# NON-DISSOCIATIVE SINGLE ELECTRON CAPTURE BY NO<sup>2+</sup> FROM NOBLE GASES

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The state-selective non-dissociative single-electron capture reactions of 6 keV NO<sup>2+</sup> ions from noble gas (He, Ne, Ar, Kr and Xe) targets are investigated by translational energy spectroscopy. Capture occurs predominantly from ground state NO<sup>2+</sup> ( $X^{2}\Sigma^{+}$ ). For the NO<sup>+</sup> ( $X^{1}\Sigma^{+}$ ) formation a shift of the peak in the translational energy distribution was found (1.3 to 1.7 eV) which suggests higher vibrational excitation of the molecular product than expected from the mutual position of potential energy curves of the NO system. A simple model assuming a dynamical perturbation of the NO<sup>+</sup> curve in the presence of He<sup>+</sup> is suggested, which accounts for the shift.

#### 1. Introduction

Charge transfer of multiply charged small molecules has attracted some recent attention [1,2]. In our earlier papers [3,4] we reported on single electron capture by the diatomic dications  $CO^{2+}$ ,  $N_2^{2+}$ ,  $O_2^{2+}$ and  $Cl_2^{2+}$  (AB<sup>2+</sup>) from noble gas targets (R), i.e. the processes

$$AB^{2+} + R \rightarrow AB^{+} + R^{+} \tag{1}$$

at projectile ion energies of 6 keV. The translational spectroscopy method was used to identify the eletronic state-to-state processes.

Largest cross sections were observed for reactions with exothermicities lying within a "reaction window" which could be estimated [3] using the semiclassical Landau–Zener formulation for charge transfer in atomic systems. Recombination energies of the dications could be well correlated with the ionization energies of the ground and excited metastable states of the doubly charged molecular ions. Peak broadening was indicative of vibrational excitation of the

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product singly charged molecular ions. Effects due to the symmetry of the potential energy surfaces involved were noted and the spin conservation rule was shown to influence the size of the cross section of electronic state-to-state processes [4].

In this communication we now report our investigation of processes (1) for 6 keV  $NO^{2+}$  dications with noble gas atoms (He, Ne, Ar, Kr, Xe). In order to interpret translational energy spectra of the NO<sup>+</sup> product, the compilation of energy levels in table 1 was used. For NO<sup>+</sup>, the summary of potential energy curve data for NO<sup>+</sup> due to Albritton, Schmeltekopf and Zare [5] was used. In addition, table 1 lists (in parentheses) several states in the region 18.5-21.5 eVwhose locations result from theoretical calculations [6,7]. Ionization energies of the noble gas atoms [8] are given for the sake of completeness. The ionization energy NO-NO<sup>2+</sup> was measured several times during the past 25 years by various methods, the values for the lowest ionization energy ranging between 38.6 and 39.8 eV [9-12]. The photoionization value recently reported by Samson et al. [10] is  $39.4 \pm 0.12$ eV. Besnard et al. [11] concluded from the tail of their double photoionization curve that the lowest ionization energy to form NO<sup>2+</sup> was  $38.6 \pm 0.1$  eV. Both results are within the error limits of the value obtained by dipole (e, e+ion) spectroscopy [12],  $39 \pm 1 \text{ eV}.$ 

There are several theoretical treatments of NO<sup>2+</sup>

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Table 1	
Spectroscopic	data

Ion	State	Ionization energies E <sub>1</sub> (eV)	Equilibrium internuclear separation (Å)	Designation	
NO <sup>2+</sup>	$X^{2}\Sigma^{+}$	39.4±0.12 <sup>a</sup> ), 38.6±0.1 <sup>b</sup> ) 39.3±0.5 <sup>c</sup> ), 39.34 <sup>d</sup> )	1.11 <sup>d)</sup>	I	
	Α <sup>2</sup> Π	40.64 <sup>d</sup>	1.22 <sup>d</sup>	п	
	$B^{2}\Sigma^{+}$	44.30 <sup>d</sup>	1.11 <sup>d)</sup>	III	
NO <sup>+ e)</sup>	$X \Sigma^+$	9.26	1.063	А	
	a <sup>3</sup> Σ <sup>+</sup>	15.66	1.281	a	
	b <sup>3</sup> Σ <sup>+</sup>	16.56	1.76	b	
	$w^{3}\Delta$	16,88	1.289	w	
	b' <sup>3</sup> Σ-	17.60	1.276	b'	
	$A' \Sigma^{-}$	17.82	1.287	Α′	
	W 'Δ	18.08	1.301	W	
	$A^{1}\Pi$	18.33	1.193	А	
	$({}^{1}\Sigma^{+})^{f}$	18.7	(1.5)		
	$(^{3}\Sigma^{+})^{f}$	20.3	(1.7)		
	$c^{3}\Pi(B^{\perp}\Pi)^{g}$	21.73	1.15	с	
	$B^{-1}\Pi(B^{-1}\Sigma^{+})^{g)}$	22.73	1.34	В	
ole gases					
He <sup>+</sup>	${}^{2}S_{1/2}$	24.59		α	
Ne <sup>+</sup>	${}^{2}P_{3/2}$	21.56		α	
Ar <sup>+</sup>	${}^{2}P_{3/2}$	15.76		α	
Kr+	${}^{2}P_{3/2}$	14.00		α	
	${}^{2}P_{1/2}$	14.67		α'	
	${}^{2}S_{1/2}$	27.51		β	
Xe+	<sup>2</sup> P <sub>3/2</sub>	12.13		α	
	${}^{2}\mathbf{P}_{1/2}$	13.44		α΄	
	${}^{2}S_{1/2}$	23.39		β	
	${}^{2}\mathbf{P}_{3/2}$	24.87		γ	

<sup>a)</sup> Photoionization [10]. <sup>b)</sup> Photoionization [11].

<sup>c)</sup> DCT, Apell et al. [9]. <sup>d)</sup> Theory [14].

<sup>c)</sup> Ref. [5]. <sup>f)</sup> Theory; a cluster of bound triplet states predicted in this region [5,7].

<sup>8)</sup> Ref. [8].

[6,7,13]. They culminate the the recent high-quality calculations of Cooper [14]: the lowest bound state of NO<sup>2+</sup> possesses  ${}^{2}\Sigma^{+}$  symmetry and the author places it at 39.34 eV. In addition, the calculations report two other bound states of NO<sup>2+</sup>, A  ${}^{2}\Pi$  and B  ${}^{2}\Sigma^{+}$ , 1.4 and 5.0 eV above the ground state, respectively. Observation on NO<sup>2+</sup> emission [11] and our recent translational energy spectroscopy results [15] provide excellent confirmation of these calculations.

#### 2. Experimental

Experiments were performed on a VG analytical ZAB-2F mass spectrometer [16]. The operation procedure has been described on many occasions (see, e.g., refs. [3,4,17]); briefly, nitric oxide dications are produced by 100 eV electron impact on NO gas, in the ionization chamber of the conventional Nier-type ion source, extracted and accelerated to 6 keV translational energy. The NO<sup>2+</sup> ions, mass selected by a sector magnet, enter a 2.00 cm long collision cell located at the intermediate focal point of the mass

spectrometer, containing a rare gas target at a pressure of  $\approx 0.2$  Pa. Translational energy spectra are obtained under high-resolution conditions, by scanning the voltage applied to the plates of the cylindrical electrostatic analyzer, located after the collision cell.

From previous studies of atomic ion-atom electron capture processes [17], the energy resolution for NO<sup>+</sup> spectra is estimated to be  $\approx 1 \text{ eV}$ , compared with a primary NO<sup>2+</sup> beam width of  $\approx 0.2 \text{ eV}$  (fwhm). As in our earlier studies [3,4], the translational energy scale is calibrated by adding a small amount of argon to the source gas and by repeatedly measuring the well known translational energy spectra for the Ar<sup>2+</sup>-no-ble gas single electron capture reactions, before and after each run of the NO<sup>2+</sup>-noble gas systems. The accuracy of the calibration was better than 0.2 eV.

#### 3. Results

As in our preceding papers [3,4], experimental results are shown as plots of product ion NO<sup>+</sup> intensity as a function of calibrated translation exothermicity,  $\Delta E$ , where

$$\Delta E = E_{\text{lab}}(\text{NO}^+) - E_{\text{lab}}(\text{NO}^{2+}) .$$
<sup>(2)</sup>

Figs. 1-5 show the translational spectra of NO<sup>+</sup> from reactions

$$NO^{2+} + R \rightarrow NO^{+} + R^{+}, \qquad (3)$$

where R is He, Ne, Ar, Kr and Xe, respectively. The exothermicities  $\Delta E_0$  of the various electronic stateto-state processes are given in table 2. They were calculated from the ionization energies of the species under the assumption of no vibrational excitation of the molecular ions. For reasons discussed later on, the value of the ionization energy NO-NO<sup>2+</sup> (X  $^{2}\Sigma^{+}$ ) was taken as 39.4 eV. As in our other papers [3,4], designation of the particular processes follows the modified Hasted notation [18]: Roman numerals (I, II, ...) refer to the ground and successive excited states of the molecular projectile (only I in  $NO^{2+}$ ), Greek letters  $(\alpha, \beta, \gamma, ...)$  to the ground and excited states of the noble gas product ion  $R^+$ . Arabic letters (X, a, b, b', ..., A, B, ...) follow the abbreviated conventional notation of the spectroscopic states of NO<sup>+</sup>. The designations are given in tables 1 and 2 as well.

(still)  $Ix - \frac{B c}{I}$  A b' b a X  $Ix - \frac{B c}{I}$  A b' b a X  $Ix - \frac{B c}{I}$  A b' b a X  $I x - \frac{B c}{I}$  A b' b a X $I x - \frac{B c}{I}$  A b'

Fig. 1. Translational energy spectrum for NO<sup>+</sup> ions produced by collisions of 6 keV NO<sup>2+</sup> with He, the exothermicities of various state-to-state processes (table 2) are shown in the upper part of the figure, for the definition of the abscissa *E*, see eq. (2).



Fig. 2. Translational energy spectrum for NO<sup>+</sup> ions produced by collisions of 6 keV NO<sup>2+</sup> with He.

# $3.1. NO^{2+} + He$

Formation of NO<sup>+</sup> in the ground state (process  $(I\alpha X)$ ) is the only exothermic process in this system and it fits into the reaction windown [3] (exothermicities 4.5–6.9 eV, peak at 5.7 eV). Accordingly, the translational energy spectrum (fig. 1) is character-



Fig. 3. Translational energy spectrum for NO<sup>+</sup> ions produced by collisions of 6 keV NO<sup>2+</sup> with Ar.



Fig. 4. Translational energy spectrum for NO  $^+$  ions produced by collisions of 6 keV NO  $^{2+}$  with Kr.

ized by a prominent peak which we ascribe to this electron capture channel. Formation of NO<sup>+</sup> excited states in endothermic processes shows up as a very weak, broad, unresolved peak on the endothermic side of the translational energy spectrum (at -1 to -7eV). There is no indication of processes involving electronically excited states of the projectile NO<sup>2+</sup>. The most interesting feature in the spectrum is that the  $(I\alpha X)$  peak is shifted from its expected position, peaking at 1.3 eV lower energy than predicted, with a clear tail towards higher energy, towards its expected position.

### 3.2. $NO^{2+} + Ne$

Exothermic processes include the formation of NO<sup>+</sup>(X  $^{1}\Sigma^{+}$ ) (process (IaX)) and several excited states of NO<sup>+</sup>, though the exothermicities of these processes are lower than 2.2 eV. Athough formation of excited states has a fairly small cross section, and, moreover, these states are closely clustered together, production of NO<sup>+</sup>(a  $^{3}\Sigma^{+}$ ) and NO<sup>+</sup>(b  $^{3}\Pi$ ) can be clearly identified (process (Iaa) and (Iab), fig. 2). The largest peak belongs to process (IaX) whose exothermicity is slightly above the calculated reaction window (4.2–6.4 eV); the peak is broadened and shifted to lower energy from its expected position by 1.5 eV. Again, there is no indication of reactions involving excited states of the NO<sup>2+</sup> projectile.

#### 3.3. $NO^{2+} + Ar$

According to the calculated reaction window (exothermicities 3.5-5.2 eV) formation of higher excited states of NO<sup>+</sup> ought to be favoured. In the overlapping structure in the translational energy spectrum (fig. 3) the largest cross section may be ascribed to the formation of NO<sup>+</sup> (A <sup>1</sup>II). Various processes leading to clustered excited states of NO<sup>+</sup> may evidently take place. A low-energy shoulder of the spectrum occurs in the region where positions of excited NO<sup>+</sup> states are not well known [5], though theoretical calculations suggest their existence [6,7] (see also table 1). The unresolved character of the spectrum in this region does not make it possible to identify their position more closely.

Process (IaX) has a small cross section; the corresponding peak exhibits a considerable shift (of about 1.5-1.7 eV) from its expected position.

#### 3.4. $NO^{2+} + Kr$

The processes with exothermicities within the reaction window (3.3-4.9 eV) require formation of NO<sup>2+</sup> in higher excited states (energies of 20.5-22.7 eV). The translational energy spectrum in fig. 4 ex-



Fig. 5. Translational energy spectrum for NO<sup>+</sup> ions produced by collisions of 6 keV NO<sup>2+</sup> with Xe.

Table 2 Reaction channel exothermicities  $\Delta E_0$  for the reaction NO<sup>2+</sup> (X <sup>2</sup> $\Sigma^+$ ) + R(<sup>1</sup>S<sup>0</sup>)  $\rightarrow$  NO<sup>+</sup> + R<sup>+</sup>

Final R <sup>+</sup> state		Final NO <sup>+</sup> state									
		$\frac{1}{X^{1}\Sigma^{+}}$	a <sup>3</sup> Σ <sup>+</sup> a	b <sup>3</sup> Π b	w <sup>3</sup> Δ w	b′ <sup>3</sup> Δ b′	A' <sup>1</sup> Σ- A'	$\mathbf{W}^{1}\Delta$ $\mathbf{W}$	Α <sup>1</sup> Π Α	с <sup>3</sup> П с	В <sup>1</sup> П В
$He^{+}(^{2}S_{1/2})$	α <sup>a)</sup>	5.55	-0.85	-1.75	-2.07	-2.79	- 3.01	-3.27	-3.52	-6.92	-7.92
$Ne^{+}(^{2}P_{3/2})$	α	8.58	2.18	1.28	0.96	0.24	0.02	-0.24	-0.49	- 3.89	- 4.89
$Ar^{+}(^{2}P_{3/2})$	α	14.38	7.98	7.08	6.76	6.04	5.82	5.56	5.31	1.91	0.91
$Kr^+(^2P_{3/2})^{b}$	α	16.14	9.74	8.84	8.52	7.80	7.85	7.32	7.07	3.67	2.67
$Kr^{+}(^{2}S_{1/2})$	β	2.63	-3.77	-4.67	- 4.99	5.71	- 5.93	-6.19	-6.44	9.84	- 10.84
$Kr^+(^2P)$	γ	1.45	-4.95	5.85	-6.17	-6.89	-7.11	-7.37	-7.62	-11.02	-12.02
$Xe^{+}(^{2}P_{3/2})^{c})$	ά	18.01	11.61	10.71	10.39	9.67	9.45	9.19	8.94	5.54	4.54
$Xe^{+}(^{2}S_{1/2})$	β	6.75	0.35	-0.55	-0.87	-1.59	-1.81	-2.07	-2.32	5.72	-6.72
$Xe^+(^2P)$	γ	5.27	-1.13	-2.03	-2.35	- 3.07	-3.29	-3.55	-3.80	7.20	-8.20

a) Hasted's nomenclature.

<sup>b)</sup> Formation of Kr<sup>+</sup> ( ${}^{2}P_{1/2}$ ) ( $\alpha'$ ): exothermicities 0.67 eV lower.

<sup>c)</sup> Formation of Xe<sup>+</sup>(<sup>2</sup>P<sub>1/2</sub>) ( $\alpha'$ ): exothermicities 1.31 eV lower. Transfer ionisation threshold  $\Delta E_0 = -3.19$  eV.

hibits a single broad peak of overlapping structures with a maximum for exothermicities  $\approx 4.9 \text{ eV}$ , indicative of formation of excited NO<sup>+</sup> in states lying at 20–20.5 eV (taking into account the spin-orbit splitting of the Kr<sup>+</sup> product). In this region, however, we emphasize that the excited states of NO<sup>+</sup> are not well identified and thus no definite conclusions can be made, except that excited bound states of NO<sup>+</sup> do exist. Processes (IaA) and (Ia'A) can be identified as a partly resolved structure on the high-energy side of the spectrum. The formation of the excited  $Kr^+({}^2S_{1/2})$  product (process I $\beta X$ ), exothermicity 2.6 eV) is not evident.

## $3.5. NO^{2+} + Xe$

The overlapping structures in the translational energy spectrum (fig. 5) indicate that NO<sup>+</sup> is most probably formed in its highest known electronic states (B<sup>1</sup> $\Pi$ , c<sup>3</sup> $\Pi$ , B'<sup>1</sup> $\Sigma$ <sup>+</sup>, table 1), with Xe<sup>+</sup> in the ground

state. In addition, processes involving formation of the Xe<sup>+</sup> product in electronically excited states may contribute. Of those, the series of Xe<sup>+\*</sup>(<sup>2</sup>S<sub>1/2</sub>), starting with (I $\beta$ X), and Xe<sup>+\*</sup>(<sup>2</sup>P), starting with (I $\gamma$ X), is plotted in fig. 5 as an example. Excited states of Xe<sup>+</sup> are then closely packed and other series with Xe<sup>+\*</sup> in higher excited states would start successively with shifts of 0.2–0.3 eV to the left.

### 4. Discussion

The most interesting feature in the spectra of  $NO^{2+}$ and He, Ne and Ar is the shift of the peak corresponding to the (IaA) process to lower energies, with respect to the peaks corresponding to the formation of the NO<sup>+</sup> in electronically excited states (processes (IaA), (Iab), etc.). The shift of the (IaX) peaks can be explained by a considerable vibratonal excitation of the NO<sup>+</sup> product and will be discussed later on.

The double ionization energy  $(NO-NO^{2+})$  has been well established in recent measurements (table 1) to be 38.6-39.4 eV. The position of clearly identifiable peaks of processes (Iaa) and (Iab) in the spectrum  $NO^{2+} + Ne$  (fig. 2) favours the value 39.4 eV which is consistent with spectral features in figs. 1-5.

There is no indication of the participation of excited states of  $NO^{2+}$  in the translational energy spectra in figs. 1-5: capture occurs exclusively from the ground state NO<sup>2+</sup> (X  $^{2}\Sigma^{+}$ ). This observation is supported by the following facts: emissions from allowed transitions  $(A^2\Pi - X^2\Sigma^+)$  and  $(B^2\Sigma^+ - X^2\Sigma^+)$  of NO<sup>2+</sup> were observed in recent spectroscopic experiments on  $NO^{2+}$  [11]. The travel time of  $NO^{2+}$  ions from the ionization chamber to the collision centre in our apparatus was about  $10^{-5}$  s, therefore, it is most probable that the excited states of  $NO^{2+}$  formed by the electron-impact ionization passed in radiative transitions to the ground state, forming either v=0 or partly v > 0 of the NO<sup>2+</sup> (X <sup>2</sup> $\Sigma$ <sup>+</sup>) state. No low-lying non-dissociative metastable states of NO<sup>2+</sup> have been reported [14]. In addition, our recent results on translational energy spectroscopy of  $NO^{2+}$  [15] show only negligible traces of inelastic transitions from electronically excited states of NO<sup>2+</sup>; the experimental arrangement in these studies was essentially the same as described here (i.e. the ions were inelastically scattered, about  $10^{-5}$  s after being formed by electron impact) and this implies that the reactant beam of NO<sup>2+</sup> in the collision zone was indeed predominantly composed of the ground state NO<sup>2+</sup> (X<sup>2</sup>Σ<sup>+</sup>) ions.

The shift of the  $(I\alpha X)$  peak to lower energies, in the translational spectra of  $NO^{2+}$  + He, Ne, Ar systems, can be explained by vibrational excitation of the product NO<sup>+</sup> (X  $\Sigma^+$ ) ion. However, reliable data on the potential energy curves of this system show (fig. 6) that electron impact double ionization of NO will lead via a vertical Franck-Condon transition, to v=0 and, to a lesser extent, v=1 states of the  $NO^{2+}(X^{2}\Sigma^{+})$  ion. Radiative transitions from the electronically excited state NO<sup>2+</sup> (A  $^{2}\Pi$ ) may somewhat increase the population of higher (v=1, 2, 3)vibrational levels of the NO<sup>2+</sup> ground state, but not much. If we could assume - in a simple model - that the electron exchange occurs via vertical transitions (i.e. "frozen" nuclei during the collision), the majority of events wouls lead to the lowest few vibrational energy levels of the product ion NO<sup>+</sup> (X  ${}^{1}\Sigma^{+}$ ), giving rise to little (0.2-0.4 eV) or no shift of the peak max-



Fig. 6. Potential energy curves [5,14] for NO(X <sup>2</sup>Π), NO<sup>+</sup>(X <sup>1</sup>Σ<sup>+</sup>) and NO<sup>2+</sup>(X <sup>2</sup>Σ<sup>+</sup>, A <sup>2</sup>Π, B <sup>2</sup>Σ<sup>+</sup>). The dotted line represents NO<sup>+</sup>(X <sup>1</sup>Σ<sup>+</sup>) which has been perturbed by a nearby cation (see text). The upward arrows show the Franck-Condon region for formation of NO<sup>2+</sup> from NO, the downward arros show the expected region of a vertical electron exchange process.

imum. However, the collision time of the 6 keV NO<sup>2+</sup> with a noble gas atom is  $3-5 \times 10^{-15}$  s, if we can take the interaction distance (Coulomb repulsion between the products) 5-10 Å. The vibrational period of NO<sup>+</sup> in the ground state is  $1.1 \times 10^{-14}$  s, corresponding to 30-50% of the collision time, implying that the position of the nuclei N-O may change during the collision. The considerable observed shift of the peak maximum (of more than 1 eV) may have a trivial explanation, namely that the positions of the potential energy curves of the NO<sup>2+</sup> ions are different than we assume. However, it is quite unlikely that the high quality calculations of Cooper [11] could lead to an error in the position of the minimum of more than 0.1 Å (required to account for the observed vibrational excitation). Moreover, our abovementioned results by translational energy spectroscopy of NO<sup>2+</sup> [15] confirm excellently the mutual positions of the NO<sup>2+</sup> curves as calculated in ref. [11].

Therefore, we suggest that the shift of the peak maximum is due to a dynamical perturbation of the potential energy curve of NO<sup>+</sup> in the presence of the positive ion R<sup>+</sup> and/or to a similar effect for the NO<sup>2+</sup>-R pair, i.e. to the actual shape of the potential energy surfaces near the transition region (see also ref. [19]), as shown schematically in fig. 6 by a dashed curve. This dynamical change will promote the population of higher vibrational states of the final NO<sup>+</sup> product.

In favour of this model is the observed trend that the shift of the  $(I\alpha X)$  peak increases in the target atom sequence He-Ne-Ar from 1.3 eV, to 1.5 eV, to about 1.5-1.7 eV, respectively. This may be explained in the following way: occurrence of the specific state-tostate process requires reaching a certain minimum separation  $(NO-R)^{2+}$  where the respective potential energy surfaces cross and where the electron capture transition takes place. In the first approximation, this is inversely proportional to the exothermicity of the process. In the sequence He-Ne-Ar the transition region can be located approximately near the  $(NO-R)^{2+}$  separation of 2.6, 1.7 and 1.0 Å, respectively. Smaller  $(NO-R)^{2+}$  separations should result in a larger dynamical perturbation and a larger ( $I\alpha X$ ) peak shift, as observed. Calculations of the potential energy surfaces near the transition region would be needed to quantitatively confirm the validity of this qualitative model.

Two possible interpretations could be forwarded to explain the main peak in the translational energy spectrum of the  $NO^{2+}$  + Xe system (fig. 5). It may result from process  $(I\gamma' X)$  in which the ground state NO<sup>+</sup>(X<sup>1</sup> $\Sigma$ <sup>+</sup>) is formed with electronically excited  $Xe^+$  in the  ${}^{2}P_{1/2}$  state (preferably to the  ${}^{2}P_{3/2}$  state as then the total angular momentum quantum number J of the process would not be conserved). The slight shift of the maximum towards lower energies might be due to the perturbation of the NO<sup>+</sup> (X  ${}^{1}\Sigma^{+}$ ) curve by the Xe<sup>+</sup> ion, as described earlier. The shoulder on the low-energy side of the peak may result from overlapping contributions of processes in which still higher excited states of Xe are formed. However, formation of the product Xe<sup>+</sup> in the excited <sup>2</sup>P state ( $\gamma$ ) or in higher-lying excited states requires a two-electron transition (ionization of one electron and excitation of another) which seems to be less likely than a single-electron transition, as in the case of formation of the ground state or  ${}^{2}S_{1/2}$  excited state of Xe<sup>+</sup>.

An alternative explanation assumes that the main peak in the spectrum is due mainly to process (I $\alpha$ B) in which the ground state Xe<sup>+</sup> is formed wih a highly excited state of NO<sup>+</sup> lying at 2.7 eV. The exact assignment of this state is not clear [5]: it is supposed to be either the (B'  $\Sigma$ <sup>+</sup>) or a (B <sup>1</sup>Π) state. If this interpretation was correct, we could say – on the basis that the total angular momentum quantum number J ought to be a good quantum number for this process – that description of this excited state as NO<sup>+</sup>(B <sup>1</sup>Π) should be favoured, as process (I $\alpha$ B) would then be an allowed process.

In both cases the high-energy tail of the peak could be ascribed to process (I $\beta$ X) in which NO<sup>+</sup> in its ground state and Xe<sup>+</sup> in its first excited state <sup>2</sup>S<sub>1/2</sub> are formed.

#### 5. Conclusions

(a) Translational energy spectra of the products of single-electron capture processes between 6 keV NO<sup>2+</sup> and noble gas atoms were measured and a series of electronic state-to-state of processes identified.

(b) A considerable shift of the translational energy peak of NO<sup>+</sup>( $X^{1}\Sigma^{+}$ ) (process (IaX)) was ob-

served, in collisions with He, Ne, and Ar; this shift indicates vibrational excitation of the product NO<sup>+</sup>, which cannot be explained from the mutual position of the existing potential energy curves of the molecular species.

(c) A simple, qualitative model has been suggested which assumes a perturbation of the potential energy curve of NO<sup>+</sup> (X  ${}^{1}\Sigma^{+}$ ) in the presence of the noble gas ion; because the N-O internuclear distance can change during the collision, the transition between the perturbed curves may result in a higher vibrational excitation of NO<sup>+</sup> than expected from the positions of the molecular potential energy curves.

(d) Studies at low collision energies and with a better energy resolution than in these experiments are likely to bring further information on the problem (resolution of populated vibrational states in the translational energy spectra). Also, theoretical calculations of potential energy surfaces for systems  $(NO-He)^{2+}$  and  $(NO-Ne)^{2+}$  would check the validity of the described model. Investigations of both types are under progress. Undoubtedly, studies of chemiluminescence of products of these processes would be very valuable.

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#### References

- D. Mathur, R.G. Kingston, F.M. Harris and J.H. Beynon, J. Phys. B 19 (1986) L575.
- [2] J.O. Pedersen and P. Hvelplund, J. Phys. B 20 (1987) L317.
- [3] Z. Herman, P. Jonathan, A.C. Brenton and J.H. Beynon, Chem. Phys. Letters 141 (1987) 433.
- [4] Z. Herman, P. Jonathan, A.G. Brenton and J.H. Beynon, Chem. Phys., submitted.
- [5] D.L. Albriton, A.L. Schmeltekopf and R.N. Zare, J. Chem. Phys. 71 (1979) 3271.
- [6] E.Q. Thulstrup ad Y. Ohrn, J. Chem. Phys. 57 (1973) 3716.
- [7] P.W. Thulstrup, E.W. Thulstrup, A. Andersen and Y. Ohrn, J. Chem. Phys. 60 (1974) 3975.
- [8] C.E. Moore, Atomic energy levels, NBS (US Govt. Printing Office, Washington, 1949).
- [9] F.H. Dorman and J.D. Morrison, J. Chem. Phys. 35 (1961) 575;
  J. Appell, J. Durup, F.C. Fehsenfeld and P.G. Fournier, J. Phys. B 6 (1973) 197;
  Y.B. Kim, K. Stephan, E. Mark and T.D. Mark, J. Chem. Phys. 74 (1981) 6771.
- [10] J.A.R. Samson, T. Masuoka and P.N. Pareek, J.Chem. Phys. 83 (1985) 5531.
- [11] M.J. Besnard, L. Heller, Y. Malinovich and G. Dujardin, J. Chem. Phys. 85 (1986) 1316;
  L. Hellner, M.J. Besnard, G. Dujardin and J. Aarts, Abstracts of Papers, 15th ICPEAC, Brighton, IK (1987) p. 57.
- [12] Y. Iida, F. Carnovale, S. Daviel and C.E. Brion, Chem. Phys. 105 (1986) 211.
- [13] A.C. Hurley, J. Mol. Spectry. 9 (1962) 18.
- [14] D.L. Cooper, Chem. Phys. Letters 132 (1986) 377.
- [15] P. Jonathan, Z. Herman, M. Hamdan and A.G. Brenton, Chem. Phys. Letters 141 (1987) 511.
- [16] R.P. Morgan, J.H. Beynon, R.H. Bateman and B.N. Green, Intern. J. Mass Spectrom. Ion Phys. 28 (1978) 171.
- [17] E.Y. Kamber, A.G. Brenton and J.H. Beynon, J. Phys. B, to be published.
- [18] E.Y. Kamber, D. Mathur and J.B. Hasted, J. Phys. B 15 (1982) 263.
- [19] M. Lipeles, J. Chem. Phys. 51 (1969) 1252.