On the excited states of N_2^+ produced in (near-) thermal charge transfer between He^+ and N_2

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1. Update of earlier work

At (near-)thermal energies, charge transfer ("CT") between helium ions (RE = 24.587 eV) and molecular nitrogen produces emission from the C $^2\Sigma_u^+$ state of N_2^+, from the B $^2\Sigma_u^+$ state, and, at low pressures, extensive emission from one or more long-lived, initially unidentified state(s) of N_2^+[1-4]. Its lifetime was estimated to be larger than $6x10^{-7}$ s, and probably of the order of 10^{-5} s [3]. Cossart et al. were able to assign the most prominent of these emissions to the transition D' $^2\Pi_g$(v') → A $^2\Pi_u$ (v" =7,8,and 9) [5]. Using a novel discharge source and photographic recording, they carried out a rotational analysis complemented by SCF ab-initio calculations. The emitting D' $^2\Pi_g$(v') vibrational levels were tentatively labeled as v' = 0,1,2 [5]. They are located at 23.698, 23.786 and 23.870 eV above the ground state of N_2 and their formation by CT from He^+ is thus exothermic by 0.889, 0.801 and 0.717 eV, respectively.

Baltzer et al. reported a weak vibrational progression starting at about 23.7 eV in the UV photoelectron spectrum (PES) of N_2 and assigned it to a N_2^+ state labeled 2 $^2\Pi_g$ [6]. Its vibrational level v'=2 was observed at 23.881 eV, in close agreement with the value D' $^2\Pi_g$ v' =2 at 23.870 eV obtained from the analysis by Cossart et al. [5]. The levels v' = 0 and 1 were not clearly seen in the PES. The difference between the corresponding energies listed by Baltzer et al. as 23.755 and 23.809 eV, and those determined by Cossart et al. for D' $^2\Pi_g$ v' =0 and 1, is probably not significant. One thus concludes that the state labeled 2 $^2\Pi_g$ by Baltzer et al. [6] and the one earlier called D' $^2\Pi_g$ by Cossart et al. [5] are one and the same electronic state of N_2^+. The vibrational numbering adopted is consistent between the two publications.

The potential curve computed for the D' state has a broad, irregular well which supports close-lying vibrational levels with initial spacings of the order of 85 meV [5-7]. From an energetics point of view it can be

populated by (near-)thermal He^+/N_2 charge transfer up to the level v'=10 located by Baltzer et al. at 24.541 eV [6] and by Yencha et al. at 24.548 eV [7]. In the spectra of refs. [1,3,4], however, only emission from the vibrational levels v'=0 and v'=1 can be clearly identified on the basis of the bandhead wavelengths determined by Cossart et al. [5], the most prominent emissions being those corresponding to the transitions from D' (v'=0) to A (v"=7 and 9) and from D' (v'=1) to A (v"= 8 and 9). Sekiya et al. also identify the transitions from v'=2 to v"= 7 and 8 [4], but overlap with v'=0 to v"=6 and 7 renders this attribution less certain. Higher vibrational levels could not be identified in any of the spectra reported in references [1,3,4]. The D' state is thus seen to be populated in a very narrow range of vibrational levels, just as in the case of the C $^2\Sigma_u^+$ state where (near-)thermal He^+/N_2 CT populates only the levels v'=3 and 4, even though CT into the lower vibrational levels would be exothermic by only a fraction of an eV [1-3]. In the case of CT into the D' $^2\Pi_g$ state, the populated vibrational levels are off-resonance by between 0.7 and 0.9 eV.

A propensity for a rather narrow range of product states can be rationalised as resulting from curve-crossings between vibronic diabates, where only a limited number of crossings will effectively lead to CT, namely those where the system "hesitates" between diabatic and adiabatic behaviour, resulting in a rather narrow range of product levels [8].

2. Implications

The main configuration of the D' $^2\Pi_g$ state differs from that of the A $^2\Pi_u$ state by two spin-orbitals [5]. Its transition strength thus relies on intensity borrowing by configuration interaction, which is consistent with the long lifetime cited above. In the absence of collisional quenching, the D' levels resulting from charge transfer between He^+ and N_2 will emit to the vibrational levels of the A state concentrated around v"=7,8 and 9. These in turn radiate to the N_2^+ electronic ground state, an emission system known as the Meinel bands. Transitions from high vibrational levels of the A state, ranging from v"=5 to 17, were identified by observing the emission from beams of N_2^+ ions; their lifetime was evaluated at about 6×10^{-6} s [9]. A detailed analysis was carried out by Maier and Holland, for both $^{28}N_2^+$ and $^{30}N_2^+$ [10]. Their paper lists vibrational branching ratios, those pertaining to transitions from A $^2\Pi_u$ (v"=7,8,9) to $X^2\Sigma_g^+(v)$ being as follows for $^{28}N_2^+$:

	$X^2\Sigma_g^+(v)$							
	0	1	2	3	4	5	6	7 and more
$A\ ^2\Pi_u$ (v")								
7	0.0031	0.0397	0.1945	0.3972	0.2698	0.0097	0.0577	0.0284
8	0.0010	0.0156	0.0964	0.2893	0.3774	0.1428	0.0017	0.0756
9	0.0003	0.0059	0.0441	0.1709	0.3485	0.3022	0.0528	0.0784
Equal 7;8;9	0.0015	0.0204	0.1117	0.2858	0.3319	0.1516	0.0374	0.0598

Vibrational branching ratios for A→X emission

It is apparent that He^+/N_2 charge transfer into the D' $^2\Pi_g$ state, followed by D'→A and A→X emission will, in the absence of collisional quenching, lead to the production of vibrationally excited N_2^+ on a timescale of the order of 10^{-5} s. More than half of this N_2^+ is produced in the levels v = 3 and 4 of the electronic ground state, and hardly any in the level v = 0. A lower limit to the reaction rate for this production can be evaluated from simultaneous optical and mass spectrometric experiments as outlined in ref. [2]. The C $^2\Sigma_u^+$ v' = 3 and 4 levels populated by thermal He^+/N_2 charge transfer decay either by emission to ground state N_2^+, or by predissociation into ground state N^+ + N. The competition between the two decay modes varies considerably depending on the N_2 isotope [11]: $k(C,N^+)/k(C,N_2^+)$ = 10.6 for $^{28}N_2$ and = 1.09 for $^{30}N_2$ [2] when summed over v'= 3 and 4. If all of the N^+ and N_2^+ was produced via the C state, the ratio k(total N^+)/k(total N_2^+) would show the same isotope effect. In fact, the latter ratio varies less than that for the C state, which imposes alternate reaction channels as indicated in the table below.

Rate constants for $He^+ + N_2 \rightarrow He + N_2^+$ or $He + N + N^+$ as specified / 10^{-9} cm^3/sec

Lower limit on k(other N^+)

	Total CT	Total N_2^+	Total N^+	N_2^+ from C	N^+ from C	Total C	Other N_2^+	Other N^+
$^{28}N_2$	1.20	0.51	0.69	0.065	0.69	0.75	0.45	0.00
$^{30}N_2$	1.20	0.79	0.41	0.34	0.37	0.71	0.45	0.04

No isotope effect on N^+/N_2^+ ratio from other than C state

	Total CT	Total N_2^+	Total N^+	N_2^+ from C	N^+ from C	Total C	Other N_2^+	Other N^+
$^{28}N_2$	1.20	0.51	0.69	0.059	0.62	0.68	0.45	0.069
$^{30}N_2$	1.20	0.79	0.41	0.31	0.34	0.64	0.48	0.073

The top of this table shows the lower limits to alternate channels obtained by imposing these to have rate constants that are zero or positive. The lower part assumes that the alternate channels do not show an isotope effect in the N^+/N_2^+ production ratio. In both cases one finds that at least

88% of the $^{28}N_2^+$ results from charge transfer into states other than the C state, the rate for production of these alternate channels representing at least 0.45 x 10^{-9} cm^3/s. Of this, at most 0.02 x 10^{-9} cm^3/s represents CT into the B $^2\Sigma_u^+$ state, followed by emission to the electronic ground state [3]. Unless yet other, unidentified, N_2^+ states are formed, CT into the D' $^2\Pi_g$ state, followed by D'→A and A→X emission is thus found to produce vibrationally excited N_2^+ at a rate of more than 0.43 x 10^{-9} cm^3/s. As CT between N_2^+ and Ar [12,8] and also between N_2^+ and Kr [13] depends very strongly on the vibrational excitation of the parent ion, SIFT experiments, e.g., should be able to use these as monitor reactions to verify the high vibrational excitation of N_2^+ produced by He^+/N_2 CT.

We note that the ratio of the rate for C $^2\Sigma_u^+$ (v') state predissociation to that for C→X emission was determined in ref.[11] using calculated "vertical' excitation and emission probabilities. Photoelectron photoion coincidence measurements on an instrument such as DELICIOUSIII [14] should be able to verify the underlying assumptions by determining this ratio directly, as a function of vibrational level and isotopic substitution.

4. References

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