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Collisional electron detachment from NO^- by rare gases

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Abstract

A model is proposed to explain earlier measurements of electron detachment from NO^- by He, Ne, and several diatomic and triatomic molecules. The measurements have been extended to include detachment by Ar with a rate constant of $2 \times 10^{-14}\,cm^3\,s^{-1}$ at 500 K. The previously puzzling inefficiencies are satisfactorily explained by a mechanism in which NO^- ($v = 0$) is vibrationally excited to NO^- ($v = 1$), followed by autodetachment. The data are analyzed with Landau–Teller theory after invoking the principle of detailed balance. Ab initio calculations of the NO^- interactions potentials with He, Ne, and Ar have been made. Range parameters derived from Landau–Teller plots and ab initio calculations are in the range expected although not in exact agreement. The ab initio potential attractive wells make clear why the necessary vibrational excitations in He and Ne collisions with NO^- (and hence collisional detachment) are far more effective than in the case for Ar. This appears to be the first application of Landau–Teller theory to a negative ion.

Keywords: Collisional electron detachment; NO^-; Rare gases

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1. Introduction

Collisional detachment of the weakly bound electron on NO^- by He, Ne, H_2, NO, CO, CO_2, N_2O, and NH_3 was reported in 1972 [1]

$$NO^- + M \rightarrow NO + M + e^- + 0.026\,eV. \qquad (1)$$

Rate constants were derived over the temperature range 193–505 K. Subsequently, kinetic energy and temperature dependent studies of NO^- detachment by N_2O, CO_2, N_2, CH_4, C_2H_6, and C_3H_8 were made in a variable temperature selected ion flow drift tube [2]. The two studies showed, with the exception of Ar, that all gases detached the electron relatively rapidly. The rate constants were $>10^{-13}\,cm^3\,s^{-1}$ at 506 K. Ar was sufficiently inefficient at detaching the electron that it was used as the non-reactive buffer gas, thereby making the studies possible.

Increasing temperature increased the detachment, as expected for endothermic reactions. The temperature dependencies could be reasonably represented by Arrhenius plots with activation energies substantially larger than the endothermicity of 26 meV [3]. The activation energies varied considerably, from 45 meV for CO to 107 meV for N_2O [1]. The drift tube results found NO^- associated with N_2O and CO_2 at low temperature. A comparison of temperature and kinetic energy dependences showed that bending modes of these molecules increased the detachment rates by about an order of magnitude [2].

The slow detachment rate of Ar compared to He and Ne has remained a mystery. Here we propose a new model for the detachment, vibrational excitation followed by autodetachment. The mechanism was inspired by the NO^- photodetachment work of Maricq et al. [4] who established the photodetachment process to be vibrational excitation followed by autodetachment. They also determined the NO^- vibrational frequency to be $1284 \pm 10\,cm^{-1}$ and the autodetachment lifetime for NO^- ($v = 1$) to be 3.5×10^{-13} s.

In addition, we report for the first time a quantitative rate constant for Ar detachment at 500 K and analyze the He and Ne results with the Landau–Teller model. Theoretical calculations of the NO^-–noble gas potentials are presented and shown to be consistent with the proposed model.

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2. Experimental and theoretical methods

While most of the experimental data discussed in this paper has been reported previously [1], there have been no accurate measurements for NO^- detachment by Ar since the rate constant is very small. In fact, flow tube measurements at room temperature and above can only be made in Ar since other gases detach the electron rapidly. Therefore, an alternative method is needed to measure Ar detachment rates. We use a scavenger method in a selected ion flow tube (SIFT) to measure the Ar detachment rate constant. Due to the inefficiency of the reaction, a measurement could only be made at 500 K.

The apparatus is described in detail elsewhere [5,6] and only pertinent details are given here. NO^- is made in an electron impact source from N_2O. The ion is mass selected and injected into a fast flow of Ar. Even at 500 K, much of the NO^- survives the length of the flow tube, although the signal is noticeably weaker at high temperatures indicating that detachment is occurring. Normal SIFT techniques do not allow for such a low rate constant measurement.

Previously, it has been shown that O_2 reacts with NO^- almost exclusively by charge transfer [1]. Therefore, adding O_2 to the flow tube in large quantities converts the NO^- into O_2^- in the vicinity of the injector. The O_2^- signal is a measure of the amount of NO^- that survives to the injector. Using several injectors (the AFRL SIFT has three) allows for determination of the rate constant for detachment. A plot of such data is shown in Fig. 1, where the most upstream injector is assumed to be at $t = 0$. A small correction to the signal for a background O_2^- signal due to impurities in the Ar buffer has been made. The exponential slope of the NO^- decay with time divided by the Ar concentration yields a rate constant. Monitoring the decay in the nose cone current yields a similar rate constant and is a check on the method. At low temperatures, NO^- partially survives the length of the flow tube in a helium buffer and allows for rate constants to be measured. The measured rate constants for He detachment are in agreement with the previous data from NOAA within experimental error (50%).

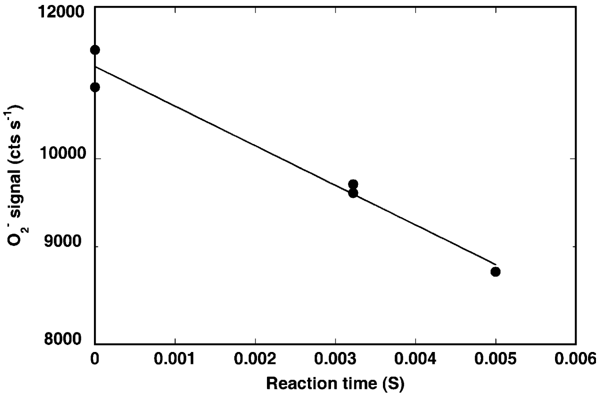

Fig. 1. O_2^- signal vs. reaction distance. The O_2^- represents the NO^- signal in the Ar detachment as explained in the text.

Ab initio RCCSD(T) [7] calculations of the He, Ne, $Ar \cdots NO^-$ ($X^3\Sigma^-$) potential energy functions (PEF) have been made in order to lend support for the proposed mechanism. Most of the calculations were for collinear geometries. The NO^- bond length was fixed at its equilibrium value of 2.3629 bohr [8]. We used the augmented correlation-consistent valence quadruple zeta basis set of Dunning and coworkers [9]. In all calculations, the MOLPRO program package was used [10]. For the $NO^- \cdots He$ complex also the two-dimensional PEF was calculated in Jacobi coordinates. Similar extensive calculations for all three complexes and variational calculations of bound states are being performed and will be reported elsewhere [11].

3. Results and discussion

Table 1 shows the present Ar rate constant at 500 K as well as previous measurements for other gases at 506 K, as well as the activation energies and range parameters to be discussed later. For the noble gases, each step in the periodic table appears to decrease the rate constant by approximately an order of magnitude. This is a substantial and an easily measured effect. The activation energies for He and Ne are 75 and 98 meV, respectively [1]. No activation energy for Ar could be measured. Other activation energies are in excess of 100 meV.

The occurrence of activation energies hugely in excess of the NO electron affinity [1,3] (by as much as a factor of 4) indicates that the process involved is not a simple collisional detachment. The variability in the activation energies makes it unlikely that a potential surface with a barrier is responsible, e.g., He and Ne would be expected to have similar barriers. At low temperatures, an association channel is seen for N_2O and CO_2, which precludes significant barriers for those reactions. As shown below, the present ab initio potential curves (Figs. 2 and 3) have no barriers. The potentials for the reactants are mainly determined by a charge–polarizability interaction at long range and repulsive

Table 1
Parameters for NO^- detachment with various neutrals

Specie	k (506 K) ($cm^3 s^{-1}$)	Activation energy (meV)	Range parameter from Fig. 2 (Å)
He	1×10^{-12}	74.5	0.49
Ne	1.6×10^{-13}	98.0	0.31
Ar	2×10^{-14}	–	
H_2	9.4×10^{-13}	82.8	0.79
CO	1.2×10^{-12}	45.5	0.20
NO	3.0×10^{-11}	105.1	0.30
CO_2	3.7×10^{-11}	81.2	0.24
N_2O	3.5×10^{-11}	107.2	0.37

The range parameters come from the Landau–Teller plots shown in Fig. 2. Except for the Ar data, all data are from McFarland et al. [1].

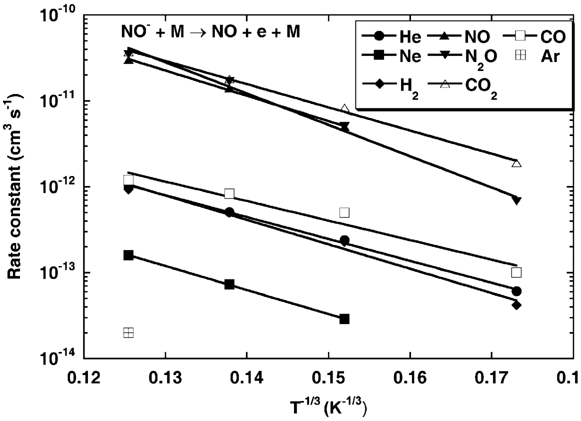

Fig. 2. Landau–Teller plots for NO^- detachment for various gases.

at short range with Van der Waals minima at intermediate distances. This indicates a mechanism other than a one-step collisional detachment is responsible for NO^- detachment. Here we propose a two-step mechanism of vibrational excitation followed by autodetachment.

One distinguishing feature in the noble gas series, He, Ne, and Ar is the decrease of their thermal velocity with increasing mass. This suggests the explanation may include consideration of the Adiabatic Principle due to Ehrenfest [12], where the probability of a non-adiabatic process (vibrational excitation in this case) increases with the speed of the applied perturbation. In the present case, the perturbation is a collision. The Adiabatic Principle is expressed as [13–15]

$$P \sim \exp\left(\frac{-a\Delta E}{hv}\right) \tag{2}$$

where P is the probability of the process occurring, ΔE is the energy exchange, v is the relative velocity, h is Planck's constant, and a is the range parameter for the repulsive interaction expressed as $V(r) \sim \exp(-r/a)$, a good approximation at high energy. The most successful application of the Adiabatic Principle is the Landau–Teller equation [16] for vibrational quenching of molecules by small non-polar molecules. For such systems, P integrated over a Maxwellian distribution yields a probability proportional to $T^{-1/3}$.

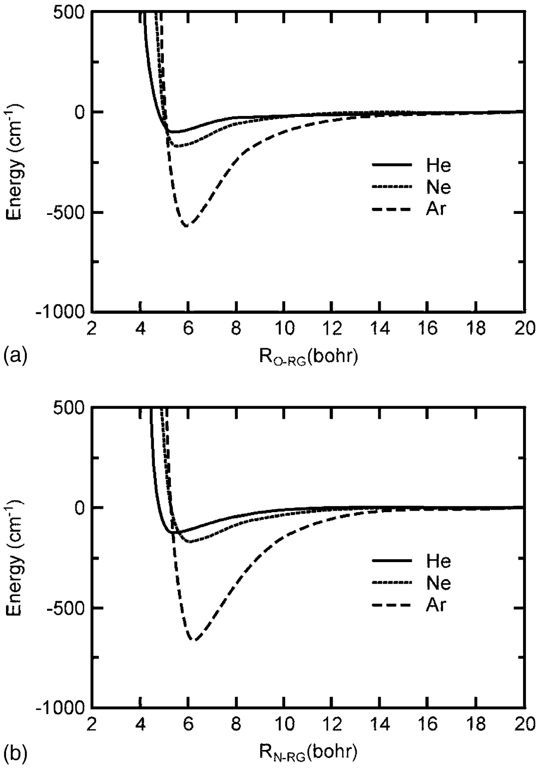

Fig. 3. Ab initio potentials for NO^- colliding with He, Ne, and Ar for collinear approaches. (a) O atom approach, (b) N atom approach.

Here we use the Landau–Teller equation as a test for the proposed vibrational excitation–autodetachment mechanism. The application of Landau–Teller theory to vibrational excitation requires some justification. The traditional application has been to vibrational quenching. Excitation and quenching are related by the Principle of Detailed Balance. For NO^- (v) + He, it can be represented as

$$\mathrm{NO^-(0) + He(KE_1)} \underset{k_q}{\overset{k_{exc}}{\rightleftarrows}} \mathrm{NO^-(1) + He(KE_2)} \tag{5}$$

with $KE_1 = KE_2 + h\nu$ (159 meV). Since the forward and reverse rates must be equal and

$$\frac{[\mathrm{He(KE_1)}]}{[\mathrm{He(KE_2)}]} = \frac{[\mathrm{NO^-(1)}]}{[\mathrm{NO^-(0)}]} = e^{-h\nu/kT}, \tag{6}$$

the rate constants must be equal. The Principle of Detailed Balance has practical applicability only in very limited cases, e.g., with polyatomic reactants the exothermic reaction might yield excited state products. Usually the product distribution would not be known and in any case would not correspond to the conditions in which the reverse reaction would be measured. In the present case, the only possibility for error would be for the NO^- to be highly rotationally excited in the vibrational excitation process. However, this is not likely, especially in light of the relatively weak anisotropy found in the potential, shown in Fig. 3. Since k_q and k_{exc} are equal at the threshold energy and above, k_{exc} must satisfy the Landau–Teller relationship (which gives only the temperature dependence not the absolute values) if k_q does. In the absence of NO^- ($v = 1$) autodetachment, it is quite sure this would be the case and the collisional dynamics of quenching would not be altered by the presence of autodetachment.

The repulsive potential energy range parameters are determined from the Landau–Teller theory

$$k_q \propto e^{-3/2(\theta/T)^{1/3}} \tag{7}$$

where $\theta = 4\pi^2\mu a^2\omega^2/k$, μ is the reduced mass, ω is the vibrational frequency, k is Boltzmann's constant, and a is the range parameter in $V(r) \sim e^{-r/a}$. Fig. 2 shows the collisional detachment rate constants for NO^- with several molecules versus $T^{-1/3}$, i.e., Landau–Teller plots. The plots are quite linear although the temperature range is limited. Range parameters derived from the data are listed in Table 1. They fall between 0.2 and 0.49 Å, except a large value is found for H_2. As shown below, these are approximately what is expected, lending support to the vibrational excitation mechanism.

The range parameter is typically 0.1–0.4 Å for simple molecules [13]. A value of 0.22 Å was obtained from the vibrational quenching of $N_2^+(v = 1)$ by He in the kinetic energy range 0.2–0.6 eV [17,18]. This is supported by ab initio calculations yielding range parameters of approximately 0.2–0.25 Å in this energy range, with a slight anisotropy of the potential [19]. Cheng et al. [20] found range parameters of 0.175 Å for NO^+–He and 0.171 Å for O_2^+–He from scattering data. Hasted [15] lists a table of range parameters for a wide variety of neutrals obtained from virial coefficients, all in the ~0.2 Å range. A Landau–Teller plot for HCN^+ (v) quenching by He yielded a range parameter of 0.21 Å [21]. The only negative ion systems for which range parameters have been derived are those for Cl^- with He, Ne and Ar. The range parameters are 0.45, 0.33, and 0.39 Å, respectively [22]. The former two values are remarkably close to the present values for NO^-.

The relative invariance of the repulsive range parameter follows from the broad qualitative applicability of the screened coulomb potential [23]

$$V(r) = \frac{Z_1 Z_2 e^2}{r} e^{-r/a} \tag{8}$$

and Bohr's [24] expression for a

$$a = \frac{a_0}{(Z_1^{2/3} + Z_2^{2/3})^{0.5}} \tag{9}$$

where Z_1 and Z_2 are the atomic numbers of the colliding atoms and a_0 is the first Bohr radius, 0.53 Å. For small Z, this is a relatively insensitive function, leading to range parameter values slightly less than a_0. In vibrational quenching of N_2^+ ($v = 1$) by He, equation 4 yields a value of $a = 0.23$ Å as compared to a value of 0.22 Å found from a Landau–Teller plot [17]. This shows the utility of the Bohr expression as a rough guide.

The condition for Landau–Teller (or more generally non-adiabatic behavior) is that the collision (or more generally perturbation) be impulsive and not involve long-lived collision complexes. Until recently, the only ionic systems to show Landau–Teller behavior involved quenching by He [17,18,21]. This is a consequence of the low polarizability yielding a shallow attractive potential, which prevents a collision complex from forming. Another criterion favoring complex formation is anisotropy of the attractive potential [25]. This presumably reflects the possibility of translational energy conversion to internal rotational energy, leading to increased complex lifetime. Recently, NO^+ (v) quenching by Ar has also been found to fit Landau–Teller theory (yielding a range parameter of 0.19 Å) in spite of the relatively large polarizability of Ar [26].

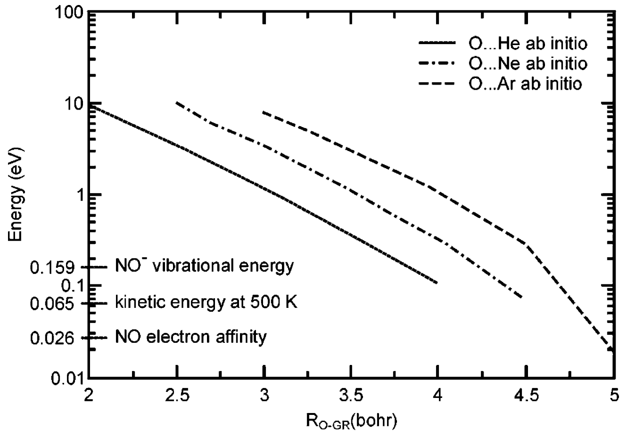

Fig. 4. Enlargement of the repulsive part of the ab initio potentials for NO^- colliding with He, Ne, and Ar for collinear approaches to the O atom.

The application of Landau–Teller theory requires the potential to have a shallow minimum at most and an exponential repulsive potential. In this regard, ab initio potential surfaces were calculated for NO^- colliding with He, Ne, and Ar. The potentials are shown in Figs. 3 and 4 and several of the parameters are listed in Table 2. Fig. 3a and b shows potentials for linear approaches to the O and N atoms, respectively. The attractive well of NO^- with Ar is almost five times larger than that with He and Ne. One can note that the polarizabilities of the rare gases follow the same trend: 0.204956 for He, 0.3956 for Ne, and 1.6411 for Ar (all values in 10^{-24} cm^3) [27]. The electric dipole moment of NO^- (relative to the center of mass) has been calculated to be 0.4157 a.u. The negative charge is mainly located on the oxygen atom. The depths of the local collinear minima are not appreciably different for both possible orientations. Although very shallow, the $NO^- \cdots$ He interaction potential exhibits three minima, which is rather unusual for such a weakly bound structure. We note that both PEF components of the neutral ArNO ($X^2\Pi$) complex [28] have bent equilibrium structure, the dissociation energy D_e of the lowest A

Table 2
The RCCSD(T) minima, dissociation energies D_e, and $1/b$ factors for collinear approaches obtained from the potentials (cf. text), for NO^-He also such parameters are given for the bent minimum

	R (bohr)	Θ (°)	E_{diss} (cm^{-1})	a (Å), range parameter
He				
$He \cdots NO^-$(bent)	6.44	77	93	0.20
$He \cdots NO^-$	7.29	180	80	0.18
$He \cdots ON^-$	6.71	0	91	0.24
Ne				
$Ne \cdots NO^-$		180	169	0.22
$Ne \cdots ON^-$		0	170	0.23
Ar				
$Ar \cdots NO^-$		180	661	0.33
$Ar \cdots ON^-$		0	568	0.28

component is only about 80 cm^{-1} by comparison to more than 600 cm^{-1} in the negatively charged Ar complex.

Fig. 4 shows in more detail the purely repulsive parts of the potential for O atom approach. The He and Ne repulsive potentials are seen to be nearly exponential down to energies as low as 0.159 eV (the energy necessary to vibrationally excite NO^-). The theoretical range parameters are compared to those derived from the Landau–Teller plots in Table 1 and are in the range expected. However, the agreement is only semi-quantitative. We have assumed the collisions to be linear with the rare gas striking the O atom. Linear collisions are favored for the necessary momentum transfer and the O end is favored since the attracting charge is concentrated there.

Perhaps a weakness of the L–T approximation to the Adiabatic Principle lies in the fact that the collisions in the detachment experiments are only marginally in the non-adiabatic regime, i.e., having collision durations short compared to the vibrational period of NO^-, 2.6×10^{-14} s. The minimum energy collisions for vibrational excitation, 0.159 eV, have collision times of the order a/v or slightly less than 0.8×10^{-14} s. The more effective collisions at higher energy are even shorter. However, a more compelling argument for the applicability of the Adiabatic Principle (which of course is more general than the Landau–Teller theory derived from it) is indicated in the attractive potentials shown in Fig. 3. The He and Ne potential wells are very small compared to the kinetic energies of the collisions and hence the interactions will be dominated by the repulsive potentials. By contrast the NO^-–Ar potential well is much deeper than kT so that orbiting, non-impulsive collisions will occur, not satisfying the criterion for a non-adiabatic transition. This results in the smaller rates observed for Ar detachment.

In any case, the use of Landau–Teller theory is somewhat questionable, since it is based on the qualitative statement of the Adiabatic Principle integrated over a Maxwellian velocity distribution, which requires approximations in the integration [29]. Nevertheless, it has proven remarkably successful over many years (yielding energy dependences, not magnitudes). For our purposes, we do not press for more than qualitative agreement. Our main goal is to show that the proposed mechanism of vibrational excitation followed by autodetachment is quite plausible.

So far, we have discussed only rare gas detachers, although data exists for other molecules. The simple picture given for the rare gases certainly does not apply to several of the molecules studied. As mentioned above, CO_2 and N_2O are known to associate with NO^- at low temperature, implying a long-lived complex and therefore the concept of a purely repulsive collision does not apply [2]. The binding energy of N_2O with NO^- has been reported to be 0.2 eV [30] in which case the electron detachment would be exothermic on collision and it is well established that non-adiabatic processes readily occur in complexes [31]. Similar situations may apply to the other molecular species, e.g., the associative detachment $NO^- + NO = ONNO + e^-$ is 43 meV [32] exothermic but does not occur [1]. With the negative charge of NO^- now known to be on the O atom, it is clear that the collision complex would have the form $NONO^-$ or $NOON^-$ rather than $ONNO^-$, a suggested explanation postulated previously [1].

A further argument for the vibrational excitation–autodetachment mechanism comes from the work comparing kinetic energy to temperature dependencies [2]. In that study, it was found that vibrational excitation of N_2O and CO_2 enhanced the detachment rate by over an order of magnitude. This would be due V–V energy transfer, generally known to be more efficient than T–V energy transfer.

4. Conclusions

Here we present arguments that indicate NO^- collisional detachment is a two-step process of vibrational excitation followed by autodetachment. This appears to be the first such example. Application of Landau–Teller theory demonstrates the applicability of the Adiabatic Principle to the vibrational excitation process. The vibrational excitation–autodetachment mechanism is severely limited in application requiring an electron affinity to be less than the vibrational energies, for example ${O_2}^-$, would require multiple quanta to detach the electron. Most weakly bound species would not be stable in a buffer gas.

Calculations of the NO^- interaction potentials with He, Ne, and Ar are reasonably consistent with the model proposed here, an application of the Adiabatic Principle of Ehrenfest. In particular, the ab initio potentials for collinear collisions are shown to be repulsive in the range of energies required for NO^- vibrational excitation, 159 meV, as required for the non-adiabatic mechanism proposed. For He and Ne, the attractive charge-induced dipole well depths are shallow compared to the experimental energies involved in the detachment studies so that the necessary impulsive collisions are expected while for Ar–NO^-, the attractive well depth greatly exceeds the kinetic energies involved so that impulsive (sudden) collisions would not occur, hence weak collisional detachment by this model.

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