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$^{15}N_2^+(D'^2\Pi_{gr}-A^2\Pi_{ui})$ Emission Resulting from the $He^+ + {}^{15}N_2$ Charge Transfer Reaction

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The $^{15}N_2^+(D'^2\Pi_{gr}-A^2\Pi_{ui})$ emission system arising from the $He^+ + {}^{15}N_2$ reaction has been observed both in a flowing afterglow and in a low-pressure chamber combined with flowing afterglow. The absolute vibrational quantum numbers for the D′−A system have been proposed by measuring isotopic shifts between $^{15}N_2^+$and $^{14}N_2^+$ bands.

1. Introduction

The $He^+ + N_2$ reaction is one of the most extensively studied charge transfer (CT) reaction. However, the structured continuum emission in the 200-320 nm region[1-4] is not fully understood. Cossart *et al.*[3] was first to identify the $N_2^+(D'^2\Pi_{gr}-A^2\Pi_{ui})$ emission system in the 220-280 nm region and carried out complete rotational analysis for the $(v'_0, 7-9)$ bands assuming that v'_0-1, v'_0, and v'_0+1 are the three first vibrational levels of the D′ state. On the basis of their vibrational assignment of the D′−A system, we have estimated the relative excitation rate constant for the D′ state to be about 30% of that of the C state in the $He^+ + {}^{14}N_2$ reaction.

Studies on the isotopic effect on the emission spectrum in the 200-320 nm region make it possible to determine the absolute vibrational quantum numbers for the D′−A system, and provide information on the formation process of the D′ state.

$$He^+ + N_2 \rightarrow {}^{14}N_2^+(D', v'_0) + He + 0.77eV \quad (1)$$

In the $He^+ + {}^{15}N_2$ CT reaction, the formation of high vibrational levels of the D′ state is expected from the exergy resonance requirements for the charge transfer reaction of rare gas ions with simple molecules,[5] while only the v'_0+1, v'_0, and v'_0-1 levels of the D′ state have been detected in the $He^+ + {}^{14}N_2$ CT reaction. It is generally acknowledged that charge transfer reaction between an atomic ion and a molecule at thermal energies is likely to populate molecular ion states lying near the recombination energy of atomic ion.[5-7] Though

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the emission spectra in the 200-320 nm region produced from the $He^+ + {}^{14}N_2$ reaction have been observed by several investigators,[1,2,4] no emission spectrum resulting from the $He^+ + {}^{15}N_2$ reaction has been reported under the conditions of low He pressure.

In the present work, we have observed the $^{15}N_2^+(D'-A)$ emission system resulting from the $He^+ + {}^{15}N_2$ CT reaction by using both a flowing afterglow apparatus and a low-pressure apparatus. The absolute vibrational quantum numbers for the D'−A transition have been proposed by measuring the isotopic shifts between $^{15}N_2^+$ and $^{14}N_2^+$ bands, and the difference in the emission spectrum in the 200-320 nm region between $^{15}N_2^+$ and $^{14}N_2^+$ transitions have been discussed.

2. Experimental

The flowing afterglow apparatus and the low-pressure apparatus used were essentially the same as those described previously.[4] The purity of the $^{15}N_2$ gas (Amersham) was 98 atom%. The emission spectra of $^{15}N_2^+$ and $^{14}N_2^+$ were measured with a Nippon Jarrell Ash M2 (f = 1 m) monochromator fitted with a cooled Hamamatsu R376 photomultiplier. The wavelength was calibrated by a low-pressure mercury pen lamp and known bandhead positions of the $N_2^+(C^2\Sigma^+_u-X^2\Sigma^+_g)$ transition.[8] The relative accuracy of measured wavelength was 0.6 Åfor the spectra measured in the flowing afterglow.

3. Results and discussion

3.1 $^{15}N_2^+(D'-A)$ emission system in the flowing afterglow and its isotopic shifts

In Fig.1a. is shown the emission spectrum in the 220-255 nm region resulting from the $He^+ + {}^{15}N_2$ reaction. For comparison, the emission spectrum arising from the $He^+ + {}^{14}N_2$ reaction is shown in Fig.1b. In our previous study,[4] double headed bands in Fig. 1b. were assigned to the$(v'_0, 7-10)$ transitions of the $^{14}N_2^+(D'-A)$ system on the basis of the assignment of Cossart *et al.* Four red degraded double headed bands appear in Fig.1a, for which spectral features closely resemble to those in Fig.1b. These bands could be assigned to the $(v'_0, 7-10)$ transitions of the $^{15}N_2^+(D'-A)$ system. As is the case for the $He^+ + {}^{14}N_2$ reaction, strong D'−A emission system of N_2^+ has been observed in the 220-260 nm region, and the $^{15}N_2^+(D-A)$ emission[8] which will be heavily overlapped with the D'−A emission is expected to be much weaker than the D'−A emission. The transitions from the v'_0+1 and v'_0-1 levels could not be identified in the present study.

In Table 1 are given the vacuum wavenumbers of the observed bandheads for $^{15}N_2^+(D'-A)$ and $^{14}N_2^+(D'-A)$. The isotope shifts of the bandheads of $^{15}N_2^+$ are calculated from the following equation by using the vibrational constants of $^{14}N_2^+$:

$$\Delta\nu = \nu(^{14}N_2^+) - \nu(^{15}N_2^+)$$

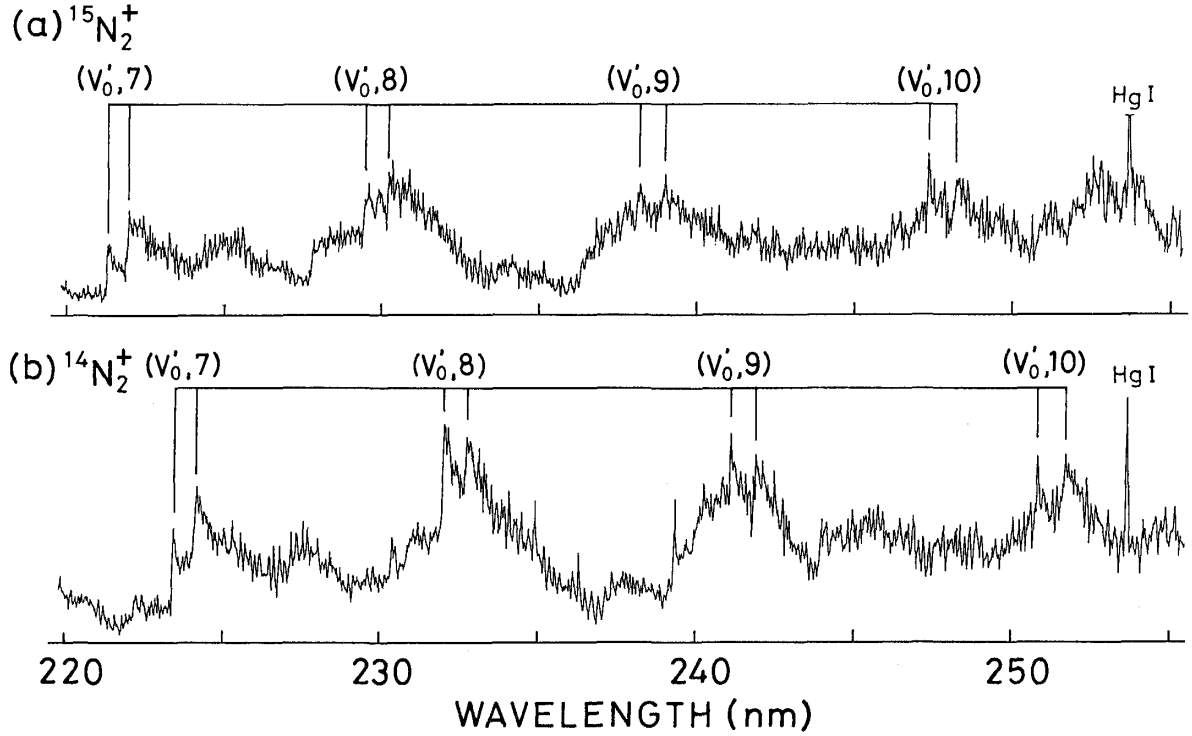

Fig.1: Emission spectra between 220 and 255 nm obtained from the $He^+ + {}^{15}N_2$ reaction (a) and the $He^+ + {}^{14}N_2$ reaction (b) in flowing afterglows. Effective spectral resolution was 0.4 Å. Experimental conditions were as follows: He, 1.2 Torr; $^{15}N_2$, 3 mTorr for (a) and He, 1.2Torr; $^{14}N_2$, 10 mTorr for (b).

Table 1. Observed bandheads and differences between observed and calculated* isotope shifts for the $N_2(D^2\Pi_{gr} - A^2\Pi_{ui})$ system (in cm^{-1})

$D^2\Pi_{3/2} - A^2\Pi_{3/2}$			$D^2\Pi_{1/2} - A^2\Pi_{1/2}$			Band assignment	
Wavenumber		$\Delta\nu_{obs.} - \Delta\nu_{cal.}$	Wavenumber		$\Delta\nu_{obs.} - \Delta\nu_{cal.}$	ν'	ν''
$^{14}N_2^+$	$^{15}N_2^+$		$^{14}N_2^+$	$^{15}N_2^+$			
46,449	46,808	6	46,316	46,677	4	0	6
44,747	45,173	−10	44,621	45,035	2	0	7
43,098	43,563	− 1	42,961	43,427	− 2	0	8
41,471	41,976	6	41,320	41,834	− 3	0	9
39,849	40,421	−17	39,712	40,284	−17	0	10

*The calculated isotope shifts have been obtained by assuming that $\omega'_e = 728$ and $\omega_e x'_e = 1.9 cm^{-1}$ (see the text).

$$= (1-\rho)\ [\omega'_e(v'+1/2) - \omega''(v''+1/2)] \qquad (2)$$
$$-(1-\rho^2)\ [\omega_e x'_e(v'+1/2)^2 - \omega_e x''_e(v''+1/2)^2]\ ,$$

where $\rho = [\mu(^{14}N_2^+)/\mu(^{15}N_2^+)]$, μ being the reduced mass. For the calculation, the ω''_e and $\omega_e x''_e$ values were taken from Ref.3. Although the ω'_e and $\omega_e x'_e$ values are not known we have attempted to determine the absolute vibrational quantum numbers for the D′−A transition on the following basis: The isotopic shift is dominated by the ω''_e value (1903.7 cm^{-1})[8] since the ω'_e value must be much smaller than the ω''_e value as suggested by the calculated ω'_e value (728 cm^{-1}) and the experimental $\Delta G_{v'_0+1/2}$ value (681 cm^{-1}). Thus, the ω'_e value has been varied between 681-728 cm^{-1}. Similarly, the $\omega_e x'_e$ value has been varied over the range of 1.9-15 cm^{-1}, where 1.9 cm^{-1} is a calculated value. It should be noted that minor changes (< 1 cm^{-1}) have been found in the calculated isotope shifts for the variations of ω'_e and $\omega_e x'_e$ over the above ranges. Satisfactory agreement between the observed and calculated isotope shifts has been obtained only when we assign $v'_0 = 0$. If we assign $v'_0 = 1$ as assumed by Cossart *et al.*[3] the calculated isotope shifts deviate from those measured by 16-39cm^{-1}. The variation of ω'_e over the more wide range (500-800 cm^{-1}) provided essentially the same result. The assignment $v'_0 = 0$ leads to $T_0 = 66178$ cm^{-1}, which has been measured by Cossart *et al.*[3]

One may imagine that v'_0-1 becomes -1 if $v'_0 = 0$, and the assignment provided here is unreasonable. However, the He pressure dependence of the emission intensity ratio between the (D′ ; $v'_0-1 \rightarrow$ A ; v'') and (D′;$v'_0 \rightarrow$ A ; v'') transitions of $^{14}N_2^+$ prefers our assignment to the assumption of Cossart *et al.*[3] The emission intensity ratio I(D′ ; $v'_0-1 \rightarrow$ A ; 9)/I(D′ ; $v'_0 \rightarrow$ A ; 8) estimated from the peak heights was almost constant (0.8 ± 0.1) at He pressures between 0.01 and 7.0 Torr, and the transitions from the v'_0 level were very intense throughout the above wide range of He pressures. On the other hand, the emission intensity ratio I(D′; $v'_0+1 \rightarrow$ A ; 8)/I (D′; $v'_0 \rightarrow$ A ; 8) decreased significantly with increasing the He pressure as described in the previous paper.[4] Since the lifetime of the D′ state has been estimated to be very long ($6\times10^{-7}-10^{-5}$s),[2] the vibrational relaxation of the D′ state in collisions with He atoms must be significant in the flowing afterglow experiment. These experimental results suggest that the v'_0-1 level is not the lowest vibrational level of the D′ state.

3.2 Emission spectrum in the 190-320 nm region produced from the $He^+ + {}^{15}N_2$ CT reaction in the low-pressure apparatus

In Fig.2 is shown a typical emission spectrum in the 190-320 nm region. The $\Delta v = -6$, -7, and -8 sequences of the $^{15}N_2^+$(C−X) emission and the structured continuum emission have been observed. The positions of the $^{15}N_2^+$(D′−A) emission are given in Fig.2 on the basis of the assignment of the D′−A emission system detected in the flowing afterglow.

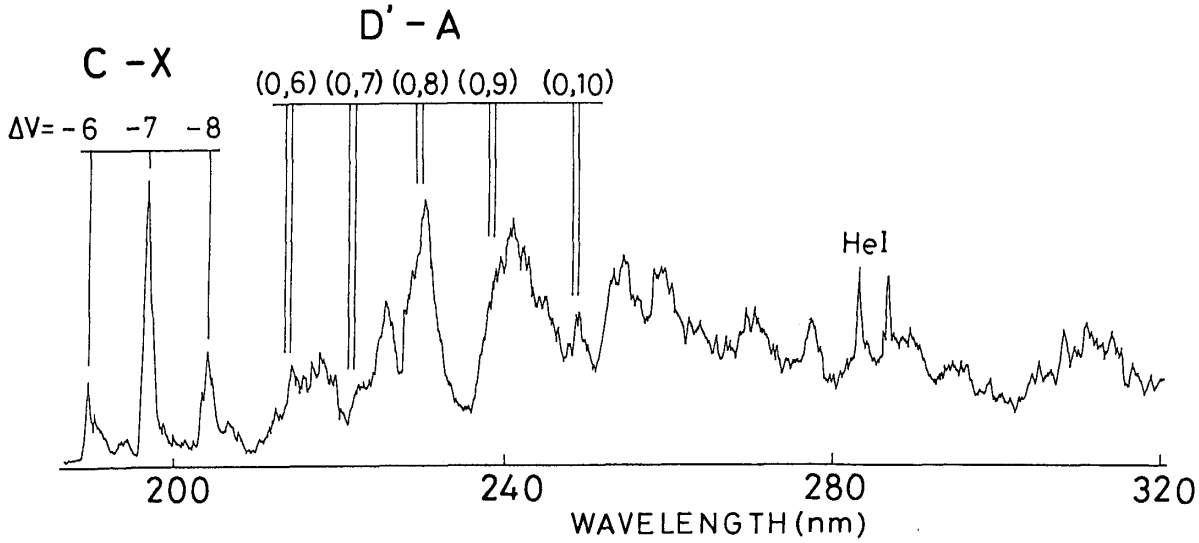

Fig.2: Emission spectrum between 190-320 nm produced from the $He^+ + {}^{15}N_2$ reaction in the low-pressure apparatus. The total pressure in the interaction chamber was 8.7×10^{-4} Torr and the partial pressure of ${}^{15}N_2$ was 5×10^{-5} Torr.

The spectral pattern of the structured continuum emission produced from the $He^+ + {}^{15}N_2$ reaction resembles to that observed in the $He^+ + {}^{14}N_2$ CT reaction, while the former spectrum is much more congested than that of the ${}^{14}N_2^+$ (D′−A) emission. However, it is clear that the intensity of the (0, 6-10) bands of the D′−A transition is very small in Fig.2, *e.g.*, the (0, 7) band appears as a weak shoulder of the band located at 226 nm. Two prominent bands are located at 230 and 241 nm. These bands are deduced to consist of several bands from their bandshapes. Relatively low intensity of the (0, 6-10) transitions of the D′−A system in the ${}^{15}N_2^+$ spectrum is different from those in the ${}^{14}N_2^+$ spectrum, where intense (0, 6-10) transitions of the D′−A system have been observed. The difference between the ${}^{15}N_2^+$and ${}^{14}N_2^+$ spectra may be due to the formation of much higher vibrational levels of the D′ state comparing with the $He^+ + {}^{14}N_2$ reaction and/or to the overlapping with intense unknown emission in the $He^+ + {}^{15}N_2$ CT reaction.

In summary, the absolute vibrational quantum numbers for the D′−A emission system of N_2^+ ion have been determined. In the $He^+ + {}^{15}N_2$ reaction, the intensity of transitions from the lowest vibrational level of the D′ state to the A state is very weak in contrast with the $He^+ + {}^{14}N_2$ reaction. It is necessary to detect higher resolution spectrum of ${}^{15}N_2^+$(D′−A) at low pressures in order to obtain the vibrational molecular constants for the D′ state and to get information on the formation process of the D′ state in the $He^+ + N_2$ CT reaction.

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