$ in angle, whereas for NO($A\tilde{\Delta}$–Kr and Xe, the minima are wider. It is the narrowness of the minimum which results in a higher zero-point correction.

This effect is similar to what we observed recently for the OH($A\tilde{\Delta}$–Ar complex, where the vibrational ground state corresponds to collinear ArOH geometry, even though the global minimum on the PES corresponds to collinear ArOH geometry. Here, the ArOH well, although deeper, is more localized in angle, so that the zero-point energy is larger.

In Table III we report equilibrium geometries and binding energies for Rg–NO($X$) complexes together with theoretical and experimental values of dissociation energies. The dissociation energies for He and Ne complexes have not been determined experimentally to date. In the case of heavier Rg atoms the agreement between theoretical and experimental values of dissociation energies is very good. The relative error between theoretical and experimental results for Rg–NO($X$) complexes is much smaller than for Rg–NO($A\tilde{\Delta}$) systems.

D. Simulated spectra

Simulated spectra were determined by assuming that all excitations occurred out of the zero-point energy level of the $\tilde{X}$ state of each complex. To calculate rovibronic Franck–Condon factors for transitions to all $J=0, 1, 2$ bound levels of the $A\tilde{\Delta}$ state of each complex we used the wavefunctions for the NO($X\tilde{\Sigma}^+$)–Rg and NO($A\tilde{\Delta}$–Rg complexes, determined as described above in Sec. III C. To obtain relative line intensities, we integrated the product of the ground and excited state vibronic wavefunctions multiplied by the $P_{10}$ and $P_{11}$ Legendre functions contained in the transition dipole moment operator and then squared the result. The $P_{10}$ and $P_{1 \pm 1}$ terms correspond to parallel and perpendicular transitions, respectively. We used the approximation of a constant transition dipole moment for the NO molecule.

1. NO–Kr

Figure 6 shows the predicted spectrum for the $\tilde{A}\leftarrow \tilde{X}$ transition of NO–Kr. The qualitative agreement is good, with all of the main intensity variations reproduced. Indeed, there is a large amount of quantitative agreement, with many features in the experimental spectrum identifiable in the calculated one. The theoretical spectrum terminates at slightly lower wavenumbers because the calculated dissociation energy $D_0$ is $\sim 7\%$ too low (Table II).

In Fig. 7, we overlay contour plots of the vibrational wavefunctions corresponding to the more prominent peaks in the simulated spectrum. It is immediately obvious that the previously suggested hypothesis that the prominent features correspond to a progression in the intermolecular stretch is incorrect. In fact the pure stretch vibrations have much smaller intensities than the main features, likely because the NO($X\tilde{\Sigma}^+$–Kr complex has a skewed T-shaped structure, while the NO($A\tilde{\Delta}$–Kr state is linear (Fig. 4). Consequently, the first strong feature at $\sim 44 230$ cm$^{-1}$ corresponds to the $\Pi$ bend. The next very strong features at $\sim 44 262$ cm$^{-1}$ are due to mixed $\Sigma^\prime$ bend/stretch combinations, with those at $\sim 44 295$ cm$^{-1}$ having very mixed character. We thus conclude that the strongly anharmonic and mixed nature of the calculated energy levels implies that only by calculation of the positions and wavefunctions of the bound levels based on an ab initio PES can one hope to assign correctly the observed spectrum.

Given an identifiable 1:1 correspondence between many calculated and experimental features, it might be possible to obtain a better agreement by scaling the radial and angular components of the calculated PES.

2. NO–Xe

As noted in Sec. I, previous attempts to make any headway with the assignment of the $\tilde{A}\leftarrow \tilde{X}$ spectrum of NO–Xe have been unsuccessful since no obvious progressions were seen in the experimental spectrum. Given the conclusions just reached for NO–Kr, this now seems unsurprising! In Fig. 8, we show our calculated ab initio spectrum for NO–Xe. As with NO–Kr, the qualitative agreement is good overall, with many features being identifiable in both...
the calculated and experimental spectra. Again, the first strong feature is assignable as mainly the \( ^2\Sigma^+ \) \( \tilde{A} \leftarrow \tilde{X} \) bend, see Fig. 9, although it is almost isoenergetic with the first stretch mode \( (\nu_i=1) \), which is calculated to have only \(~20\%\) of the intensity. This accounts for two of the features in the experimental spectrum at about this energy. It is possible that the weaker experimental feature to the red may be a hot band, since NO–Xe would be the most difficult to cool in a supersonic expansion.

Interestingly, a strong band at 44 211 cm\(^{-1}\) appears only in the \( J=2 \) calculations, suggesting that it most likely arises from \( n=2, K=2 \) (a component of the first overtone of the \( \Pi \) bend, which has \( \Delta \) vibrational symmetry)—a fact confirmed by the contours of the corresponding wavefunction. Again, we note that the calculated spectrum terminates at slightly lower wavenumbers than the experimental one, consistent with the fact that the calculated dissociation energy is 8\% too low (Table II). Higher energy levels become very mixed as can be seen in the wavefunctions shown for selected features in Fig. 9.

As with NO–Kr, we conclude that the complexity of the bound states necessitates, as a first step in the assignment of this spectrum, determination of an accurate PES followed by calculation of the energies and wavefunctions of the bound states.

FIG. 7. (Color online) Calculated \( \tilde{A} \leftarrow \tilde{X} \) spectrum of NO(\( ^2\Sigma^+ \))–Kr, with vibrational wavefunction contours indicated for selected features. The stick spectrum from Fig. 6 is reproduced. For all of the wavefunction contours the ordinate is the Jacobi distance \( R \) in \( a_0 \), and the abscissa is the Jacobi angle in degrees. The three displayed wavefunctions with the lowest energies are the ground level, the first intermolecular stretch, and the first \( \Pi \) bending mode, respectively; see text for details. Features to higher energies become mixed, and identification of the number of intermolecular stretch and bend quanta becomes progressively difficult.

FIG. 8. Comparison between simulated (lower trace, stick spectrum) and experimental (Ref. 4; upper trace) \( \tilde{A} \leftarrow \tilde{X} \) spectra of NO(\( ^2\Sigma^+ \))–Xe.
3. NO–Ar

The calculated spectrum, determined with the unscaled \textit{ab initio} PES, is shown in Fig. 10 and compared to experiment. The agreement is not as good as in the cases of NO–Kr and NO–Xe. The qualitative features are the same though, namely, a strong origin, weaker features at low energies, and then strong features toward the high energy end of the spectrum. However, the simulated spectra show fewer features to higher energies than seen experimentally. As shown in Fig. 11, agreement with experiment is better with the scaled PES.

We discussed in Sec. I how, to date, there has been a fairly consistent interpretation of the NO(A $^2\Sigma^+$)–Xe spectra.\textsuperscript{2,5,14,15} However, there has been no explanation of the weak features appearing above the origin and of the apparently disproportionate magnitude of the stretch vibration compared to the dissociation energy. As seen in Fig. 12, the calculated vibrational wavefunctions reveal stark differences when compared to the previous assignments.

The intermolecular stretch vibration is now seen to be very low in energy, $\sim 12 \text{ cm}^{-1}$ (it appears in spectrum at $\sim 44 253 \text{ cm}^{-1}$). Comparing with the contour plot of the NO–Ar PES (Fig. 3), we see that the corresponding wavefunction extends to large angles, where the PES has only a low barrier, with a saddle point at $\sim 38^\circ$. This suggests that the stretch is mixing with the $\Sigma$ bend. This is confirmed by the contour plot of the next bend-stretch wavefunction, which has a node in the angular direction and an apparent node in the stretch direction (suggesting that this is mainly the $\Sigma$ bend but mixed with the intermolecular stretch).

There is a calculated vibration at 44 258.2 cm$^{-1}$ which is straightforwardly identifiable as the $\Pi$ bend, but its intensity is very weak (in contrast to the situations for Rg=Kr and Xe). There are then a number of vibrations which appear to be mixtures of the overtones of the intermolecular stretch and $\Sigma$ bend. The most intense vibrations at higher energy have very mixed bend and stretch character, as can be seen in Fig. 12.

FIG. 9. (Color online) Calculated $\bar{A} \rightarrow \bar{X}$ spectrum of NO(A $^2\Sigma^+$)–Xe, with vibrational wavefunction contours displayed for selected features. The stick diagram from Fig. 8 is reproduced. For all of the wavefunction contours, the ordinate is the Jacobi distance $R$ in a$_0$, and the abscissa is the Jacobi angle in degrees. The three displayed wavefunctions with the lowest energies are the ground level, the first $\Pi$ bending mode, and the first intermolecular stretch, respectively (with the latter two being almost isoenergetic); see text for details. In the upper spectrum, the zero-point level may be easily seen; the bottom trace shows that the first two features are due to the $\Sigma$ bending mode and the intermolecular stretch, which are mixed with each other. Features to higher energies become mixed, and identification of the number of intermolecular stretch and bend quanta becomes progressively difficult.

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Even though we have scaled the surface to match the previously reported dissociation energy, the experimental features extend to higher wavenumbers than the last calculated feature. These high-wavenumber experimental features have been noted and discussed previously, and were suggested as arising from quasibound levels lying above the dissociation asymptote. Also, it is possible that a more sophisticated scaling of the radial and angular dependences of the PES would improve the agreement with experiment, but this is beyond the scope of the present work.

The present study therefore implies that all previous assignments of the features in the NO–Ar spectrum are incorrect: the weak features, seen clearly only in Ref. 5, are now understood to arise from fundamentals, combination bands, and overtones of stretch and bend vibrations, with some stretch/bend mixing. The stronger features to higher energy arise from highly mixed energy levels which have larger overlap with the state vibrational wavefunction. The “anomalously high” stretch vibrational frequency assignment of the features. For the heavier two species the anisotropy is even more pronounced.

Previous assignments of the high energy regions have been based on application of either the model of Fawzy and Hougen or the model of Dubernet et al. As noted earlier herein, the model of Fawzy and Hougen assumes a semirigid molecule. Both models attempt to correlate the observed spectra to the angular anisotropy of the NO–Rg potential, which is expressed as a standard expansion in Legendre polynomials. Our calculated bend-stretch wavefunctions show that by contrast the NO(A $^2\Sigma^+$)–Ar complex is quite floppy.

McQuaid et al. applied the model of Dubernet et al., which depends on assigning values of several constants which define the lowest order anisotropies of the NO–Ar PES. As has been discussed in Sec. I, it was impossible to find a single set of constants which allowed a fit to all regions of the observed spectrum. In Sec. III D 4 we shall show that the assumption of a fixed anisotropy, independent of R, is overly simplistic.

4. Anisotropy

In Figs. 13–15, we show plots of the variation with R of the Legendre components of the angular anisotropy, V$_{l0}$(l=0–5), for NO(A $^2\Sigma^+$)–Ar, Kr, and Xe, respectively. For NO(A $^2\Sigma^+$)–Ar we see that for stretch levels which are localized close to the bottom of the well, both V$_{10}$ and V$_{20}$ are large and negative and vary strongly with R. However, for levels which sample larger intermolecular separations (>10a$_0$), the effective value V$_{10}$ becomes close to zero, and V$_{20}$ becomes much smaller, somewhat consistent with the most recent work. However, in some ways, comparison with the previous determinations of the V$_{l0}$ terms is pointless, since in both cases the determination relied on an incorrect assignment of the features. For the heavier two species the anisotropy is even more pronounced.

The PES contours in Figs. 1–5 indicate that the interaction in these species changes from largely isotropic in NO(A)–He to significantly anisotropic in NO(A)–Xe. This increased anisotropy both leads to a stronger interaction as well as forces the complex into a linear geometry. This is in line with the suggestions made in Refs. 4 and 10. For both He and Ne, there appears to be a balance between repulsive interactions of the 3s Rydberg electron and the electrons on the Rg atom.

For the heavier species, however, the significant dipole moment of NO(A $^2\Sigma^+$) [~1.1 D (Ref. 47)] interacts more strongly with more polarizable Rg atom, and this might be hypothesized as leading to the linear geometry. Clearly this interpretation is simplistic and ignores the quadrupolar, dipolar, and dispersive interactions in these species, and their magnitudes are all likely significant. A further comment is that the larger electron affinity of O leads the Rg atom to prefer the N end of the molecule, where the electron density is less.
FIG. 12. (Color online) Upper panel: calculated $\tilde{A} - \tilde{X}$ spectrum of NO($A^2\Sigma^+$)–Ar, determined using the scaled PES, with vibrational wavefunction contours displayed for selected features. The stick diagram from Fig. 11 is reproduced. For all of the wavefunction contours, the ordinate is the Jacobi distance $R$ in $\text{a}_0$, and the abscissa is the Jacobi angle in degrees. For all of the wavefunction contours, the ordinate is the Jacobi distance $R$ length in $\text{a}_0$, and the abscissa is the Jacobi angle in degrees. Lower panel: Enlarged view of the weaker features in the center of the spectrum in the lower portion of the figure. In the upper spectrum, the zero-point level may be easily seen; the bottom trace shows that the first two features are due to the $\Sigma$ bending mode and the intermolecular stretch, which are mixed with each other. Features to higher energies become mixed, and identifying intermolecular stretch and bend quanta becomes progressively difficult.
IV. CONCLUSIONS

In the present work we have presented, for the first time, the first principles calculation of electronic absorption spectra for the $\tilde{A} \rightarrow \tilde{X}$ transition for NO–Rg binary complexes (Rg=Ar–Xe). For the two heavier species the agreement is better than qualitative. Good agreement for NO–Ar was achieved only after a global scaling of the PES. The assignments of the spectra are far from intuitive, with previous attempts for NO–Kr being seen to be rather far from the mark. For NO–Xe, for the first time, the complexity of the spectrum can be understood.

Previous assignments of the NO–Ar (Refs. 5, 14–16, and 20) spectra were reasonable, but with some major discrepancies. We now see that these discrepancies arose because the previous assignments were incorrect. The present calculations, while not providing a complete 1:1 assignment of all features, do suggest that by separately scaling radial and angular contributions to the PES one could obtain a near-quantitative fit of the positions of the major features. By iteration the whole spectrum could then be completely assigned. This should be the focus of future work.

As mentioned above, for NO–Ar a global scaling led to much better agreement with experiment. However, there are still features in the predicted spectrum which lie above the currently accepted experimentally derived dissociation energy.\textsuperscript{15} At the present time, the nature of the high-lying features in the $\tilde{A} \rightarrow \tilde{X}$ spectrum of NO–Ar is still not understood. We note that recently anomalous photodissociation behavior of NO(A)–Ar near threshold has been reported, where it was suggested that this was attributable to thermal population of the $\tilde{X}$ state.\textsuperscript{48}

The calculated dissociation energies (Table I) lie close to the extrapolated basis set limits. However, these convergence tests were carried out only at the minima of the PESs. The unscaled NO(A)–Ar surface (despite the apparently good $D_e$ value in comparison to the complete basis set extrapolated value) gives the worst agreement (of the three heavier Rg atoms) between the simulated and experimental spectra. Further work is needed to determine what methodologies will guarantee “spectroscopic” accuracy in all regions of the PES, although we appear to be close for NO–Kr and (to a slightly lesser extent) for NO–Xe.

An approach similar to that reported here will be the only way to tackle the interaction of NO(A) with diatomic targets, such as NO–N$_2$ (Ref. 49) and NO–CO,\textsuperscript{50} where \textit{ab initio} identification of potential energy minima has been carried out or, eventually, for the interaction of NO with CH$_4$, where the vibrational energy level structure has recently been examined.\textsuperscript{51} The latter system has been considered in some detail but has the extra challenge of being a complex whose ground state has Jahn–Teller character.\textsuperscript{51,52} Higher electronic states of the NO–Rg (Refs. 1, 9, and 53) complexes could also be future targets of study.

Figures 13–15 show that the anisotropic terms in the NO(A)–Rg PESs are far from negligible in regions near the equilibrium. Consequently, it is clear that the isotropic empirical potentials that have been used in MD simulations of NO-doped Rg matrices,\textsuperscript{26–29} cannot be expected to represent...
accurately the interactions that occur upon photoexcitation. It would be interesting to perform new MD simulations taking into account the anisotropy of the NO–Rg interaction.

ACKNOWLEDGMENTS

T.G.W. is grateful for the provision of computer time from the EPSRC-GB under the auspices of the NSCCS. R.H.-L. would like to acknowledge support from Conacyt under Grant Nos. 44117-F and SESIC-SEP-FOMES2000 for unlimited time on the IBM p690 supercomputer at UAEM. M.H.A. wishes to thank the U.S. National Science Foundation for partial support under Grant No. CHE-0848110. He would also like to thank David King for conversations, many years ago, which stimulated his interest in the interaction of NO(A) with noble gases.