# CHARGE-TRANSFER EXCITATION OF $CO^+$ COMET-TAIL BANDS BY SLOW $N_2^+$ IONS

Nyle G. Utterback

General Motors Defense Research Laboratories, Santa Barbara, California

and

H. P. Broida*

Department of Physics, University of California, Santa Barbara, California

(Received 2 August 1965)

Optical spectra have been observed from collisions between low-velocity $N_2^+$ ions and CO molecules in a beam-type experiment under thin-target conditions. The reaction has been identified as charge transfer to an excited state,

$$N_2^+ + CO \rightarrow N_2 + CO^+(A\,^2\Pi). \quad (1)$$

Although this excitation reaction is endothermic by 1 eV, the cross section decreased less than a factor of two when the kinetic energy in the center-of-mass system was decreased from 100 to 8 eV, indicating that translational energy was efficiently converted to excitation energy. The excitation cross section was large, of the order of $10^{-16}$ cm$^2$, which is 10 to 100 times the cross sections typically found at ion energies of many hundred eV. All light emission observed was identified as bands belonging to the $CO^+$ comet-tail system ($A\,^2\Pi_u - X\,^2\Sigma_g^+$). The distribution of population in the vibrational states of the $A\,^2\Pi$ state of $CO^+$ was found to be Boltzmann, and to correspond to a temperature near 2500°K. Since this distribution of population is not expected on the basis of the Franck-Condon principle, it appears that intermediate states are involved in the charge transfer. The result of the $N_2^+ + CO$ interaction is surprising, since so little radiation was observed at low collision energy for $N_2^+ + N_2$, $N_2^+ + NO$, and $N_2^+ + O_2$. (Also, weak radiation has been observed from $He^+$ on CO, NO, $N_2$, $O_2$, and He, but the work is not definitive at this time.) The present work shows the feasibility of using optical techniques to study collision processes in this very interesting energy range, at least for some species.

The $N_2^+$ ions were produced by electron bombardment.[1] In order to assess possible effects of electronically excited ions in the beam, bombarding electron energies were varied from less than 18 eV to 24 eV. Electron energies were calibrated by determining the appearance potentials of $Ar^+$ and $N_2^+$. Although detailed optical spectra could not be obtained at the lower electron energies, the integrated light output for 98-eV ions (normalized to equal ion-beam intensity) did not vary more than 20% when the bombarding electron energy was varied from 18 to 24 eV. Since no long-lived $N_2^+$ excited electronic states may be produced by 18-eV electrons, it is unlikely that electronically excited $N_2^+$ ions grossly affected the measurements.

The $N_2^+$ ions were accelerated and focused as described earlier.[1] The ion beam was directed axially through a reaction chamber formed from a cylinder 1.6 in. long with internal diameter 0.5 in. The CO target gas, quoted to be 99.5% pure, was admitted at the center of the chamber. The pressure at the center was maintained at approximately $5\times10^{-3}$ Torr. One side of the cylinder was cut along a $\frac{1}{4}$-in. chord. The cut was covered with clear flat quartz, forming a window $1.6\times0.25$ in., parallel to the ion beam. The remainder of the inside chamber walls was covered with aluminum foil. A quartz lens imaged an area of the window about $0.1\times0.25$ in. on the monochromator entrance slit.

After passing through the reaction chamber, the ion beam struck a plate connected to an electrometer. This electrometer was used to monitor the ion-beam intensity. Because no provision was made to control secondary electrons, this method of beam monitoring was reliable only to about 300-eV beam energy.[1]

Two types of measurement were made. The first involved direct use of the monochromator, and provided detailed optical spectra. Because of the signal-to-noise ratio, it was necessary to use ion-beam energies above 30 eV and ion-source electron energies above 22 eV to obtain well-defined spectra. In the second type of measurement, a photomultiplier was placed at the position of the monochromator entrance

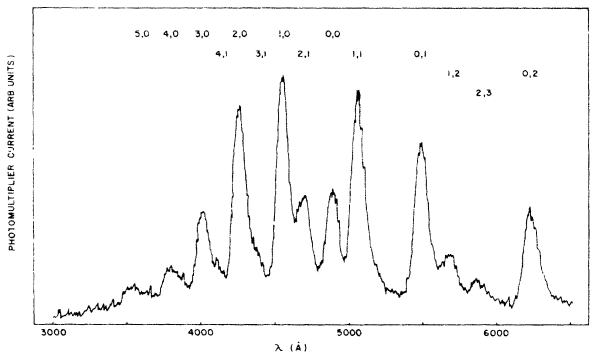


FIG. 1. Spectrum of light emitted in the interaction $N_2^+ + CO$.

slit. Integrated intensity measurements were then possible down to 10-eV ion-beam energy (24-eV electrons) and less than 18-eV ion source electron energy (98-eV ions). Light emission from neutral-neutral collisions and from ion-surface collisions was found to be unimportant.

For spectral measurements, a $\frac{3}{4}$-m Ebert grating monochrometer was used. This instrument was equipped with 5-mm slits, an S-20 surface photomultiplier tube, and an $85 \times 85$ mm grating with 90 000 grooves blazed at 5000 A in the first order. The instrument resolution in the first order was 100 A. Figure 1 shows an uncorrected recorder tracing of a spectrum obtained at an ion energy of 250 eV and bombarding electron energy of 24 eV.

Wavelengths and vibration band transitions for $CO^+ A\,^2\Pi - X\,^2\Sigma$ are shown. Identification of the emitter was obtained from wavelengths of the bands and the proper relative intensities. Peak heights of the bands were used with transition probabilities obtained from Nicholls[2] to measure relative populations of the first six vibrational levels. These populations show a distribution which is Boltzmann, corresponding to a temperature of $2500 \pm 500°K$. Band-intensity ratios did not vary significantly over the ion energy range for which spectra were obtained, i.e., 30 to 250 eV.

Figure 2 shows the results of the second type of measurement, where the total light output

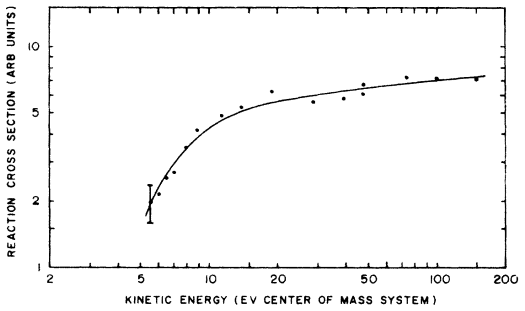


FIG. 2. Relative cross section for excitation in the interaction $N_2^+ + CO$.

was integrated by the photomultiplier. The ordinate is proportional to the photomultiplier output divided by the ion-beam intensity. The ordinate is thus proportional to the excitation cross section, under the assumption that the photon spectrum did not vary with ion energy. The abscissa is the kinetic energy in the center-of-mass system, and is just half the laboratory beam energy. The bombarding electron energy was 24 eV. These results are similar to those obtained in cross-section measurements for endothermic ion-molecule and charge-transfer measurements reported by Maier,[3] and again show that in certain cases translational energy is efficiently converted to electronic energy.

In order to estimate the excitation cross section, spectra also were taken for the reaction

$$N_2^+ + N_2 \rightarrow N_2 + N_2^+(B\,^2\Sigma). \qquad (2)$$

Since the cross section for this process ($N_2^+$ first negative excitation) has been measured previously,[4] a comparison of intensities showed that the cross section for Reaction (1) was about $10^{-16}$ cm$^2$.

*Supported in part by the Advanced Research Projects Agency and the Office of Naval Research.

[1]N. G. Utterback and G. H. Miller, Rev. Sci. Instr. 32, 1101 (1961).
[2]R. W. Nicholls, Can. J. Phys. 40, 1772 (1962).
[3]W. B. Maier, II, J. Chem. Phys. 42, 1790 (1965).
[4]J. P. Doering, Phys. Rev. 133, A1537 (1964).