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Electron Affinity of NO[†]

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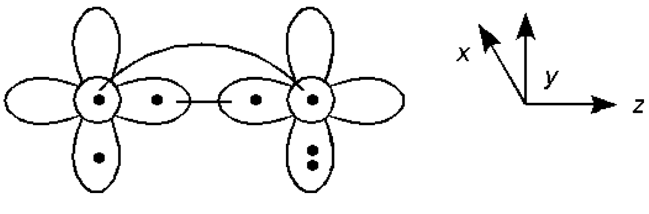
The electron affinity of NO has been measured to be 0.026 eV by laser photodetachment experiments. This low electron affinity (just 2.5 kJ/mol or 210 cm^{-1}) presents a computational challenge that requires careful attention to several aspects of the computational procedure required to predict the electron affinity of NO from first principles. We have used augmented correlation consistent basis sets with several coupled cluster methods to calculate the molecular energies, bond dissociation energies, bond lengths, vibrational frequencies, and potential energy curves for NO and NO$^-$. The electron affinity of NO, EA$_0$, using the CCSD(T) method and extrapolating to the complete basis set limit, is calculated to be 0.028 eV. The calculated bond dissociation energies, D_0, for NO and NO$^-$ are 622 and 487 kJ/mol, respectively, compared with experimental values of 626.8 and 487.8 kJ/mol. From the calculated potential energy curves for NO and NO$^-$ the vibrational wavefunctions were determined. The calculated vibrational wavefunctions predict Franck−Condon factor ratios in good agreement with the values determined in the photodetachment experiment.

Introduction

The electron affinity of NO was measured in an elegant experiment using laser photodetachment spectrometry of the gas-phase NO$^-$ anion and found to be 0.024 eV.[1] Later work using the same experimental technique, but with more sensitive and accurate instrumentation, provided a value of 0.026 ± 0.005 eV for the electron affinity of NO.[2] A more recent report of electron capture measurements gave a value for the ground-state adiabatic electron affinity of 0.084 ± 0.05 eV.[3] These authors suggest that the photodetachment spectroscopy results giving the electron affinity value of 0.026 eV arise from transitions from the $^1\Delta$ excited state of NO$^-$ rather than from the $^3\Sigma$ ground state. However, Ervin et al.[4] have sharply refuted the conclusion drawn by Chen and Chen[5] for O$_2^-$ from the electron capture measurements.

At the zeroth order of approximation, one might expect the electron affinity of NO to be close to zero. The electron affinity of the N atom is zero,[6] and that of the O atom is 1.461 eV.[7] The valence bond orbital structure of the neutral molecule NO can be written as



which in molecular orbital terms is $\pi_x^2\pi_y^2\pi_y^*$. The electron added to NO to form NO$^-$ is expected to go into an antibonding π_x^* orbital, giving a $^3\Sigma^-$ state, as is observed experimentally. Because the extra electron is in an antibonding orbital with substantial nitrogen character (the π_x orbital is strongly polarized toward oxygen), one would expect an electron affinity for NO close to zero as is indeed the case.

The calculation of accurate electron affinities for atoms and molecules has represented a significant challenge for computational chemistry and has received significant attention over the past three decades. The major issue has been the incorporation of electron correlation and the use of basis sets that provide a balanced description of the neutral molecule and anion. The major techniques for treating electron correlation in *ab initio* calculations have been configuration interaction, perturbation theory, and coupled cluster methods. Several comprehensive reviews have covered the developments in this effort.[8,9] Calculation of the electron affinity of NO, which is close to zero, has been of particular interest. Several calculations have reported values for the NO electron affinity NO that lie reasonably close to the experimental value.[10−13]

Computational Approach

We have undertaken a careful study of the electron affinity of NO following the road map described by Dunning, Peterson, and Van Mourik in their study of the electron affinities of O$_2$ and CN.[14] These authors showed that for these two species, which have moderate and large electron affinities (0.422 and 3.862 eV, respectively), the only electronic structure methods that provided a well balanced description of the neutral molecule and the anion were coupled cluster methods that explicitly included triple excitations, namely, CCSD(T) and CCSDT. Therefore, in this paper we focus only on coupled cluster methods but consider the CCSD[T][15] and CCSD-T[16] methods as well as the CCSD(T) method.

To calculate the equilibrium electron affinity of NO [EA$_e$(NO) is the difference in the energies of NO$^-$($^3\Sigma^-$) and NO($^2\Pi$) at their respective equilibrium bond distances (R_e)], we

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TABLE 1: Calculated Equilibrium Electron Affinities, EA_e (eV), for NO Using Several Coupled Cluster Methods and the Augmented (av*n*z) and Doubly Augmented (dav*n*z) Correlation Consistent Basis Sets

	CCSD		CCSD(T)		CCSD[T]		CCSD-T		
n	av*n*z	dav*n*z	av*n*z	dav*n*z	av*n*z	dav*n*z	av*n*z	dav*n*z	CCSDT[a] av*n*z
2	−0.0413	−0.0321	−0.0478	−0.0350	−0.0261	−0.0086	−0.0523	−0.0411	−0.0410
3	−0.0247	−0.0210	−0.0106	−0.0041	0.0042	0.0133	−0.0120	−0.0061	−0.0060
4	−0.0219	−0.0174	−0.0018	0.0039	0.0108	0.0184	−0.0022	0.0031	
5	−0.0177	−0.0142	0.0044	0.0086	0.0166	0.0220	0.0043	0.0082	
6	−0.0149	−0.0133	0.0080	0.0099	0.0202	0.0229	0.0080	0.0097	
CBS Limit		*−0.011 ± 0.002*		*0.010 ± 0.001*		*0.023 ± 0.002*		*0.010 ± 0.001*	

[a] Calculations performed at the RCCSD(T) equilibrium distances for the same basis set for NO and NO^- (see Table 2).

TABLE 2: Equilibrium Internuclear Distances (R_e), Vibrational Frequencies (ω_e), and Dissociation Energies (D_e) for NO and NO^- from Valence Electron CCSD(T) Calculations with the d-aug-cc-pV*n*Z Sets

	R_e (Å)		ω_e (cm^{-1})		$\omega_e x_e$ (cm^{-1})		D_e (kJ/mol)	
n	NO	NO^-	NO	NO^-	NO	NO^-	NO	NO^-
2	1.1686	1.2829	1876	1363			562	440
3	1.1569	1.2715	1889	1376			608	477
4	1.1530	1.2662	1907	1392			625	489
5	1.1520	1.2647	1911	1396			630	493
6	1.1517	1.2641	1912	1390			632	494
a			1906.8	1394.4	13.1	11		
exptl[b]	1.15077	1.258	1904.04	1363.3	14.1	8	626.8	487.8

[a] Values obtained from the Dunham analysis of the CCSD(T) calculated potential curve using the aug-cc-pV5Z set. [b] See ref 21. Bond energies given are for D_0.

used augmented correlation consistent basis set up to aug-cc-pV6Z and d-aug-cc-pV6Z[17] for the valence electron calculations. These basis sets have been shown to provide a balanced description of neutral molecules and anion (see, e.g., ref 14). The calculated EA_e's were then extrapolated to the complete basis set (CBS) limit using both simple exponential and (exponential, $1/n^3$) functions; the quoted Δ's represent the observed variations in the various extrapolations. Core−valence effects were taken into account by comparing valence electron and all electron calculations with the aug-cc-pwCV5Z sets.[18] Corrections for relativistic effects were estimated by calculating the spin orbit coupling in the $^2\Pi$ state and using the Douglass−Kroll method to estimate the scalar relativistic effect.

Optimum bond lengths were calculated by geometry optimization, and vibrational frequencies were determined. The vibrational frequencies were used to calculate EA_0, the equilibrium electron affinity corrected for zero point vibrational effects, as well as D_0.

Potential energy curves for both NO and NO^- were determined by calculating the energies at a series of bond lengths about the equilibrium internuclear distance using the aug-cc-pV5Z set and the CCSD(T) method. These points were fit to an eighth-order polynomial function as well as a Morse function. Dunham analysis of the polynomial fits of the potentials gave the values for ω_e and $\omega_e x_e$ also listed in Table 2. The vibrational wave functions were obtained from the polynomial functions using a MathCad program developed by Metz.[19] We then calculated Franck−Condon factors for photodetachment to compare with those from experiment.

All electronic structure calculations were carried out using MOLPRO,[20] except for the CCSDT calculations, which were performed with Aces II (Mainz-Austin-Budapest version).[22]

Results

Calculated Equilibrium Electron Affinities (EA_e). The calculated equilibrium electron affinities, EA_e, from CCSD, CCSD(T), CCSD[T], and CCSD-T and CCSDT calculations with the aug-cc-pV*n*Z and d-aug-cc-pV*n*Z sets, along with the extrapolated CBS limits for the doubly augmented sets, are listed in Table 1. (The calculated R_e's for NO and NO^- are reported in Table 2.) From the calculations with the d-aug-cc-pV*n*Z sets, the CBS limit for EA_e(NO) is estimated to be 0.010 ± 0.001 eV for both the CCSD(T) and CCSD-T methods, with the uncertainty coming from the extrapolation to the CBS limit. For the CCSD[T] method, the predicted CBS limit is over twice this value, namely, 0.023 ± 0.002 eV. The CCSDT calculations increase the CCSD(T) electron affinities, by 0.0043 eV for the aug-cc-pVTZ set, but the magnitude of the correction appears to be decreasing with increasing *n*.

The CCSD calculations do not predict NO^- to be bound relative to NO for any of the basis sets considered. (Note that the negative numbers for EA_e listed in Table 1 are nonzero only because of the lack of sufficiently diffuse functions in the basis set.) In fact, the extra electron in NO^- is predicted to be unbound even at the CBS limit for the CCSD method. NO^- is not bound relative to NO for the CCSD(T), CCSD-T and CCSDT methods for the double and triple-ζ basis sets, becoming progressively more bound with increasing *n*. In line with the larger EA_e predicted by the CCSD[T] calculations, the CCSD[T] calculations predict that NO^- is bound relative to NO for all of the sets beyond $n = 2$.

In the work on O_2 and CN,[14] it was found that doubly augmented basis sets were not required to properly describe O_2^- and CN^-. However, in NO^- the extra electron is so weakly bound that the more diffuse functions in the doubly augmented sets have a more pronounced effect; see Figure 1, in which the basis set error is plotted for CCSD(T) calculations with the singly and doubly augmented sets. The singly augmented sets significantly underestimate EA_e(NO), especially for the smaller basis sets. In addition, as can be seen in Figure 1, the electron affinities calculated with the doubly augmented sets converge more quickly and consistently to the CBS limit. This increases the reliability of the extrapolation to the CBS limit.

The core−valence correlation correction was calculated by comparing the CCSD(T) energy using the aug-cc-pwCV*n*Z basis set in an all-electron calculation with the CCSD(T) energy obtained using the same basis set in a valence-electron calculation. This correction decreases the EA_e(NO) by just 0.0001 eV, which is consistent with the very diffuse nature of charge distribution for the extra electron. The correction is larger for the smaller aug-cc-pwCV*n*Z sets, decreasing with increasing *n* beyond $n = 2$.

Because of the small size of the electron affinity of NO, we also investigated relativistic corrections to EA_e(NO), in particular, the spin orbit correction and scalar relativistic correction. The spin orbit energy of the $^2\Pi$ state must be taken into account because the coupled cluster calculations give the average of the energies of the $^2\Pi_{1/2}$ and the $^2\Pi_{3/2}$ states. The $^2\Pi_{1/2}$ state lies lower than the $^2\Pi_{3/2}$ state by a calculated spin orbit energy of

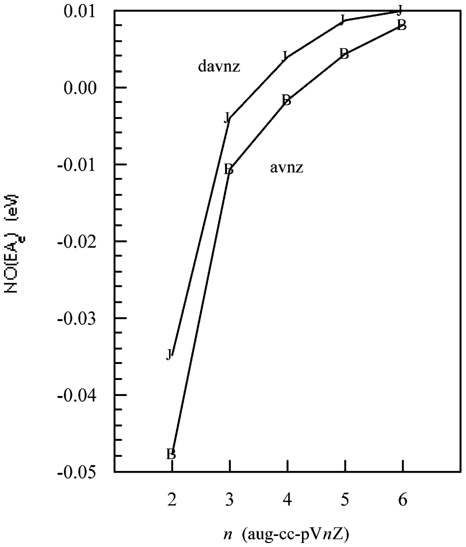

Figure 1. Basis set errors for the calculated equilibrium electron affinity of NO, EA_e(N), from CCSD(T) calculations with the aug-cc-pV*n*Z and d-aug-cc-pV*n*Z basis sets.

120 cm^{-1} (the experimental spin orbit splitting is 119.82 cm^{-1}).[18] The calculated energy is the midpoint between these two values. Thus, the spin orbit energy correction lowers the NO energy and decreases EA_e(NO) by 60 cm^{-1} or 0.0074 eV. The scalar relativistic energy correction for NO and NO^- determined using the Douglass−Kroll method reduces the electron affinity of NO by another 0.0058 eV.

The final calculated equilibrium electron affinity is the sum of each of the terms discussed in the preceding paragraphs, namely:

$$\begin{aligned} EA_e(\mathrm{NO}) = {} & \\ & 0.0100 - 0.0001 - 0.0074 - 0.0058\ (\pm 0.001)\ \mathrm{eV} \\ & = -0.0033 \pm 0.001\ \mathrm{eV} \end{aligned}$$

(because the CCSDT calculations could not be performed with the larger basis sets, we use the CCSD(T) results in this equation). In summary, the nonrelativistic electronic energy of NO^- at its equilibrium internuclear distance lies below that of NO at its equilibrium internuclear distance by 0.0009 eV. However, including relativistic effects, the situation is reversed and NO lies below NO^- by 0.0033 eV.

Vibrational Correction to Equilibrium Electron Affinities. The potential energy curve for NO^- has a lower curvature than that of NO, consistent with a weaker bond: $\omega_e(\mathrm{NO}) = 1907$ cm^{-1} and $\omega_e(\mathrm{NO^-}) = 1392$ cm^{-1}. The higher vibrational frequency (energy) of NO means that EA_0(NO), the energy difference between $v = 0$ of NO^- and $v = 0$ of NO, will be greater than EA_e(NO), the difference between the energies at the two potential minima. Thus, the vibrational correction will increase the calculated electron affinity of NO. The calculated vibrational frequencies and anharmonicities for NO and NO^- are listed in Table 2.

The final calculated electron affinity is

$$\begin{aligned} EA_0(\mathrm{NO}) &= -0.0033 + 0.0317\ (\pm 0.001)\ \mathrm{eV} \\ &= 0.0284 \pm 0.001\ \mathrm{eV} \end{aligned}$$

Inclusion of anharmonicity has a negligible effect on the vibrational energy correction. Thus, numerically, the largest contribution to the electron affinity of NO is from the change in zero point vibrational energy.

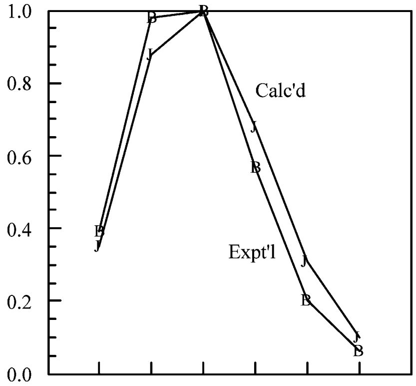

Figure 2. Experimental and calculated Franck−Condon factors for the photodetachment spectrum of NO^-.

The energy of the $^1\Delta$ state of NO^- from CCSD(T) calculations with the aug-cc-pV5Z basis set is 1.02 eV higher than the energy of the $^3\Sigma^-$ state. The experimental value is 0.7514 eV.[19] This energy for the $^1\Delta$ state is not consistent with the suggestion of Chen[6] that the electron affinity value of 0.026 eV[5] must be that of the $^1\Delta$ state rather than the $^3\Sigma^-$ state.

Dissociation Energies of NO and NO^-. Table 2 includes the calculated dissociation energies, D_e, for NO and NO^-, determined from the difference between the calculated energies of NO and those of the N and O atoms and the difference between the energy of NO^- and those of N and O^-. CCSD(T) calculations with the d-aug-cc-pV*n*Z basis sets were extrapolated with a simple exponential function to give the calculated D_e's: 634 kJ/mol (NO) and 495 kJ/mol (NO^-). The D_e values were decreased by the calculated zero point energies ($^1/_2\omega_e - {}^1/_4\omega_e x_e$) to obtain the D_0 values, yielding 622 and 487 kJ/mol, respectively. The calculated values for D_0 are in good agreement with the experimental values of 626.8 and 487.8 kJ/mol.[19]

Calculated Franck−Condon Factors for Photodetachment. The calculated potential energy curves were used to determine the vibrational wave functions and hence the Franck−Condon factors for the photoelectron detachment. These Franck−Condon factors were determined experimentally and are given the paper by Siegel et al.[1] Figure 2 shows the experimental and calculated Franck−Condon factors. For each set the most intense transition, 0−2, is assigned the value 1.0, and other values are expressed as a fraction of that value. The calculated Franck−Condon factors are in good agreement with the measured values.[1]

Conclusions

The present study of the electron affinity of NO (EA = 0.026 eV), combined with previous studies of the electron affinities of O_2 and CN (EA = 0.422 and 3.862 eV, respectively), convincingly show that coupled cluster methods that include triple excitations can accurately describe the negative ions of a wide range of molecules. The CCSD(T) and CCSD-T methods yield similar predictions for EA_e(NO), 0.028 eV, but that predicted by the CCSD[T] method is 0.013 eV larger. Full accounting for triples in CCSDT calculations increase the electron affinity, although the magnitude of the increase appears to be decreasing with increasing basis set size.

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