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The binding energies of NO–Rg (Rg = He, Ne, Ar) determined by velocity map imaging

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We report velocity map imaging measurements of the binding energies, D_0, of NO–Rg (Rg = He, Ne, Ar) complexes. The $\tilde{X}$ state binding energies determined are 3.0 ± 1.8, 28.6 ± 1.7, and 93.5 ± 0.9 cm^{-1} for NO–He, –Ne, and –Ar, respectively. These values compare reasonably well with *ab initio* calculations. Because the $\tilde{A}$–$\tilde{X}$ transitions were unable to be observed for NO–He and NO–Ne, values for the binding energies in the $\tilde{A}$ state of these complexes have not been determined. Based on our $\tilde{X}$ state value and the reported $\tilde{A}$–$\tilde{X}$ origin band position, the $\tilde{A}$ state binding energy for NO–Ar was determined to be 50.6 ± 0.9 cm^{-1}. © *2011 American Institute of Physics*. [doi:10.1063/1.3601924]

I. INTRODUCTION

Because of their experimental accessibility, the NO–Rg complexes have come to serve as benchmarks for dispersion interactions involving open shell-closed shell systems.[1,2] The small number of electrons associated with He and Ne makes the dispersion interactions in the NO–He and NO–Ne systems particularly weak, especially in the case of He, and sophisticated calculations are required for accuracy. These systems thus provide excellent test cases for high level calculations. *Ab initio* calculations have been reported for both the $\tilde{X}$ and $\tilde{A}$ states of the NO–Rg complexes. These were summarised by Kim and Meyer in their 2001 review of the multiphoton spectroscopy of the NO–Rg complexes.[2] A recent overview is given by Klos *et al.*[3] Comparison with experiment is crucial for establishing the suitability of different *ab initio* approaches. However, experimental measurements of the dissociation energies have not been reported for NO–He, –Ne and the value for NO–Ar has recently been called into question.[4]

Experimental values for the $\tilde{X}$ and $\tilde{A}$ states binding energies, D_0, of NO–Ar,[5] NO–Kr (Refs. 6 and 7), and NO–Xe (Refs. 7 and 8) were reported some time ago. The term binding energy is used throughout this paper to refer to D_0, the dissociation energy measured from the zero point energy, appropriate to experiment. Where the energy is measured from the minimum of the potential energy surface, the symbol D_e is used. D_0^0 refers to the ground electronic state, $\tilde{X}$, while D_0^1 refers to the first excited electronic state, $\tilde{A}$. In the case of NO–Ar, recent work by Roeterdink *et al.*[4] has cast doubt on the accepted values of 88 and 44 cm^{-1} for D_0^0 and D_0^1, respectively,[5] with the authors suggesting that excitation from low-lying states has compromised previous measurements. They do not give a value for the binding energy; however, they report an appearance energy for the products from which a binding energy can be determined. Their results imply an almost 8 cm^{-1} increase in both D_0^0 and D_0^1, with the revised values being 96 and 52 cm^{-1}, respectively. It is not known whether a similar problem affects the reported NO–Kr and –Xe values. Additionally, several groups have determined, via *ab initio* computation, D_0 values for these systems. In the case of NO–Ar, an $\tilde{X}$ state value of 83.16 cm^{-1} for D_0 was determined by Alexander using coupled-cluster single double triple CCSD(T) calculations.[9] Subsequently, Sumiyoshi and Endo,[10] using RCCSD(T) level calculations and an aug-cc-pYTZ + bf basis set, determined a value of 87.6 cm^{-1} when their surface was adjusted via a least squares fit to observed microwave transitions. Klos *et al.*,[3] using the same level of theory, obtained a potential energy surface for the $\tilde{A}$ state. These authors found it necessary to scale the surface to match the experimental D_0^1 value in order to provide an improved comparison with the observed $\tilde{A} \leftarrow \tilde{X}$ spectrum.

In contrast, the NO–He and NO–Ne $\tilde{X}$ and $\tilde{A}$ state binding energies have not been experimentally measured. Early molecular beam scattering data suggested a NO–Ne well depth (D_e) of 50 cm^{-1} in the $\tilde{X}$ state,[11] while subsequent ion-current spectra by Sato *et al.*[12] gave an upper limit of D_0^0 of 100 cm^{-1}. Alexander *et al.*[13] determined a RCCSD(T) level potential energy surface to give $D_0^0 = 29.4\ \text{cm}^{-1}$ when simulating the $v = 0$–2 infrared spectrum of the complex for comparison with the experimental measurements of Kim *et al.*[14] Klos *et al.*[3] report that they have undertaken RCCSD(T) level calculations that predict a D_0^0 value of 35 cm^{-1}. Recently, Sumiyoshi and Endo[15] determined an *ab initio* potential energy surface using RCCSD(T) level calculations. The surface was adjusted using a least squares fitting process to improve the match with the Fourier transform microwave spectrum. The authors determined the binding energy, D_0^0, to be 33.7 cm^{-1} for the resulting surface.

While several excited electronic states of NO–Ne have been extensively studied through multiphoton excitation,[16–18] the $\tilde{A} \leftarrow \tilde{X}$ band origin has not been observed despite several attempts.[7,17–21] *Ab initio* studies predict an extremely shallow potential, with a D_0^1 as low as 2 cm^{-1}.[3,21,22] Very small Franck-Condon factors are predicted for excitation from the

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zero point vibrational level in $\tilde{X}$ to bound levels in $\tilde{A}$.[21] These results explain the difficulty of obtaining spectra attributable to the $\tilde{A}$–$\tilde{X}$ transition of the complex.

Data for NO–He are particularly sparse. Parsons *et al.*[23] reported seeing NO products from NO–He dissociation in their velocity map imaging (VMI) study of NO–Ar dissociation, suggesting that the complex is bound. There have been no reports of spectra arising from the NO–He complex to date. *Ab initio* calculations predict a binding energy, D_0^0, of 7 cm^{-1} in the $\tilde{X}$ state[24] while that of the $\tilde{A}$ state is predicted to be less than a wavenumber.[3]

To date then, D_0^0 values for the NO–He and NO–Ne complexes have not been determined experimentally, although *ab initio* calculations have predicted values for these systems. The accepted value for NO–Ar (Ref. 5) is in some doubt, with the most recent experiments[4] suggesting that it has been underestimated due to excitation from thermally populated rotational levels. We here provide experimental measurements of the dissociation energies for these three systems.

II. EXPERIMENTAL DETAILS

The dissociation energies are measured using velocity map imaging (VMI). The apparatus has been described in detail as has the analysis of the images to produce translational energy distributions.[25,26] Those details pertinent to the present series of experiments are as follows. Gas mixtures of 5% NO in the rare gas were used to create the NO–Rg complexes via supersonic expansion. The complexes were photodissociated following excitation via the $\tilde{A}\leftarrow\tilde{X}$ transition. A key measurable for determining the dissociation energies in these experiments is the photon energy and hence, an accurate determination of the photolysis wavelength is critical. This was measured using a commercial wavemeter (Bristol 821). The NO *A* products produced were probed using one colour resonance enhanced multiphoton ionisation (1C-REMPI) via the $E\leftarrow A$ NO transition, producing NO^+ ions that are detected using VMI.[27] The momentum change in NO on loss of the electron during ionisation is negligible and hence, the detected NO^+ ions reflect the NO (*A*) velocity. The photolysis and probe laser systems are those previously described.[25] The probe laser was delayed by between 120 and 150 ns following the photolysis pulse to separate the probe-generated signal from the background signal arising from NO products ionised by the photolysis pulse.

III. RESULTS

The binding energies were determined using two, related techniques that rely on measuring the translational energy of NO *A* fragments in particular *N* states following photodissociation of NO–Rg $\tilde{A}$. *N* is the sum of the molecular rotational angular momentum and the electron orbital angular momentum. The photon energy, $E_{Excitation}$, provides energy in excess of that required to dissociate the complex, $E_{Dissociation}$, and this excess energy is partitioned amongst the products rotational (NO only) and translational (NO and Rg) energies

$$E_{Excitation} - E_{Dissociation} = E^{\text{NO}}_{Rotation} + E_{Translation}. \tag{1}$$

Here, $E_{Translation}$ refers to the total translational energy, which is the sum of the NO and Rg translational energies. Since the NO rotational energy is quantised, $E_{Translation}$ takes a single value for a particular NO *N* product state. Conservation of momentum enables $E_{Translation}$ to be expressed in terms of the NO translational energy

$$E_{Translation} = \frac{m_{\text{NO}} + m_{\text{Rg}}}{m_{\text{Rg}}} E^{\text{NO}}_{Translation}$$

and thus

$$E_{Excitation} = E_{Dissociation} + B'N(N+1) + \frac{m_{\text{NO}} + m_{\text{Rg}}}{m_{\text{Rg}}} E^{\text{NO}}_{Translation}, \tag{2}$$

where we have explicitly expressed the NO rotational energy in terms of the rotational constant, B', in the *A* state, 1.9965 cm^{-1},[28] and quantum number, *N*.

The first method (hereafter referred to as Method 1) involves measuring the NO translational energy for a given *N* state as the excitation energy is varied while the second, Method 2, involves measuring the NO translational energy in each *N* state at fixed excitation energy, as discussed below.

In our application of Method 1, NO *A* fragments are monitored in $N = 0$ by probing via the $R(0)$ band of the *E*–*A* 0–0 transition. Thus $E^{\text{NO}}_{Rotation} = 0$ and Eq. (2) becomes

$$E_{Excitation} = E_{Dissociation} + \frac{m_{\text{NO}} + m_{\text{Rg}}}{m_{\text{Rg}}} E^{\text{NO}}_{Translation}. \tag{3}$$

Thus, plotting excitation energy against the NO translational energy allows the dissociation energy to be extracted as the y-intercept. Determining the NO translational energy from the measured velocity map image requires the pixel positions to be calibrated with energy; however, this step can be obviated as follows. In the inverse Abel transformed image, the NO velocity is proportional to the radius from the image centre, *R*, and thus $E^{\text{NO}}_{Translation}$ is given by

$$E^{\text{NO}}_{Translation} = cR^2, \tag{4}$$

where *c* is a constant. Equation (3) thus simplifies to

$$E_{Excitation} = E_{Dissociation} + c'R^2, \tag{5}$$

where c' is a constant. The units used for *R* are arbitrary. Given the measurement is made on a CCD camera, *R* is most conveniently expressed in pixels and this is the unit we use. While in principle a single velocity, and hence radius, is expected, in practice the peak is broadened by resolution limitations and the radius of the centre of the peak is the value of *R* determined. A plot of $E_{Excitation}$ *vs.* R^2 yields $E_{Dissociation}$ as the y-intercept.

During the experiment, velocity map images of NO *A* in $N = 0$ are acquired following excitation of NO–Rg over a range of photolysis energies. A typical image is shown in Fig. 1. The images are inverse Abel transformed and converted to radial plots. Each radial plot is converted to a distribution in R^2. This distribution is fitted to a Gaussian whose

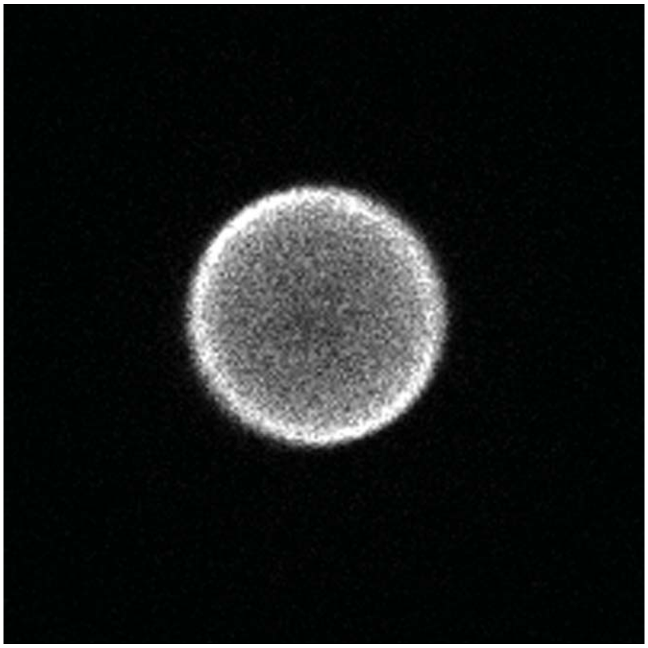

FIG. 1. A VMI image typical of those observed for NO A product in a single N state following NO–Rg $\tilde{A}$ dissociation. The image shown is of the NO A $N = 0$ product produced in the dissociation of NO–Ne at $E_{Excitation} = 44\,394.0$ cm^{-1}.

position is the value of R^2 at the excitation energy of the experiment. Figure 2 shows the distribution and fit for the Fig. 1 image. The plots of $E_{Excitation}$ *vs.* R^2 for the NO–He, –Ne, and –Ar complexes are shown in Fig. 3. The uncertainties in laser position and image radius are less than the size of the circle used to identify the experimental points. $E_{Dissociation}$ for each of the three complexes is given by the intercept of the corresponding plot.

From $E_{Dissociation}$ and the NO A–X energy separation, ν_{00}, the $\tilde{X}$ state binding energy for the complex is extracted as

$$D_0^0(\tilde{X}) = E_{Dissociation} - \nu_{00}.$$

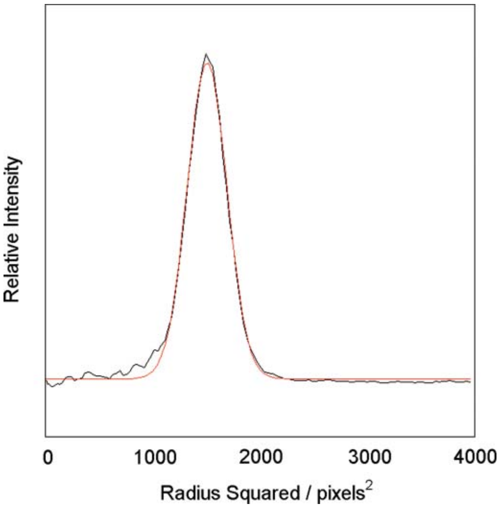

FIG. 2. The NO translational energy distribution as a function of R^2 and the Gaussian fit to this distribution for the image shown in Fig. 1.

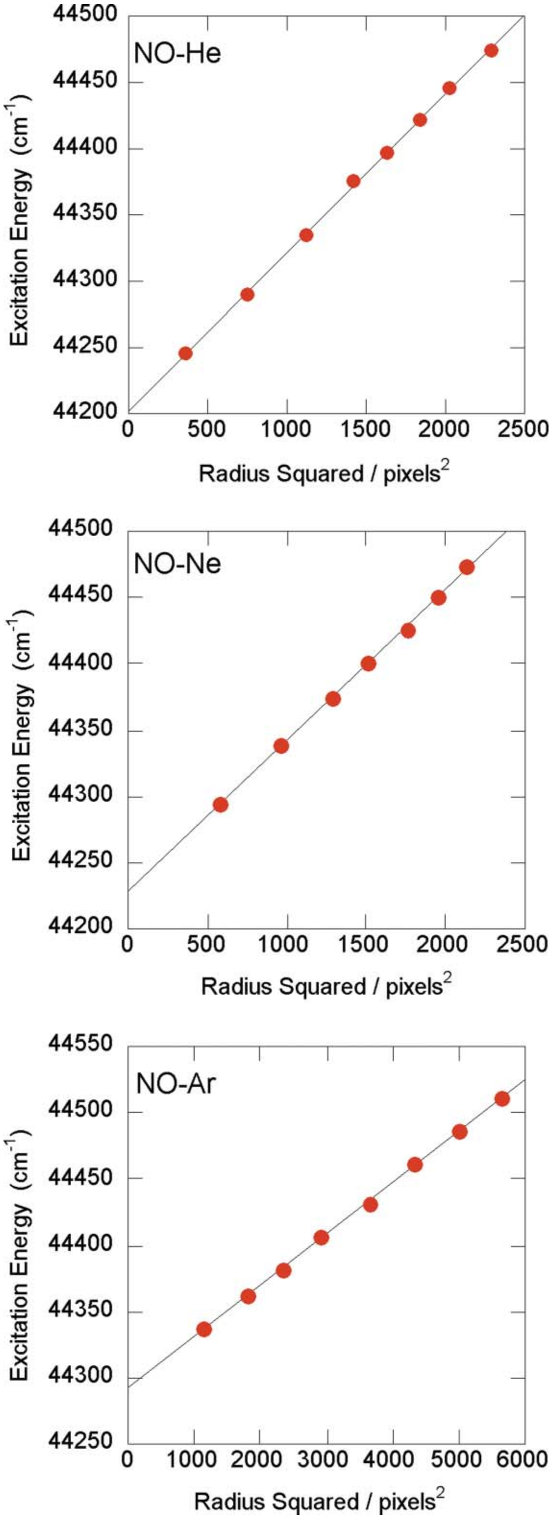

FIG. 3. Plots of $E_{Excitation}$ *vs.* R^2 for NO–He (upper), NO–Ne (middle), and NO–Ar (lower). $E_{Dissociation}$ is extracted from the plots as the y-intercept.

Interestingly, different authors have used different values for $\nu_{00,}$ which complicates comparisons of the reported NO–Ar binding energies. Tsuji *et al.*[5] use $\nu_{00} = 44\,198.9$ cm^{-1} based on the spectroscopic study by Engelman *et al.*, who report the $Q_{11}(0.5)$ transition at $44\,198.9$ cm^{-1}.[29] This provides a small (0.3 cm^{-1}) shift from the earlier value of $44\,199.2$ cm^{-1} reported by Herzberg in his compilation of

TABLE I. Experimentally determined dissociation and binding energies, D_0, for the NO–He, –Ne, and –Ar complexes. D_0^0 refers to the $\tilde{X}$ state while D_0^1 refers to the $\tilde{A}$ state.

		Complex		
		NO–He	NO–Ne	NO–Ar
Method 1	$E_{Dissociation}/\text{cm}^{-1}$	44 202.2 ± 1.8	44 228.4 ± 2.5	44 292.3 ± 1.2
	D_0^0/cm^{-1}	3.3 ± 1.8	29.5 ± 2.5	93.4 ± 1.2
	D_0^1/cm^{-1}	…	…	50.2 ± 1.2
Method 2	$E_{Dissociation}/\text{cm}^{-1}$	…	44 227.1 ± 2.4	44 293.4 ± 1.5
	D_0^0/cm^{-1}	…	28.2 ± 2.4	94.5 ± 1.5
	D_0^1/cm^{-1}	…	…	51. 3 ± 1.5
Weighted average[a]	$E_{Dissociation}/\text{cm}^{-1}$	44 202.2 ± 1.8	44 227.7 ± 1.7	44 292.7 ± 0.9
	D_0^0/cm^{-1}	3.3 ± 1.8	28.9 ± 1.7	93.8 ± 0.9
	D_0^1/cm^{-1}	…	…	50.6 ± 0.9

[a] Determined as described in the text.

diatomic molecule spectroscopic constants.[30] Parsons *et al.* use a value of 44 200.7 cm^{-1}, simply noting this as the "well-known value". The NIST web site,[28] which collates spectroscopic constants, provides a value of 44 200.2 cm^{-1} to the hypothetical $J'' = 0$ level in the $\tilde{X}\ ^2\Pi_{1/2}$ state. ν_{00} is less than this value by the energy of the $J'' = 1/2$ level, the lowest level accessible. Our binding energies are determined using the value $\nu_{00} = 44\,198.9$ cm^{-1}, the same as that used by Tsuji *et al.*,[5] as this appears to be the most reliable experimental value available. The binding energies determined are listed in Table I.

Method 2 was applied as follows. Using Eq. (4), Eq. (2) can be rearranged as

$$R^2 = c''(E_{Excitation} - E_{Dissociation}) - c''B'N(N+1), \tag{6}$$

where c'' is a constant. By plotting the square of the radius of the ring observed for each NO N product as a function of $N(N+1)$, we obtain a linear plot whose intercept allows $E_{Dissociation}$ to be extracted once c'' is determined from the slope.

As for Method 1, images of the NO N products were obtained using excitation through the R branch, which allows all N to be observed. Unfortunately, this method proved unsuitable in the case of He because (i) there are a limited number of N states populated and these are skewed to low N, and (ii) with He being of low mass the velocity of NO is low and the small change in NO translational energy, and hence velocity, between the low N states observed leads to rings whose radii do not vary significantly. These effects conspire to cause the plots for NO–He to have too large an uncertainty in the slope and intercept for extraction of an accurate binding energy for this partner. The plots for Ne and Ar are shown in Fig. 4. As for Fig. 3, the measurement uncertainties are contained within the experimental data points.

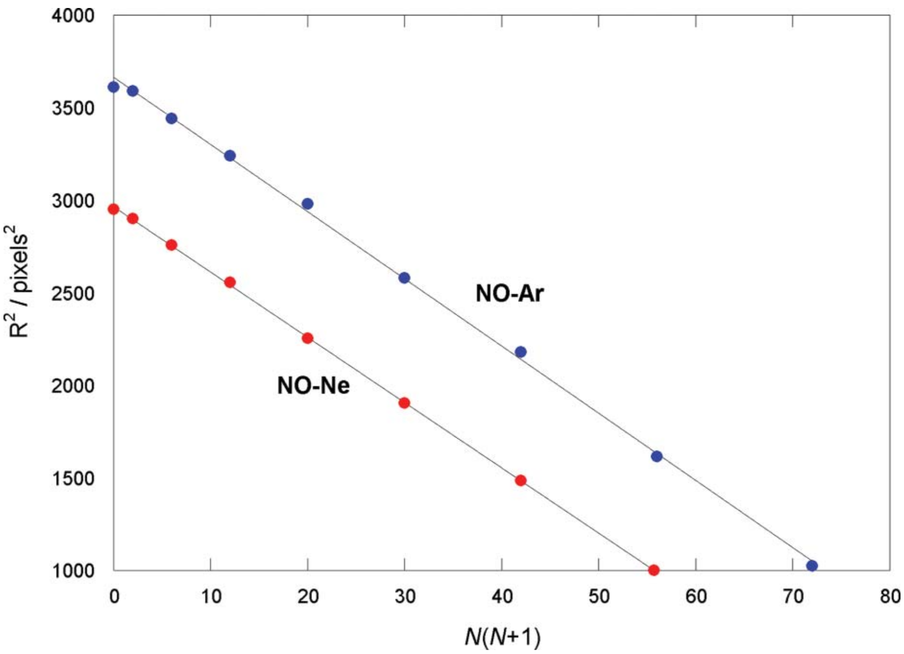

FIG. 4. Plots of R^2 *vs.* $N(N+1)$ for NO–Ne and NO–Ar at $E_{Excitation} = 44\,394.0$ cm^{-1} and 44 481.7 cm^{-1}, respectively.

TABLE II. Dissociation energy measurements for the $\tilde{A}\leftarrow\tilde{X}$ transition of NO–Ar, the $\tilde{X}$ state binding energy (D_0^0) values reported by the authors, and the corresponding D_0^0 based on $\nu_{00} = 44\,198.9$ cm^{-1}.

Authors	Dissociation energy/cm^{-1}	D_0^0 reported/cm^{-1}	D_0^0 determined using $\nu_{00} = 44\,198.9$ cm^{-1}
Tsuji *et al.* (Ref. 5)	44 286.7 ± 0.3	87.8 ± 0.3	87.8 ± 0.3
Parsons *et al.* (Ref. 23)	44 291 ± 2	90 ± 2	92 ± 2
Roeterdink *et al.*(Ref. 4)	44 294.3 ± 1.4[a]	Not reported	95.4 ± 1.4
Holmes-Ross and Lawrance (Ref. 25)	44 287.0 ± 0.5	87.8 ± 0.5	88.1 ± 0.5
Present work	44 292.7 ± 0.9	93.8 ± 0.9	93.8 ± 0.9

[a] The authors report an appearance energy for the products rather than a dissociation energy.

The dissociation energies determined from these data are translated to binding energies as described above for Method 1. The values are shown in Table I. Our final values and errors, where the error represents three standard deviations, are also included in this table. These values were determined using the weighted average of Methods 1 and 2, a calculation which determines the mean of two values based on the uncertainty in each value.[31] Method 1 relies on measuring changes in the translational energy of the products arising from changes in the photolysis photon energy while Method 2 relies on measuring the changes in the translational energy of the products associated with changes in the NO rotational energy at fixed photolysis photon energy. By using both Methods, we are able to ensure consistency in the determined value. The values determined by the two Methods are the same within experimental uncertainty.

The $\tilde{A}$ state binding energy, D_0^1, can also be extracted if the $\tilde{A}$–$\tilde{X}$ energy separation is known for the complex. For NO–He and NO–Ne the values are not known. We tried to determine them by measuring $\tilde{A} \leftarrow \tilde{X}$ spectra for the NO–He and NO–Ne complexes, however, like those who have trodden this path before us[7,17–21] we were unable to observe signal attributable to the parent ions. We are thus unable to provide binding energies for the $\tilde{A}$ state of the NO–He and NO–Ne complexes. In the case of NO–Ar, the $\tilde{A}$–$\tilde{X}$ separation is 44 242.1 cm^{-1}.[32] The $\tilde{A}$ state binding energy determined using this and our measured $E_{Dissociation}$ is 50.6 ± 1.2 cm^{-1}.

IV. DISCUSSION

Consistent with the earlier comment by Parsons *et al.*,[23] dissociation products are observed for NO–He, demonstrating that the $\tilde{X}$ state is bound. We have determined D_0^0 to be 3.3 ± 1.8 cm^{-1}, revealing that the potential well is quite shallow. There are no previous experimental values with which to compare our value. The most recent *ab initio* calculations, which were performed at the RCCSD(T)/aug-cc-pVTZ + bf level of theory, predict $D_0^0 = 7$ cm^{-1},[24] in reasonable agreement.

Here, D_0^0 for the NO–Ne complex was measured to be 28.6 ± 1.7 cm^{-1}. As for He, there are no experimental values with which to compare; however, there have been a number of *ab initio* calculations reported, including very recent work. Sumiyoshi and Endo,[15] using calculations at the [UCCSD(T)-FIZ(b)] level of theory and an aug-cc-pVQZ basis set, determined a value of 33.7 cm^{-1} for D_0^0 through a least squares fitting of their calculated potential energy surface to microwave spectral data. Earlier calculations by Alexander[13] reported a D_0^0 value of 29.4 cm^{-1}, determined using RCCSD(T)/aug-cc-PVQZ, while Klos *et al.* report[3] that they have determined a value of 35 cm^{-1}. Our value is at the lower end of the range of *ab initio* values reported. We were unable to detect the $\tilde{A}\leftarrow\tilde{X}$ transition in NO–He or NO–Ne and so the $\tilde{A}$ state binding energies for these two complexes remain undetermined.

As noted earlier in Sec. III, different NO *A*–*X* ν_{00} values have been used to extract D_0 values from the measured NO–Ar dissociation energies. We have used the dissociation energies reported by previous authors and the ν_{00} value of 44 198.9 cm^{-1} determined by Engleman *et al.*,[29] as used in the present work, to provide a self-consistent tabulation of D_0^0 values. These are given in Table II.

The results of Roeterdink *et al.*[4] led these authors to suggest that earlier measurements of the dissociation energy of NO–Ar may have been confounded by excitation of population in thermally populated rotational levels. These earlier measurements reported a D_0^0 value of 88 cm^{-1}.[5] The dissociation energy reported by Parsons *et. al.*[23] suggests a value of 92 ± 2 cm^{-1} while the appearance energy for NO products reported by Roeterdink *et al.*[4] points to a value of 95.4 ± 1.4 cm^{-1}. Our value of 93.8 ± 0.9 cm^{-1} is within the uncertainties of both Parsons *et al.*[23] and Roeterdink *et al.*[4] We had made an earlier measurement of 88 cm^{-1},[25] consistent with the accepted value,[5] and since then have altered our apparatus, significantly increasing the nozzle to skimmer distance to sample the expansion after further collisional cooling, with the intent of producing a colder NO–Ar sample. Our new observation of a value closer to Roeterdink *et al.*[4] is thus consistent with their hypothesis that excitation from thermally populated levels has led to a lowering of the measured value relative to the true value. Wen and Meyer recently reported IR-UV constant photon energy sum spectra of NO–CH$_4$ complexes produced in a NO/CH$_4$/Ar expansion.[33] They note that their spectra show features consistent with the appearance threshold for NO–Ar dissociation products determined by Roeterdink *et al.*[4]

While the NO–Ar value reported here is quite close to that suggested by the results of Roeterdink *et al.*,[4] we cannot rule out a residual influence of the thermal population affecting our value. It should thus be regarded as a lower limit. In the cases of NO–He and NO–Ne, the values should also be viewed as lower limits since we cannot discount a similar influence from thermally populated levels for these two complexes. However, in this regard we note that the NO–Ne complex does not display the high energy "tails" seen in the NO translational distributions following dissociation of NO–Ar,[25,34] suggesting that the influence of higher energy, thermally populated levels is significantly diminished in this more shallowly bound system. In the case of NO–He, the well is so shallow that such a tail would be unobservable.

Comparison of NO–Ar D_0^0 values determined using high level *ab initio* calculations shows a tendency towards the value of 88 cm^{-1} reported by Tsuji *et al.*[5] Alexander's CCSD(T) (Ref. 9) potential gives a D_0^0 of 83.16 cm^{-1}. Most recently, Sumiyoshi and Endo report a potential energy surface obtained by least squares fitting an RCCSD(T) calculated surface to microwave spectral data.[10] This gives a slightly increased D_0^0 value of 87.6 cm^{-1}. Our value of 93.8 ± 0.9 cm^{-1} lies somewhat above these values. In the $\tilde{A}$ state, Klos *et al.*[3] scaled their surface to the 44 cm^{-1} binding energy of Tsuji *et al.*[5] and found that this improved comparisons with the observed absorption spectrum. It would be interesting to explore whether the comparison is improved by scaling the surface to our value of 50.6 ± 0.9 cm^{-1}.

V. CONCLUSIONS

We have undertaken velocity map imaging measurements of the binding energies of the three lowest mass NO–Rg (Rg = He, Ne, Ar) complexes. The $\tilde{X}$ state binding energies, D_0^0, determined are 3.3 ± 1.8, 28.9 ± 1.7, and 93.8 ± 0.9 cm^{-1} for NO–He, –Ne, and –Ar, respectively. These values compare reasonably well with *ab initio* calculations. The $\tilde{A} \leftarrow \tilde{X}$ transition could not be observed for NO–He and NO–Ne and consequently values for the binding energies in the $\tilde{A}$ states remain undetermined for these species. The $\tilde{A}$ state binding energy for NO–Ar, D_0^1, was determined to be 50.6 ± 0.9 cm^{-1}.

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