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Collisions of doubly charged nitrogen molecules with rare gas atoms

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Abstract. We report on single electron capture in slow collisions of doubly charged nitrogen molecules with the rare gases He, Ne and Ar. The vertical double ionization energy of N_2 as well as vertical excitation energies of N_2^{2+} have been calculated by means of the multiconfiguration coupled electron pair approximation (MC-CEPA) method. Furthermore, experiments have been carried out applying the technique of translational energy spectroscopy. The energy gain spectra of the resulting N_2^+ molecules have been analysed, showing the single electron capture to be dominated by $N_2^{2+}(X\,^1\Sigma_g^+)$ projectile ions, as well as by N_2^{2+} ions in the low-lying metastable $c\,^3\Sigma_u^+$ state. The position of the experimentally observed reaction window is discussed in terms of Franck–Condon transitions and is compared with predictions of classical descriptions.

1. Introduction

Single electron capture in slow collisions between ions and atoms has been investigated in detail for many years. The method of translational energy spectroscopy allows an identification of the initial as well as the final states of the colliding particles. This type of measurement has been performed by different groups, and many state-selective capture cross sections have been derived. The experimental results are well reproduced within either the classical over-barrier model (Niehaus 1986, Mack 1987) or by Landau–Zener calculations using multichannel models (Lebius *et al* 1989, Fukuroda *et al* 1989). The common aspect of single electron capture reactions is described in terms of a reaction window, i.e. a range of energy gains which is favoured in a collision system. Recent experiments on electron capture by multiply charged molecular ions (Mathur *et al* 1986, 1987a, b, Hamdan *et al* 1989) show the existence of a reaction window, too.

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In the following we report on collision studies which we have performed with doubly charged nitrogen molecules. On the one hand, we have calculated the vertical double ionization energy of the neutral nitrogen molecule and several vertical excitation energies of the dication N_2^{2+} with high accuracy. On the other hand, we present translational energy spectra of N_2^+ ions formed in single electron capture collisions with different rare gases. The results are discussed in terms of the molecular potential curves and a comparison is made with predictions of the classical model as well as with previous experimental results.

2. Experiment

The experiments were carried out using the translational energy spectrometer which is described in detail in previous publications (see for example Huber 1987 or Koslowski *et al* 1988). The N_2^{2+} ions, which are produced by electron impact ($E_{el} = 200$ eV) are extracted from the ion source and accelerated to a final beam energy of $E_0 = 400$ eV, which has been used throughout the experiment. The ion beam can be characterized by a diameter of about 0.5 mm and an ion current of several pA. A magnetic sector field selects the required mass over charge ratio (m/q). The ions enter a collision cell filled with the target gas at a pressure sufficiently low in order to ensure single collision conditions. The N_2^+ product ions are analysed with respect to their kinetic energy with a double hemispherical electrostatic analyser and are detected with the aid of a channeltron. The effective energy resolution $E/\Delta E$ of the energy analyser is 3000 yielding an energy spread of 130 meV; together with the finite width of the primary beam an overall resolution of about 200 meV is obtained.

Unfortunately, the N_2^{2+} molecular ions and the atomic N^+ ions do have the same m/q ratio which is selected in the magnetic field. Generally, this problem may be overcome by using an isotope enriched nitrogen gas, as the $^{14}N^{15}N$ isotope is well separated in the mass spectrum. On the other hand, at an electron impact energy of 200 eV the cross sections for the reactions

$$e^- + N_2 \rightarrow 3e^- + N_2^{2+} \tag{1}$$

and

$$e^- + N_2 \rightarrow N^+ + \ldots \tag{2}$$

are about 3.2×10^{-18} cm^2 and 5×10^{-17} cm^2, respectively (the ionization cross sections are taken from the compilation of Tawara and Kato (1987)). Therefore, with an ordinary N_2 gas we may expect that at least 6% of the particle current at $m/q = 14$ is due to N_2^{2+} ions. In fact, we have found the fraction of N_2^{2+} ions in the extracted ion beam to be greater than 80% (Lebius 1989). This is explained as follows. The N^+ ions are created via repulsive molecular states and have kinetic energies which are large compared with the thermal energy of the molecules in the gas target. The N_2^{2+} ions are formed without any additional energy gain, thus, they are easily extracted from the ion source by electrical fields in the order of several 100 mV cm^{-1}. Under these conditions, only those N^+ ions can be extracted and detected which are emitted in a small solid angle in the direction towards the extraction aperture.

Furthermore, concerning the measurement of the translational energy gain spectra of secondary N_2^+ ions, no interference with the primary N^+ ions occurs. As the product

ions N_2^+ have a kinetic energy of more than 400 eV, they can be separated easily from the 200 eV N^+ ions by means of the electrostatic energy analyser.

3. Results and discussion

3.1. Potential curves

The dication N_2^{2+} has been studied extensively during the recent decade due to its importance in energetic reactions in the ionosphere. Nevertheless, the potential curves of various states of this molecular ion and the identification of its ground state configuration are still being discussed.

A stable state of the doubly charged nitrogen molecule was identified for the first time by Hagstrum and Tate (1941). These authors determined the double ionization energy (IE) of N_2 to be 49.5 ± 0.5 eV. Later measurements led to much smaller values. Märk (1975) studied the double ionization cross section of N_2 and found an ionization threshold of 42.9 ± 0.3 eV. He attributed this threshold to a transition into the $X\,^3\Pi_u$ ground state of the N_2^{2+} ion, since early calculations of Hurley (1962) indicated that N_2^{2+} has a $X\,^3\Pi_u$ ground state. On the other hand, photofragment spectroscopy measurements of Cosby *et al* (1983) yielded a threshold energy of 43.6 ± 0.3 eV which was attributed to the $X\,^1\Sigma_g^+$ state of N_2^{2+}. It is not obvious whether the same or two different electronic states have been observed in these measurements. A recent overview of the experimentally observed states of N_2^{2+} and possible assignments has been given by Besnard *et al* (1988); a similar discussion is also contained in the theoretical paper of Wetmore and Boyd (1986).

Several *ab initio* calculations on low-lying electronic states of N_2^{2+} have been recently published: Thulstrup and Anderson (1975), Cobb *et al* (1980), Taylor (1983), Cossart *et al* (1985), Wetmore and Boyd (1986), Taylor and Partridge (1987), Olsson *et al* (1988). The by far most complete work—regarding the covered range of interatomic distances—is that of Wetmore and Boyd (1986); we, therefore, have based our discussion on their potential curves. However, their basis set is rather modest (a [3s2p1d] contracted Gaussian basis set) and not flexible enough for very precise predictions. For instance, they find that the $^3\Pi_u$ state with an equilibrium distance of 2.36 a_0 is the ground state of N_2^{2+}, while the lowest $^1\Sigma_g^+$ state with a shorter equilibrium distance of 2.19 a_0 is 0.1 eV higher in energy (adiabatically). Later, Taylor and Partridge (1987) performed extended CI and multireference CI calculations with basis sets up to [5s4p3d2f1g] and stated that $^1\Sigma_g^+$ is definitely the ground state, but the adiabatic excitation energy of the $^3\Pi_u$ state is less than 0.1 eV. Therefore, we have used the labelling as given by Taylor and Partridge (1987) in our later discussion.

There are no reliable *ab initio* calculations for the double ionization energies of N_2. Wetmore and Boyd (1986) only performed calculations for the various states of N_2^{2+} and normalized their energies such that the $v = 0$ level of the $^3\Pi_u$ state (the ground state in their calculations) is set to 42.80 eV, the experimental minimum threshold energy. In the older CASSCF calculations of Taylor (1983) a vertical appearance potential energy (VAP) of 39.8 eV has been given. This value is certainly much too low, since the CASSCF treatment neglects dynamic correlation effects which lower the ground state of N_2 relative to N_2^{2+}. Likewise, Taylor's CASSCF value for the asymptotic limit $2 * N^+(^3P)$ relative to $2 * N(^4S)$ is 26.83 eV, much too low compared with the experimental value of 29.08 eV (Moore 1971).

In order to determine accurate values for the vertical ionization energies of N_2 we have performed a series of *ab initio* calculations on various states of N_2^{2+} as well as for the ground state of N_2. All calculations have been performed for a N–N distance of 2.074 32 a_0 which is the equilibrium distance of N_2 in its $X\ ^1\Sigma_g^+$ ground state (Huber and Herzberg 1979). The single-reference CEPA method as described by Staemmler and Jaquet (1981) and, in particular, for the $X\ ^1\Sigma_g^+$ state of N_2^{2+} the multireference CEPA method (Fink 1991, Fink and Staemmler 1991) were used. It should be noted that there are only minor differences (0.1 eV) between the single-reference and the multireference CEPA calculations for those states (all but $X\ ^1\Sigma_g^+$) which are essentially single reference states. The CASSCF calculations for $X\ ^1\Sigma_g^+$ on which the multireference CEPA calculations for this state are based included $2\sigma_u$ and $3\sigma_g$ as active orbitals; a larger active space was not necessary.

Our calculations were performed with two different basis sets: a medium-sized basis of TZ2P quality (a [6s3p2d] contracted set) and an extended basis ([8s5p2d1f] contracted set) with reasonably chosen exponents of the polarization functions.

Our calculated vertical double ionization energies are given in table 1 together with an extrapolation of our values to infinite basis sets, the results of Taylor (1983), Wetmore and Boyd (1986) and experimental values from different sources. Our extrapolation is based on the observation that the CEPA results for the vertical IE rise by 0.2–0.3 eV when the basis is augmented from TZ2P to the extended set. Another 0.2–0.3 eV will probably be gained in the limit of a complete basis; this is in line with

Table 1. Vertical double ionization energies of N_2 (in eV) relative to the minimum of the potential curve of $N_2(X\ ^1\Sigma_g^+)$ at $R_e = 2.074\ 32\ a_0 = 1.097\ 68$ Å.

States of N_2^{2+}	TZ2P basis		Extended basis		Extrap[b]	Taylor[c]	Wetmore and Boyd[d] CI	Expt
	SCF[a]	CEPA	SCF[a]	CEPA	VAP	CASSCF		
$X\ ^1\Sigma_g^+$	42.07	42.44	42.03	42.70	42.9	(42.9)	43.0	42.9 ± 0.3[e] 43.1 ± 0.1[f]
$a\ ^3\Pi_u$	42.53	43.35	42.50	43.59	43.7	44.4	(43.9)	43.6 ± 0.3[g]
$b\ ^3\Sigma_g^-$	42.44	45.00	42.47	45.29	45.4	46.6	45.9	
$c\ ^3\Sigma_u^+$	42.95	43.83	42.91	44.12	44.4	44.6	44.5	
$A\ ^1\Pi_u$	43.87	44.84	43.85	45.08	45.2	46.0	45.4	45.2 ± 0.3[h]
$B\ ^1\Delta_g$	43.87	46.13	43.86	46.38	46.5	47.6	47.2	46.1 ± 0.3[h]
2* 1st IE(N)[i]	27.95	28.64	27.92	28.80	29.1	26.83		29.08[j]

[a] CASSCF with two active orbitals $2\sigma_u$, $3\sigma_g$ for $X\ ^1\Sigma_g^+$, single reference restricted Hartree–Fock for all other states.

[b] Relative to $N_2(X\ ^1\Sigma_g^+, v = 0)$; the method of extrapolation is explained in the text; the estimated error for all states ±0.2 eV, VAP = vertical appearance potential energy.

[c] Taylor (1983); since no vertical ionization energies are given in this paper, we took the experimental VAP of 42.9 eV for $X\ ^1\Sigma_g^+$ and added the vertical excitation energies of N_2^{2+} from his figures 1 and 2.

[d] Wetmore and Boyd (1986). No vertical IE are given in this paper. We interpolated linearly between the values at $R = 1.06$ Å and 1.12 Å in table 2.

[e] Märk (1975).

[f] Hellner *et al* (1988).

[g] Cosby *et al* (1983).

[h] Besnard *et al* (1988); our assignment of the peak at 46.1 eV is different from the experimental paper.

[i] Two times the first ionization energy of the N atom.

[j] Moore (1971).

the behaviour of the IE of the N atom. This estimate has to be reduced by 0.15 eV (zero-point energy of the $X\,^1\Sigma_g^+$ ground state of N_2 (Huber and Herzberg 1979)) to obtain the vertical appearance potentials. The estimated errors are ±0.2 eV, partly caused by the extrapolation and partly by the CEPA estimate of unlinked cluster contributions.

Table 1 shows that our results agree perfectly with the experimental VAP as far as they are known, and with the results of Wetmore and Boyd (1986). The CASSCF results of Taylor (1983) show larger deviations, in particular for the higher states. But it should be stressed that only our calculations are true calculations of the IE; both in Taylor's work and in that of Wetmore and Boyd only relative energies of the states of N_2^{2+} were calculated and the position of the ground state adjusted to experiment. The assignment of the states $X\,^1\Sigma_g^+$, $a\,^3\Pi_u$, $A\,^1\Pi_u$ seems unambiguous, that of $B\,^1\Delta_g$ is questionable since there are several other states in this energy range which we have not included.

Figure 1 shows the potential curves of singly and doubly charged nitrogen molecules. The potential curves for various states of N_2^+ are taken from Gilmore (1965); those for the five states of N_2^{2+} being important for the charge exchange reactions discussed below are taken from Wetmore and Boyd (1986), corrected with our calculated vertical ionization and excitation energies. The additional full curve labelled as $N^+ + N^+$ represents the Coulomb repulsion between two N^+ ions, normalized to twice the ionization energy of atomic nitrogen plus the dissociation energy of the nitrogen molecule.

If the ionization process proceeds via vertical transitions (this assumption is quite natural since the ionization takes place on a time scale which is short compared with the relaxation time of the nuclei), the states $X\,^1\Sigma_g^+$ and $c\,^3\Sigma_u^+$ will be dominantly populated in low vibrational levels while the $a\,^3\Pi_u$, $b\,^3\Sigma_g^-$ and $A\,^1\Pi_u$ states will be populated in highly excited vibrational states. In the case of the $b\,^3\Sigma_g^-$ state and the higher electronic states of N_2^{2+} (which are not shown in figure 1, but can be taken from the paper of Wetmore and Boyd (1986)) the vertical excitation energies lie above the barriers of the respective potential curves at larger distances. Therefore, these states, if populated in the ionization process, will dissociate immediately.

Higher excited vibrational levels of the $A\,^1\Pi_u$ state, which are dominantly populated in the ionization process, are known to predissociate (Cosby *et al* 1983, Gibson *et al* 1989, Masters and Sarre 1990). Therefore, this state is believed to be of minor importance. The $c\,^3\Sigma_u^+$ state cannot decay into the low-lying $a\,^3\Pi_u$ state nor into the $X\,^1\Sigma_g^+$ ground state. From these arguments we conclude, that the majority of the N_2^{2+} ions entering the collision region are in the $X\,^1\Sigma_g^+(v=0\text{–}2)$ ground state and in the excited metastable states $a\,^3\Pi_u(v=2\text{–}11)$ and $c\,^3\Sigma_u^+(v=0,1)$. This conclusion will give a consistent interpretation of the measured energy gain spectra, as we will see in the following discussion.

3.2. N_2^{2+}/He

Figure 2 shows the energy gain spectrum of N_2^+ ions formed in collisions of N_2^{2+} with He. Displayed is the counting rate for secondary ions versus the energy gain Q. The broken curve is the result of a model calculation discussed in a paragraph further below. The measured energy gain of 4.3 eV is too large to be explained by electron capture of ground state projectiles. N_2^{2+} ions being excited in the metastable $c\,^3\Sigma_u^+$ state dominate the capture process. Two reactions are contributing, namely

$$N_2^{2+}(c\,^3\Sigma_u^+(v=0,1)) + He \rightarrow N_2^+(X\,^2\Sigma_g^+(v'=v)) + He^+ + 4.3\ \text{eV} \qquad (3)$$

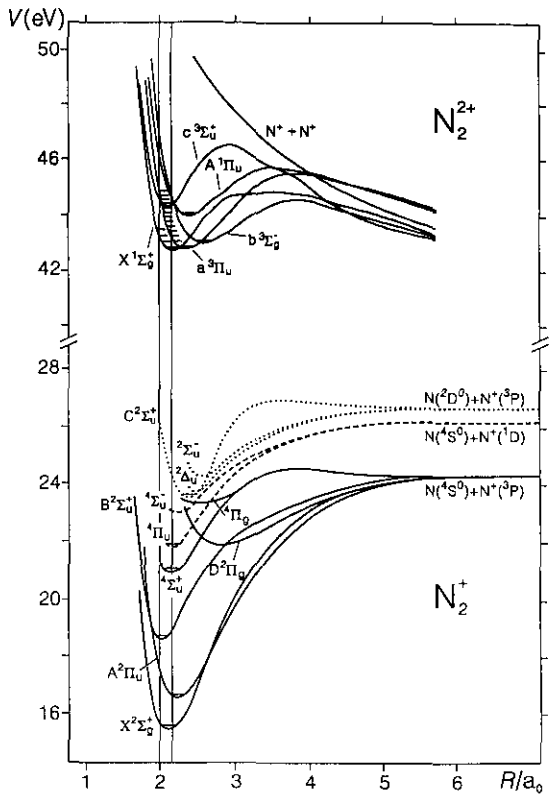

Figure 1. Potential curves for various electronic states of singly and doubly charged nitrogen molecules. The lower part of the figure shows the potential curves for N_2^+, taken from Gilmore (1965). The full, broken and dotted curves indicate that the states result from nitrogen atoms and ions in the ground states ($^4S^o$ and ^3P) as well as in metastable states ($^2D^o$ and ^1D). The upper part of the figure shows the potential curves of the ground state $X\,^1\Sigma_g^+$ as well as of four metastable states $a\,^3\Pi_u$, $b\,^3\Sigma_g^-$, $A\,^1\Pi_u$ and $c\,^3\Sigma_u^+$ of the N_2^{2+} ion, taken from Wetmore and Boyd (1986), but with a different labelling (see text); the potential curve for the $a\,^3\Pi_u$ state is shifted by 0.1 eV according to the results of Taylor and Partridge (1987). Full curve labelled $N^+ + N^+$: Coulomb potential of two nitrogen ions. The vertical lines indicate the equilibrium region of the N_2 molecule in its ground state.

and to a minor extent

$$N_2^{2+}(c\,^3\Sigma_u^+(\nu=0,1)) + He \rightarrow N_2^+(A\,^2\Pi_u(\nu')) + He^+ + (2.5\text{–}3.2)\ \text{eV}. \qquad (4)$$

The energetic positions of these reactions ($\nu = \nu' = 0$) are indicated in the upper part of figure 3 by vertical bars. The corresponding reactions with molecular projectiles in the ground state $X\,^1\Sigma_g^+$ are characterized by smaller energy gains and hence by curve crossings which occur at large internuclear distances (11 a_0 and 19 a_0, respectively). In order to estimate the contributions of these channels, we have performed a multichannel Landau-Zener calculation treating reactions with different vibrational levels but the same electronic state as one reaction channel only. The corresponding method of calculation is described in a previous publication (Lebius *et al* 1989). The results which are given in table 2 show clearly the dominance of the metastable reaction.

At energy gains between 3 eV and 4 eV additional contributions from N_2^{2+} ions in the vibrationally excited $a\,^3\Pi_u$ state are possible and may explain the small structure

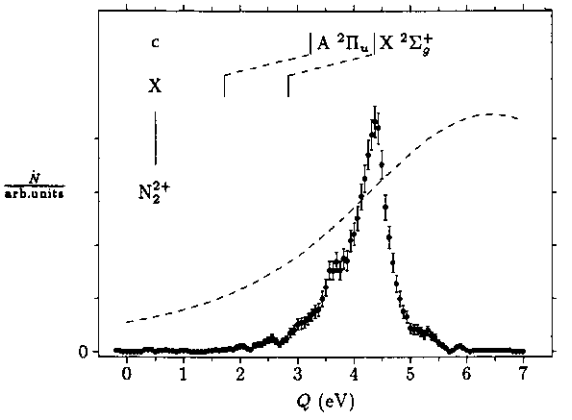

Figure 2. Translational energy spectrum of N_2^+ ions produced in N_2^{2+}/He collisions measured at $E_0 = 400$ eV and at a scattering angle of $\vartheta = 0°$. The energy defects of reaction channels leading to N_2^+ ions in the $A\,^2\Pi_u$ and $X\,^2\Sigma_g^+$ states are indicated in the upper part of the figure. The letters c and X label the projectile ion states. The broken curve represents the predictions of the classical over-barrier model.

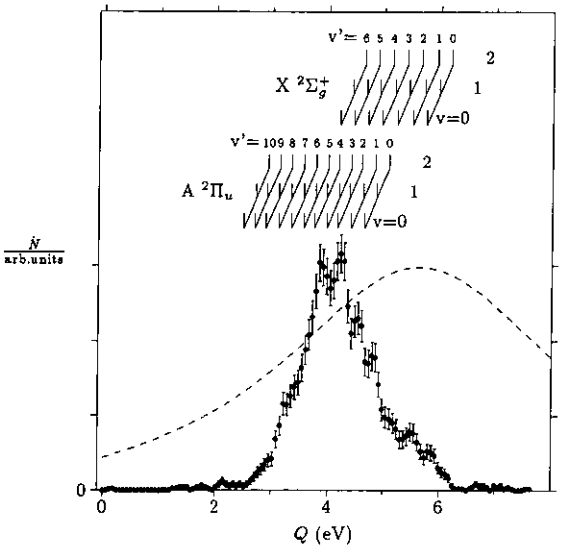

Figure 3. Translational energy spectrum of N_2^+ ions resulting from N_2^{2+}/Ne collisions at $E_0 = 400$ eV and $\vartheta = 0°$. The spectrum shows the counting rate of the secondary N_2^+ ions plotted against the energy gain Q. The bars in the upper part of the spectrum mark the positions of the reaction channels for capture into the $X\,^2\Sigma_g^+$ and $A\,^2\Pi_u$ states of the N_2^+. The letters c and X label the projectile ion states. The broken curve represents the predictions of the classical over-barrier model.

measured at $Q = 3.6$ eV:

$$N_2^{2+}(a\,^3\Pi_u(\nu = 2\text{–}11)) + He \rightarrow N_2^+(X\,^2\Sigma_g^+(\nu')) + He^+ + (3\text{–}4)\,\text{eV}. \qquad (5)$$

This explanation is in agreement with our theoretical result (see table 2). Due to the

Table 2. Cross sections for state-selective single electron capture in N_2^{2+}/He and N_2^{2+}/Ne collisions according to multichannel Landau-Zener calculations (ΔE = experimentally observed energy defect, E_0 = collision energy, σ_{21} = single electron capture cross section).

Projectile	Initial projectile state (N_2^{2+})	Final projectile state (N_2^+)	ΔE (eV)	σ_{21} (cm^2)	
				$E_0 = 400$ eV	$E_0 = 6$ keV
He	$X\,^1\Sigma_g^+$	$X\,^2\Sigma_g^+$	2.5	$<10^{-19}$	$<10^{-19}$
		$A\,^2\Pi_u$	1.5	$<10^{-20}$	$<10^{-20}$
	$a\,^3\Pi_u$	$X\,^2\Sigma_g^+$	3.6	6.2×10^{-17}	1.6×10^{-17}
		$A\,^2\Pi_u$	2.5	$<10^{-19}$	$<10^{-19}$
	$c\,^3\Sigma_u^+$	$X\,^2\Sigma_g^+$	4.1	4.2×10^{-16}	1.2×10^{-16}
		$A\,^2\Pi_u$	3.1	4.9×10^{-18}	1.3×10^{-18}
Ne	$X\,^1\Sigma_g^+$	$X\,^2\Sigma_g^+$	5.5	1.5×10^{-16}	9.0×10^{-16}
		$A\,^2\Pi_u$	4.2	9.7×10^{-16}	3.1×10^{-16}
	$c\,^3\Sigma_u^+$	$X\,^2\Sigma_g^+$	7.1	$<10^{-20}$	1.7×10^{-18}
		$A\,^2\Pi_u$	5.8	2.6×10^{-17}	6.2×10^{-16}

expected vibrational excitation of the primary projectiles in the $a\,^3\Pi_u$ state, the reaction is more exoergic than that for projectiles in the $X\,^1\Sigma_g$ ground state, although both states are nearly degenerate for $\nu = 0$.

We have measured the counting rate for reaction channel (3) in dependence on the electron energy in the ion source close to the ionization threshold ($E_{el} = 40$–50 eV). The threshold value for the production of the relevant projectile state is found to be 45 ± 1.1 eV. This value agrees very well with the vertical ionization energy for the production of $N_2^{2+}(c\,^3\Sigma_u^+)$ (see figure 1) and hence supports the identification of the dominant reaction channel given above.

We may compare our results with those of Hamdan and Brenton (1989) obtained at a collision energy of 6 keV. Although there is some ambiguity between the energetic peak positions in the spectrum and the values given in the table of their paper, the identification of the dominant peak agrees well with our interpretation (reaction (3)).

In addition, the authors have found further reaction channels to contribute to the single electron capture process. Two of them are attributed to N_2^{2+} projectiles in the $a\,^3\Pi_u$ state, characterized by energy defects of 1.3 eV and 2.4 eV. As the energetic halfwidth of these structures is very small (<300 meV), one may expect the number of active vibrational levels to be very small either. Hence, a correlation with projectiles in the $X\,^1\Sigma_g^+$ seems to be more likely than with those in the $a\,^3\Pi_u$ state, which are formed primarily in a wider range of vibrational levels ($\nu = 2$–11).

The fact, that both peaks do appear only in the high energy spectrum, is not obvious to explain. According to our calculation the cross section should even decrease at higher energies as the coupling matrix elements are rather small. On the other hand, the measured signals are proportional to the product of the cross section and the metastable fractions. The experimental finding can be explained, if the absolute metastable fractions are much smaller in the experiment of Hamdan and Brenton (1989) than in the present case. In fact, their excitation-de-excitation spectrum does not show any superelastic peak, which is a monitor for the presence of ions in metastable excited states.

3.3. N_2^{2+}/Ne

The translational energy spectrum of N_2^+ ions due to N_2^{2+}/Ne collisions is shown in

figure 3. The dominant reaction channels are characterized by energy gains close to 4 eV, some weaker contributions occur at about 5.5 eV. The energetic width of the measured distribution is found to be much larger than the experimental resolution, which corresponds to about 200 meV. This is due to the fact, that many different vibrational levels in the entrance as well as in the exit channel are involved in the capture reaction.

In the upper part of the figure the possible reaction channels are marked by vertical bars which correspond to single electron capture into specific vibrational levels ν' of the $X\,^2\Sigma_g^+$ and $A\,^2\Pi_u$ states of N_2^+ assuming the primary N_2^{2+} projectile to be in the vibrational level $\nu = (0\text{-}2)$ of the $X\,^1\Sigma_g^+$ state. According to this assignment we may specify as dominant reaction channels:

$$N_2^{2+}(X\,^1\Sigma_g^+(\nu = 0\text{-}2)) + Ne \rightarrow N_2^+(A\,^2\Pi_u(\nu' > \nu)) + Ne^+ + 4.2\ eV \qquad (6)$$

and

$$N_2^{2+}(X\,^1\Sigma_g^+(\nu = 0\text{-}2)) + Ne \rightarrow N_2^+(X\,^2\Sigma_g^+(\nu' \sim \nu)) + Ne^+ + 5.5\ eV. \qquad (7)$$

The capture into higher vibrationally excited levels in reaction (6) can be explained in terms of Franck–Condon transitions. As the potential curve for the $N_2^+(A\,^2\Pi_u)$ state has its minimum at 2.23 a_0, which is larger than that for the $N_2^{2+}(X\,^1\Sigma_g^+)$ state, transitions into vibrational excited states are favoured.

In addition, further contributions are possible at energy gains between 5 eV and 6 eV due to reactions of N_2^{2+} projectiles in the metastable $c\,^3\Sigma_u^+$ state:

$$N_2^{2+}(c\,^3\Sigma_u^+(\nu = 0\text{-}2)) + Ne \rightarrow N_2^+(A\,^2\Pi_u(\nu')) + Ne^+ + 5\text{-}6\ eV. \qquad (8)$$

However, these contributions are believed to be of minor importance for two reasons. On the one hand, at a collision energy of 400 eV our MCLZ calculation yields a very small cross section for this reaction (see table 2). The dominant reaction channel is found to correspond to equation (6), reaction (7) is expected to contribute in the order of 10%.

On the other hand we have measured the spectrum in dependence on the electron energy close to the threshold for the production of N_2^{2+} ions from N_2. An analysis of these data yields a value for the ionization threshold of 43.3 ± 1.1 eV, which is in agreement with the production of N_2^{2+} ions in the ground state $X\,^1\Sigma_g^+(\nu = 0\text{-}2)$.

Hamdan and Brenton (1989) find in accordance with our measurements the dominant reactions to be characterized by $Q \sim 4$ eV and $Q \sim 5.5$ eV, whereby the latter one gives the dominant contribution. This change in intensity is in agreement with our theoretical calculation, as may be seen in table 2.

However, the authors attribute both reactions to N_2^{2+} projectiles in the $a\,^3\Pi_u$ state. An argumentation, similar as given before in the N_2^{2+}/He system, favours an identification with the $X\,^1\Sigma_g^+$ state due to reactions (6) and (7).

3.4. N_2^{2+}/Ar

The energy gain spectrum, measured in the collision system N_2^{2+}/Ar, is shown in figure 4. The halfwidth of the spectrum, which is centred at an energy gain of 3 eV to 4 eV, is rather large compared to the systems discussed before. Therefore, a large number of reactions is expected to contribute. As in the previous figures, possible reaction channels are marked by vertical bars indicating transitions between individual vibrational levels of the following reaction:

$$N_2^{2+}(X\,^1\Sigma_g^+(\nu = 0\text{-}2)) + Ar \rightarrow N_2^+(C\,^2\Sigma_u^+(\nu' = 0\text{-}5)) + Ar^+ + (3\text{-}4)\ eV. \qquad (9)$$

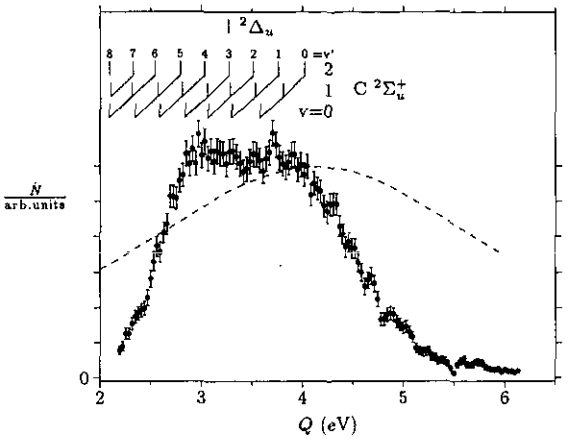

Figure 4. Energy gain spectrum of N_2^+ ions resulting from N_2^{2+}/Ar collisions at an energy of 400 eV and $\vartheta = 0°$. The reaction has an exoergicity of 3.4 eV and can be attributed to the capture of the electron into the $N_2^+(C\ ^2\Sigma_u^+)$ state as well as into the $^2\Delta_u$ state. The letters c and X label the projectile ion states. The broken curve represents the predictions of the classical over-barrier model.

Capture into the highly excited $C\ ^2\Sigma_u^+$ state of N_2^+ is explained by the lower binding energy of the electron in the Ar atom. Also the strong vibrational excitation may be expected, if Franck–Condon transitions are involved.

In addition, further capture reactions may contribute to the measured spectrum. On the one hand, capture by ground state projectiles can populate other highly excited doublet states like $^2\Delta_u$, the energetic position of which is shown in figure 4 for the $\nu = 0 \rightarrow \nu' = 0$ transition. The population of quartet states is not expected, as the total spin is not conserved in such a reaction. On the other hand, projectiles in the metastable $c\ ^3\Sigma_u^+$ and $a\ ^3\Pi_u$ states may contribute as well at energy gains above 4 eV.

3.5. Discussion in terms of the 'reaction window'

Single electron capture by doubly and triply charged molecular ions has been described recently in terms of a reaction window. Mathur *et al* (1986, 1987a, b) have found, that its position with respect to ΔE or with respect to the nuclear distance R_C, which characterizes the effective potential curve crossings, depends on the structure of the molecular ion. Whereas in the case of CS_2^{2+} and OCS^{3+} projectiles the reaction window is centred at $R_C \sim 12\ a_0$, they found for CS_2^{3+} a smaller value: $R_C \sim 5\ a_0$ (erroneously a value of 2.5 a_0 instead of 5 a_0 is given in the original paper). The reason for this different behaviour is not explained so far.

In the present system of N_2^{2+} the dominant reaction channels are always characterized by ΔE values between 3 eV and 5 eV, independent of the target ionization energy. This value corresponds to a crossing distance of $R_C \sim 7\ a_0$, which agrees with the values obtained for atomic ion/atom collisions.

In figures 2 to 4 we have included reaction windows as calculated from the Niehaus model, shown as dashed curves. The applicability of this model to a triatomic system is not very obvious, however, it has been applied successfully for the description of electron capture from molecular hydrogen (Mack 1987). On the one hand, the representation of molecular states with different vibrational and rotational levels by a single effective quantum number seems to be very crude. On the other hand, the nuclear

distance R_0 between the projectile and target, being required for a classical transfer of the target electron to the projectile, is not very large compared to the equilibrium distance R_e of the N_2 molecule: $R_e = 2.1\ a_0$, $R_0(\mathrm{He}) = 4.2\ a_0$, $R_0(\mathrm{Ne}) = 4.8\ a_0$, $R_0(\mathrm{Ar}) = 6.6\ a_0$. Due to the large width of the calculated window a comparison with the measured spectra is not very conclusive; the agreement seems to be best in the case of the Ar target, where the value of R_0 is largest.

In all three targets the measured reaction channels occur at smaller energy defects, which means $R_C > R_0$, than predicted by the classical consideration. In the case of He this might be due to the absence of suitable reaction channels with curve crossings at $R_C = R_0$. In the other systems, however, outer crossings are more important. A similar shift towards less exoergic reactions has been seen recently in the C^{2+}/H_2 system and has been explained by the influence of the Franck-Condon factors describing the transition in the molecular target system (Unterreiter *et al* 1991). This interpretation is supported by earlier measurements in Xe^{2+}/H_2 and Ne^{2+}/H_2 collisions (Huber and Kahlert 1985, Fukuroda *et al* 1989). Another reason may be the large number of final states in the molecular ion, which reduces the incoming flux before reaching the inner curve crossings although the individual transition probability is pretty small for each curve crossings at large internuclear distances.

4. Conclusion

We have investigated slow collisions of N_2^{2+} ions with the rare gases He, Ne and Ar by means of translational energy spectroscopy. On the one hand, we have determined vertical double ionization energies of the N_2 molecule performing multireference CEPA calculations. The results obtained for several low-lying states of the dication N_2^{2+} are characterized by an absolute error of ≤ 0.2 eV. On the other hand, the dominant single electron capture channels have been analysed.

Whereas in the Ar target capture occurs into high-lying excited states of $N_2^+(C\,^2\Sigma_u^+, {}^2\Delta_u)$, with the Ne target the ground state $X\,^2\Sigma_g^+$ and the first excited state $A\,^2\Pi_u$ are populated. In both cases projectile ions in the ground state $X\,^1\Sigma_g^+$ are dominantly contributing. In the He target, due to the high binding energy of the electron the ground state reaction is characterized by a very small energy gain corresponding to a curve crossing located at a large nuclear distance. Therefore no contributions from such a reaction are found. Instead, projectile ions in an excited metastable state ($c\,^3\Sigma_u^+$) are responsible for the capture reaction.

Electron capture into molecular ions is in agreement with the assumption of Franck-Condon transitions. In comparison with the predictions of the classical model the experimental spectra are found to be much narrower and to be shifted towards smaller energy defects. This may be explained by different arguments: (i) the basic assumptions of this model do not hold any longer; a serious description requires a triatomic representation of the collision system; (ii) the inclusion of Franck-Condon factors leads to a change of the important reaction channels; (iii) the large number of reaction channels with curve crossings located at large internuclear distances reduces the flux reaching the inner curve crossings.

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