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CHEMILUMINESCENCE IN COLLISIONS OF N^+ IONS WITH CO MOLECULES

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Chemiluminescence which is presumed to be due to the transitions of excited CN^+ ions formed by the reaction of N^+ ions with CO molecules in the LAB energy range 40 - 150 eV was observed in the spectral range shorter than 3100 Å. Two line spectra due to the transitions of excited C atoms were clearly found. The C atom (^1P) is thought to be produced also by an N^+-CO reaction.

Reactions of open-shell atoms like C, N, and O, whether ionized or not, are of interest in that their open-shell structures give rise to many potential surfaces, and therefore, the reactions provide a number of neutrals or ions as products. These products may be either in the ground state or in low-lying excited states. Recently, the system $N^+ + CO$ has drawn special attention and some experimental[1-3] and theoretical[4,5] researches were published on this system. Frobin et al.[1] made mass spectroscopic study on the reaction of N^+ with CO in the LAB energy range 0.2 - 20 eV and measured reaction cross sections of the five ionic products, CO^+, NO^+, CN^+, C^+, and O^+, using the guided beam technique. Ottinger and Zimmermann[3] attempted a research on optical emission from N^+-CO collisions, and found only emission from excited CO^+ produced by charge transfer between the reactants. They also measured the translational energy distribution of the ionic reaction products, and discussed excitation of the products.

The work presented in this article is an extension of the works on luminescence in collision of C^+ with N_2[6] and C^{2+} with H_2[7] and aimed at observation of collisional luminescence of N^+ with CO. We expected that we might be able to observe chemiluminescence from excited reaction products. This expectation has been fortunately realized and we ceratinly observed light emission from excited molecules and excited C atoms formed in reactions of N^+ ions with CO molecules.

Details of the experimental apparatus used in this work have been already published,[6] but a brief description will be given here. N^+ ions are formed from N_2 gas at a discharge voltage of 40 V in an arc discharge ion source. Ions produced are extracted from the ions source, accelerated to a specified energy, and then introduced into a magnetic 90° mass analyzer to select N^+ ions. Use of the 90° mass analyzer is to prevent the light in the ion source from directly entering the scattering chamber. After being refocused and decelerated with a series of einzel lenses, the N^+ ions enter the scattering chamber with an energy determined by the potential difference between the anode and the scattering chamber. Beam energy (E_{LAB}) employed in this experiment is 10 to 300 eV in the LAB frame. Typical N^+ currents were

about 3×10^{-9} amp. Target gas pressure was held at about 5×10^{-3} Torr. The fraction of metastable states that might be involved in the incident beams was determined by means of a beam attenuation method.[8] Only a metastable state N^+(perhaps ^1D) is found in the primary beams by an amount of 10% at a discharge voltage of 40 V. Participation of N_2^{2+} ions (of the same mass m/e = 14 as N^+) into the incident N^+ beams can be ignored since the discharge voltage is below the appearance potential 43.5 eV of N_2^{2+} from an N_2 molecule.

Light emitted from the excited reaction products is observed through a quartz window perpendicularly to the beam axis by a scanning monochromator equipped with a photomultiplier (Hamamatsu TV, R585S) cooled below 0°C. The spectral resolution was usually 20 Å, and was raised to 10 Å for observing chemiluminescence. Light intensity was measured with a pulse-counting method and the pulses were accumulated for 100 sec per channel in a multichannel analyzer. Collision induced spectra in Ar^+-CO and N_2^+-CO systems were also observed for comparison with the result of N^+-CO system.

In Fig.1 is displayed a spectrum covering 1900 to 5900 Å obtained in this work, in which collision energy of N^+ ions is E_{LAB} = 80 eV. This spectrum may be divided into two regions. The first region is that longer than 3100 Å and shows the vibrational progression of the comet-tail system $CO^+(A\,^2\Pi - X\,^2\Sigma^+)$ formed by charge transfer between the projectile ion N^+ and the target molecule CO. The second region is that between 2400 and 3100 Å, and consists of a series of small band peaks. The structure in this region appears at a collision energy of 40 eV, and becomes more distinct with increasing energy up to 70 - 80 eV, at which the structure gets most eminent. More increase of the collision energy brings about gradual smearing of the structure. At about 150 eV it disappears completely. The emission is presumed to be due to chemiluminescence provided by the reaction of N^+ ions with CO molecules, because there is no emission system of CO or CO^+ in this spectral region, except

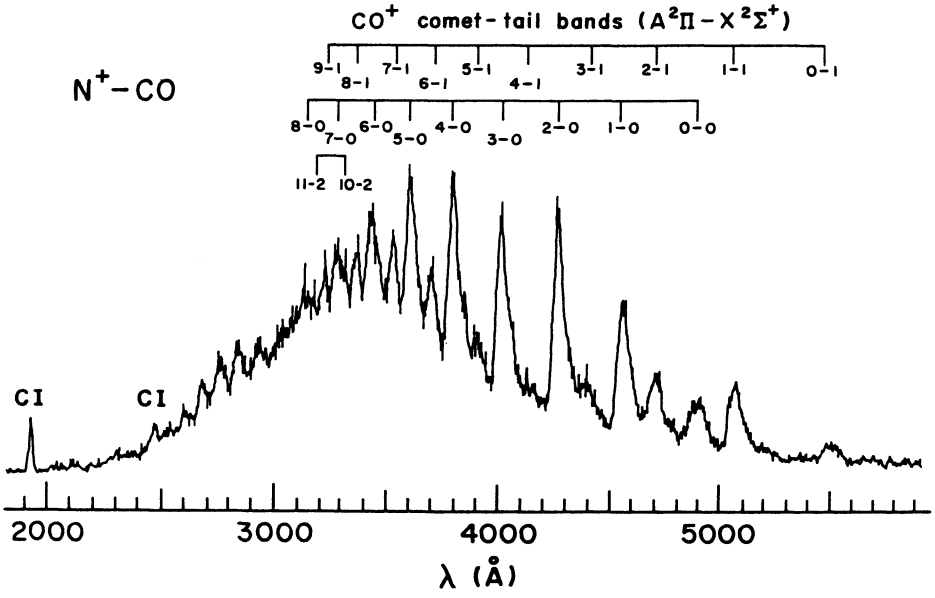

Fig. 1. Overall emission spectrum observed in collisions of N^+ ions with CO molecules. Resolution is 20 Å. E_{LAB} = 80 eV.

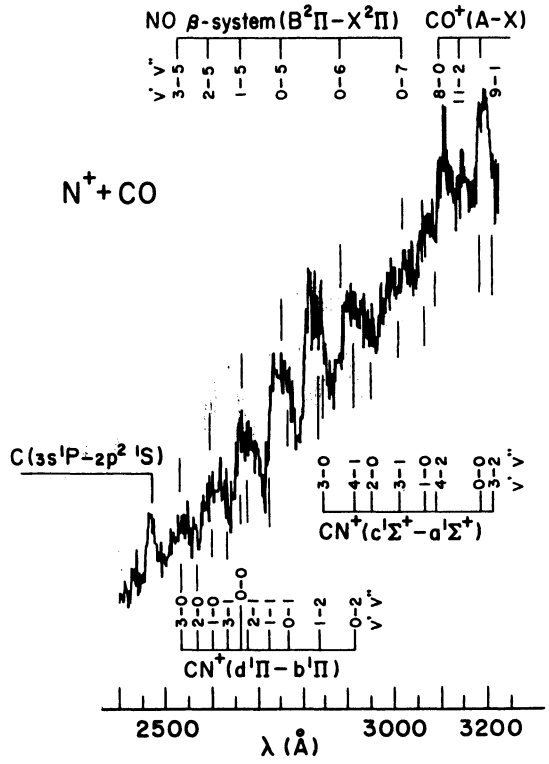

Fig. 2. Emission spectrum of Chemiluminescence produced by the reaction of N^+ ions with CO molecules. Resolution is 10 Å. E_{LAB} = 80 eV.

the transitions from very high vibrational levels ($v \approx 20 - 30$) of $CO^+(A\,^2\Pi)$, but the occurrence of such high vibrational levels is uncertain.[9] Besides, the structure is never observed in Ar^+-CO and N_2^+-CO systems. Ionic reaction products of N^+ with CO were mass spectroscopically observed.[1,3] Diatomic neutrals, NO and CN, are supposed to be produced by the reactions:

$$N^+ + CO \rightarrow CN + O^+, \quad (1)$$

and

$$\rightarrow NO + C^+. \quad (2)$$

If these reaction products are formed in excited electronic states, optical emission may be observed.

Among the candidates for the emission in the spectral region concerned, CN(Douglas and Routly's system), NO(β and γ systems), and CN^+ ($c\,^1\Sigma^+ - a\,^1\Sigma^+$ and $d\,^1\Pi - b\,^1\Pi$),[9] CN may be excluded, since strong emission from lower-lying excited states of CN(the violet system) was not observed. Between the remaining two candidates, we have presumed that CN^+ is more appropriate than NO, because the β system (and γ system, too) of NO does not satisfactorily explain all of the band sequence over the region. Particularly, the system does not provide the prominent bands around 2830 Å. On the other hand, the singlet CN^+ emission is likely to well fit the observed structure over all the concerned region. Formation of excited CN^+ in the $N^+ + CO$ reaction has been suggested also by Ottinger and Zimmermann.[3] In Fig. 2 vibrational progressions of NO($B\,^2\Pi - X\,^2\Pi$) and CN^+($c\,^1\Sigma^+ - a\,^1\Sigma^+$ and $d\,^1\Pi - b\,^1\Pi$) are schematically dispalayed for comparison with the reproduced spectrum. More precise discussion requires the experimental data with much better resolution.

In Figs. 1 and 2 are found CI emission lines at 1931 and 2479 Å, which correspond to the transitions $3s\,^1P - 2p^2\,^1D$ and $3s\,^1P - 2p^2\,^1S$, respectively.[10] They are also found in collisions of Ar^+ and N_2^+ with CO above E_{LAB} = 100 eV. Owing to reduced sensitivity of our optical instrument including the photomultiplier in the region shorter than 3000 Å, the CI emission lines look very weak at first sight. If an appropriate correction is made for the sensitivity, however, the intensity of the CI emission will become much stronger (perhaps by a factor of 3-5). These C atoms, which are excited up to $3s\,^1P$ (7.7 eV above the ground state ^3P), may be produced not only by collisional dissociation of CO or CO^+, but also by a reaction of N^+ with CO:

$$N^+(^3P) + CO(X\,^1\Sigma^+) \rightarrow NO^+(a\,^3\Sigma^+) + C(^1P) - 13.5 \text{ eV}. \quad (3)$$

If the reactants N^+ and CO are both in the ground state and a C atom is formed in a

singlet excited state (^1P), the partner ion must be formed in a $^3\Sigma$ state by the spin and orbital symmetry conservation. The a $^3\Sigma^+$ state is the lowest state of the triplet system, and above 6.5 eV above the ground state $^1\Sigma^+$.[11] This result corroborates the inference by Ottinger and Zimmermann in their research of the translational energy distribution that NO^+ produced in the N^+-CO reaction would be excited into the a $^3\Sigma^+$ state.[3] Whereas the emission of CI disappears below 100 eV in the Ar^+-CO and N_2^+-CO syatems, it disappears only below 40 eV in the N^+-CO system. At least, CI emission due to N^+-CO interaction in the energy range 40 - 100 eV seems to be chemiluminescence produced by a reaction yielding the metastable NO^+ and a singlet C atom.

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