

Excitation of nitrogen and carbon monoxide ionic emissions by $\text{He}(2^3\text{S})$, He^+ , and He_2^+

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The $\text{N}_2^+(B\ ^2\Sigma_u^+-X\ ^2\Sigma_g^+)$, $\text{CO}^+(B\ ^2\Sigma^+-X\ ^2\Sigma^+)$, and $\text{CO}^+(A\ ^2\Pi-X\ ^2\Sigma)$ emission spectra excited by reaction of He^+ and $\text{He}^+ + \text{He}_2^+$ mixtures with N_2 and CO are compared with the spectra from the reaction with $\text{He}(2^3\text{S})$ metastable atoms. The experiments were done in a room temperature flowing afterglow apparatus. Charge exchange between He^+ and N_2 gave $\text{N}_2^+(B)$ and a small amount of $\text{N}_2^+(D)$ in addition to $\text{N}_2^+(C)$; the yield of $\text{N}_2^+(A)$ was insignificant. The vibrational population distribution of $\text{N}_2^+(B)$ excited by He^+ differed greatly from that given by the reaction with $\text{He}(2^3\text{S})$. No CO^+ emission could be identified from the $\text{He}^+ + \text{CO}$ reaction. The reaction of He_2^+ with N_2 and CO gave strong emissions from $\text{N}_2^+(B)$, $\text{CO}^+(B)$, and $\text{CO}^+(A)$ with vibrational populations resembling the distributions expected for Franck-Condon transitions from neutral N_2 and CO . Although the $\text{N}_2^+(A-X)$ emission could not be studied in detail, $\text{N}_2^+(A)$ appeared to be a product from reaction of He_2^+ and N_2 .

INTRODUCTION

Results from several laboratories¹⁻³ are in general agreement regarding the optical emission spectra from thermal reactions between $\text{He}(2^3\text{S})$ with N_2 and CO . The $\text{N}_2^+(B)$ and $\text{CO}^+(A$ and $B)$ state vibrational populations are generally in accord with the Franck-Condon factors relating the neutral molecular state and the excited ionic states.¹⁻⁴ However, the emission spectra excited by He^+ and He_2^+ with these molecules are understood less well and the various reports are incomplete and/or in partial conflict. A recent claim⁵ that the $\text{N}_2^+(B)$ vibrational populations from thermal charge exchange between He^+ and N_2 were similar to those from $\text{He}(2^3\text{S}) + \text{N}_2$ disagreed with our own experience and with prior published suggestions.^{1,2} An understanding of the $\text{N}_2^+(B)$ vibrational populations is important for utilization of the $\text{He}(2^3\text{S})$ Penning ionization method for measurement of vibrational temperatures of N_2 because He^+ and He_2^+ are often impurities with the $\text{He}(2^3\text{S})$. The discrepancy⁵ of the $\text{N}_2^+(B)$ vibrational populations from He^+ excitation, the possibility of comparing ion product state populations from thermal collisions to those from beam experiments,⁶ and our need to more carefully define the operating conditions which minimize $[\text{helium ions}]/[\text{He}(2^3\text{S})]$ in our cold hollow-cathode discharge flow apparatus³ prompted the present investigation of the optical emission spectra excited by $\text{He}(2^3\text{S})$, He^+ , and He_2^+ with N_2 and CO at room temperature. Our results also are of interest to the mechanism of the recently reported $\text{N}_2^+(B-X)$ laser system⁷ pumped via charge exchange with He_2^+ , as well as for other potential laser systems.

The rates of reaction of He^+ and He_2^+ with N_2 and CO are more than tenfold^{8,9} faster than that for $\text{He}(2^3\text{S})$ at room temperature¹⁰; the energies (eV) provided by the species are 19.818(He^+ , ^3S), ≤ 22 (He_2^+),¹¹ and 24.58(He^+). The $\text{He}(2^3\text{S})$ limit is not quite sufficient to produce $\text{N}_2^+(B)$ $v' = 4$ (19.90 eV) or $\text{CO}^+(B)v' = 1$ (19.879 eV) without utilization of some thermal energy of the collision.^{3a, 5b} The $\text{N}_2^+(C-X)$ emission can be used as a diagnostic¹² indication of He^+ in the presence of $\text{He}(^3\text{S})$ and He_2^+ because 23.6 eV are required to form $\text{N}_2^+(C)$. The competition

between emission and predissociation¹³ for $\text{N}_2^+(C)$ has been characterized^{12b} and for $^{14}\text{N}_2$ the ratio of predissociation to emission is 9.8, but for $^{15}\text{N}_2$ the ratio is only 1.1. The overall ratio of the nitrogen atomic and molecular ions from charge exchange with He^+ under thermal condition is 1.3 for the $^{14}\text{N}_2$ case^{12b}; N_2^+ must arise from states other than $\text{N}_2^+(C)$. However, a satisfactory mechanism for describing the N_2^+ product states has yet to be formulated.^{12b, 14} In the current work we have assumed that conditions which effectively remove He^+ also remove He_2^+ , for which a simple unique diagnostic test based upon emission spectra in the presence of $\text{He}(^3\text{S})$ and He^+ has not been discovered. Our basic approach was to adjust experimental conditions so as to first obtain reference spectra from excitation by only $\text{He}(2^3\text{S})$. Spectra with varying concentrations of ions, monitored by the $\text{N}_2^+(C-X)$ emission intensity, then were contrasted to the $\text{He}(2^3\text{S})$ reference spectra in order to deduce the role played by the He^+ and He_2^+ reactions. Our spectral range was ~ 190 – 800 nm; since the $\text{N}_2^+(A-X)$ emission is in a difficult wavelength region, this transition was observed but not studied in detail. No attempt was made to monitor rotational populations.

EXPERIMENTAL

The helium species were generated using a cold-cathode discharge and associated discharge-flow apparatus which was similar to that previously used^{3a} for study of $\text{He}(2^3\text{S})$ reactions. Some care should be given to selection of the proper operating conditions (see below) to ensure that the desired helium species is present in the reaction zone.^{3b} As before, the electrodes were constructed from rolled tantalum foil and were placed inside a 12 mm o.d. Pyrex tube; the discharge tube was joined by a right angle bend (light trap) to the concentric mixing zone (28 mm o.d. tubing) to which N_2 and CO were added. The gas flow was maintained by a mechanical pump of 1000 l min⁻¹ capacity. Pressure was measured at the mixing zone with a silicone oil manometer. The tank helium was purified by passage through two liquid-nitrogen cooled molecular sieve traps, which removed all N_2 , CO , and CO_2 as judged by the absence of N_2^+ , CO^+ ,

and CO_2^+ emissions when the mixing zone was viewed in the absence of added reagent gas. The principal residual impurity was Ne, which was easily detected by the red Ne lines arising from the interaction of $\text{He}(^3\text{S})$ and Ne. Under conditions such that the $[\text{He}^+]$ was significant, some Ne^+ may also be formed via charge exchange.

For Condition I (400 V, 15 mA, and ≤ 1 torr) the contribution from He^+ to the excitation spectra was at the barely detectable limit, i. e., the $\text{N}_2^+(C-X)$ emission was at the noise level. Further reduction of the discharge power to ~ 250 V and ~ 5 mA tended to slightly reduce the $[\text{He}^+]/[\text{He}(^3\text{S})]$ relative to Condition I, but the low signal from $\text{He}(^3\text{S})$ excitation prevented the collection of good data at this low power setting. In general, high voltage, high current, and especially high He pressure give enhanced yields of ions, and two sets of conditions (II and III) which had appreciable ion concentrations were employed. Ion-collector electrodes were used for studies under Conditions II and III, and the application of a potential to the electrodes greatly reduced the ion concentrations. Hence, observation of the emission intensities with the voltage on and off the collector electrodes permitted assignment of the excitation to either ions or metastables. Collector electrodes also could be used with Condition I but they produced no change in the emission intensities, which is further evidence for low $[\text{He}^+]$ and $[\text{He}_2^+]$. For Condition II, which was the same geometry as I, the distance between the discharge and mixing zone was only 8 cm and the collector electrodes consisted of two parallel wires inserted at the right angle bend (light trap) and extending to the edge of the mixing zone. For III the distance between the discharge and mixing zone was extended to 17 cm and the ion-collector electrodes, which were a second pair of rolled tantalum foil electrodes, were placed between the light trap and the discharge. The main difference between Conditions II and III seemed to be the enhanced yield of He_2^+ , presumably formed during the longer time required for the gas to flow from the discharge to the mixing zone. The data from Condition II were collected over a six month period, and the ion collection efficiency varied from 40% to 90% for the same apparent operating conditions. Toward the end of the study it was discovered that "proper" grounding of the two pairs of electrodes enhanced both the collection efficiency and the reproducibility. The effect of the collector electrodes upon the $[\text{He}(^3\text{S})]$ was monitored by observing the Ne 703.2 nm line and, later in the work, the $\text{N}_2^+(B, v'=0-X)$ emission. For certain experiments some of the ion concentration actually appeared to be converted to metastable concentration by the application of voltage to the electrodes, as judged by the increase in the $\text{N}_2^+(B, v'=0-X)$ emission intensity. However, the data for this report are based on experiments for which the diagnostic emissions from $[\text{He}(^3\text{S})]$ were unchanged ($\pm 5\%$) for operation with and without potential on the electrodes.

The spectra, which were recorded with a 0.75 m Jarrell-Ash monochromator fitted with an EMI 9558QA photomultiplier tube and an SSR photon counter, were corrected for the relative response of the detection system. The system was calibrated from the visible region to 250 nm by use of an Electro Optics Associates

L-101 quartz-iodine standard lamp. Branching ratios from the $\text{NO}(A, v'=0, 1-X)$ transitions^{15a} were used to calibrate the region from 280 to 215 nm; this calibration was normalized to that of the standard lamp in the regions of overlap. The branching ratios of the $\text{CO}(a, v'=0, 1-X)$ transitions^{15b} were used to extend the calibration to 198 nm. The branching ratios of the $\text{CO}^+(B, v'=0, 1-X)$ transitions were used to confirm the calibration curve based on the $\text{CO}(a)$ and $\text{NO}(A)$ transitions; agreement to within $\pm 15\%$ was obtained for strong bands. The $\Delta v = -8, -7, \text{ and } -6$ sequences of $\text{N}_2^+(C-X)$, which comprise 65% of the emission intensity,¹³ are at 206, 198.5, and 191.3 nm, respectively; the calibration curve was extrapolated to obtain the relative response for the $\Delta v = -6$ bands. The corrected band areas of the $\text{N}_2^+(B-X)$, $\text{CO}^+(B-X)$, and $\text{CO}^+(A-X)$ transitions were converted to relative vibrational populations using the Franck-Condon factors of Ref. 15(c).

RESULTS

Nitrogen

The results from N_2 are summarized in Tables I and II; for the first entry the $\text{N}_2^+(C-X)$ emission was either very weak or not observable and the $\text{N}_2^+(B-X)$ intensity was not altered when the ion-collector electrodes were activated. Thus, for Condition I these relative populations can be assigned as arising mainly from $\text{He}(2^3\text{S})$ excitation. Although the $\text{N}_2^+(B)$ vibrational populations are based only on the $\Delta v = -2$ sequence and, hence, are not as reliable as a summation over all bands,^{3a} the $\text{N}_2^+(B) v'=0$ and 1 populations from $\text{He}(2^3\text{S})$ excitation are in agreement with earlier results and, hence, serve as a satisfactory reference. The present data extend to higher v' levels and may be compared with the Franck-Condon, $\text{N}_2(X, v=0)-\text{N}_2^+(B, v=0-4)$, values^{15c} (1000:134:2.4:0.03:0.002). The excess population for $v' \geq 3$ (a trace of $v'=6$ also was noted in the spectrum) probably reflects the presence of residual concentrations of He^+ or $\text{He}(2^1\text{S})$. No rotational intensity anomalies were found to suggest that the populations of the $\text{N}_2^+(B, v'=0-4)$ levels were being affected by perturbations¹⁶ from high vibrational levels of $\text{N}_2^+(A)$. This conclusion is based on photographic spectra from a higher dispersion instrument than the 0.75 m Jarrell-Ash in which the rotational lines were resolved. Since we¹⁷ previously have observed intensity anomalies for $\text{CN}(B-X)$ at similar pressures, rotational relaxation would not have obscured such effects if they were present.

For Conditions II and III the $\text{N}_2^+(C-X)$ intensity was monitored and the ratio of this signal with (I_c^e) and without (I_c^0) a potential applied to the collector electrodes was used to separate the other emission intensities into contributions from metastables and from ions, i. e.,

$$I_B(\text{He}^+ + \text{He}_2^+) = (I_B^0 - I_B^e)/F,$$

$$I_B(\text{He}^*) = I_B^0 - I_B(\text{He}^+ + \text{He}_2^+),$$

$$F = (I_c^0 - I_c^e)/I_c^0.$$

The relative contributions from He^+ and He_2^+ can be qualitatively identified by comparing results from II, for which the ion species is largely He^+ , and III, for which

TABLE I. Results^a for N₂.

Experimental conditions	Relative intensities ^{b,c} N ₂ ⁺ (B-X), Δv = -2							Relative intensity ^c N ₂ ⁺ (C-X)Δv = -6, -7 and 8	
	v' = 0	1	2	3	4	5	13		
I ^d He(³ S); 1.2 torr	7.1(4)	1.2(4)	4.2(2)	8.5(1)	3.8	4.2	•••	2.73(3)	
II-A ^e He(³ S) + He ⁺ ; 2.7 torr	3.1(5)	6.2(4)	8.2(4)	1.1(4)	8.0(3)	4.4(3)	1.7(3)	9.7(5)	
II-B ^e II-A with ion collection	3.3(5)	5.7(4)	5.7(3)	4.1(3)	2.9(3)	1.6(3)	5.1(2)	3.4(5)	
III-A ^f He(³ S) + He ⁺ + He ₂ ⁺ ; 3.6 torr	6.4(3)	1.1(3)	1.0(2)	9.1(1)	6.4(1)	2.3(1)	2.6(1)	5.1(3)	
III-B ^f III-A with ion collection	4.5(3)	7.4(2)	4.0(1)	1.1(1)	7.1	2.1	1.5	4.5(2)	

^aConversion of the total relative emission intensities assigned to ionic and metastable excitation into a [He(³S)]/[ions] ratio is not straight forward because of the uncertainty in product branching ratios for He⁺ and He₂⁺ reactions. It should be remembered that the product ratios must be inversely weighted by the total rate constants to obtain reactant ratios.

^bThe intensities of the Δv = -2 sequence were converted to relative populations using the Franck-Condon factors of Ref. 15c. For Conditions II and III the contribution from metastables and ions were separated (see text) and the relative populations were assigned to the ions and the metastables in Table II.

^cIntegrated band areas have been corrected for monochromator-detector response; the N₂⁺(C-X) intensity is the sum of the band areas at 206, 198.5, and 191.3 nm. The relative intensities of I, II, and III should not be compared because viewing geometry, slit width, scan rate, etc. are not necessarily the same. The number in parenthesis is the power of 10 to be associated with the preceding number.

^dSee text for description of Condition I.

^eThe physical arrangement of the cell and the operation of the discharge were the same as for I; however, the pressure was increased to 2.7 torr.

^fThe discharge arrangement consisted of two consecutive sets of hollow tantalum foil electrodes. The first set of electrode (17 cm from the mixing zone) was operated at 300 V and 15 mA; a potential difference of 40 V was used on the second set to collect ions.

He₂⁺/He⁺ has been enhanced. Presumably the metastable He⁺(2s²S) state with 40.8 eV of energy would be rapidly quenched by the He carrier gas and is not an important energy source.

The following observations from Tables I and II are pertinent for Condition II with N₂: (1) Application of the collector voltage hardly altered the N₂⁺(B, v' = 0, 1) band intensities; however, all other N₂⁺(B) bands are strongly attenuated and, except for v' = 2, by roughly the same factor as for the N₂⁺(C) emission. (2) Separating the contributions from ions and metastables as just described gives N₂⁺(B, v') populations from He(²S) in close accord with the results of the first entry of Table II. (3) The populations assigned to He⁺ excitation extend to higher vibrational levels than for He(³S). In addition to the systematic study of the Δv = -2 sequence summarized in Table I (many other experiments in the 2-3 torr pressure range gave similar results) numerous "tail bands" from high vibrational levels were observed under Condition II. The intensities of these "tail bands" were attenuated by the collector potential in the same way as

N₂⁺(C-X) and they can be attributed to excitation by He⁺. The bands which were not overlapped by other emissions were used to obtain the relative populations of v' = 11, 12, 14, 16, 17, and 19 shown in Table II. Unfortunately no information could be obtained for the v' = 7-10 levels because of the headless nature of the majority of these transitions. It is evident that the thermal He⁺ reaction gives a broad vibrational excitation in the N₂⁺(B) state.

The photon emission rate from the N₂⁺(B) Δv = -2 sequence, which was assigned to He⁺ excitation, was scaled to represent the total N₂⁺(B) emission rate from v' = 0-5 and 13 and this was compared to the N₂⁺(C-X) emission intensity; the average N₂⁺(B)/N₂⁺(C) ratio from several experiments was ~0.4. Correcting this for the higher vibrational levels of N₂⁺(B) and for the unobserved N₂⁺(C-X) emission intensity suggests that the ratio of *photon emission rates* from N₂⁺(B) and N₂⁺(C) is ~0.2-0.5 from the thermal charge exchange reaction between He⁺ and N₂. The difficulty of obtaining a good monochromator response calibration, as well as the corrections just mentioned, prevent a more accurate assessment of the

TABLE II. Relative vibrational populations of N₂⁺(B).

Helium species-condition	Relative vibrational population ^{a,b}												
	0	1	2	3	4	5	11	12	13	14	16	17	19
He(² S)-I	1000	93	2.8	0.5	0.3	0.3	•••	•••	•••	•••	•••	•••	•••
He(² S)-II	1000	82	5.9	0.01	0.02	0.03	•••	•••	•••	•••	•••	•••	•••
He ⁺ -II ^c	•••	•••	5.2	15	12	7.6	2.0	3.4	4.6	2.6	0.5	1.8	1.4
He(² S)-III	1000	88	3.5	0.3	0.2	•••	•••	•••	•••	•••	•••	•••	•••
He ⁺ and He ₂ ⁺ -III ^d	488	51	6.6	8.7	6.9	3.0	•••	•••	1.9	•••	•••	•••	•••

^aVibrational levels 0-5 and 13 are based upon the Δv = -2 sequence. Levels 11, 12, 14, 16, 17, and 19 are based upon the 11-10, 12-11, 14-12, 17-12, 16-14, and 19-13 bands which were normalized to the population of v' = 13 (using the 13-11 band). The populations in the second set of levels are the average results of several experiments.

^bThe populations from the metastables and ions are normalized to the level with the largest population, which was the v = 0 level from He(²S) excitation in all experiments.

^cSince the N₂⁺(v' = 0, 1) populations are large from He(³S) excitation, assignment of excitation to these levels from He⁺ excitation is uncertain.

^dThe tail bands were not monitored in this experiment; however, the relative populations of levels 11, 12, 14, 16, 17, and 19 can be estimated by referring to He-II and the population of v' = 13.

$N_2^+(B)/N_2^+(C)$ ratio.

Searches were made for the $N_2^+(D-A)$ and $N_2^+(A-X)$ emissions. Very weak bands in the 200–320 nm region were found which corresponded to transitions of $v' = 2-10$ of the $N_2^+(D-A)$ system.¹⁸ These band intensities correlated with the $N_2^+(C-X)$ intensity and were reduced by application of voltage to the collector electrodes; thus, $N_2^+(D)$ appears to be produced by charge exchange between N_2 and He^+ . It is difficult to estimate the relative importance of $N_2^+(D)$ as a product because a significant portion of the emission intensity is presumably too far to the red to be observed with our apparatus. The intensity of the observed transitions was more than an order of magnitude weaker than the $N_2^+(B)$ emission intensity. Qualitative observations of the 5–1, 6–2, 3–0, and 4–1 bands of the $N_2^+(A-X)$ system were made in the apparatus used for Conditions I and II. As far as could be ascertained, the presence of He^+ did not enhance the residual $N_2^+(A)$ excitation from $He(2^3S)$. High pressure experiments in the apparatus used for II, which enhance the He_2^+/He^+ ratio, strongly suggested that the $N_2^+(A-X)$ bands were reduced by ion collection. Thus charge exchange between He_2^+ and N_2 apparently yields $N_2^+(A)$ as a product. Unfortunately no observations of the $N_2^+(A-X)$ system were made under Condition III (to be described next) and, since those experiments actually were done first, that apparatus was not reassembled in order to make additional measurements.

The important new observation for N_2 under Condition III was the large effect that removal of the ions had upon the $N_2^+(B, v' = 0, 1)$ band intensities (see Table I). As shown in Table II, the relative populations assigned to the metastable excitation are very similar to the results of I and II; however, the $v' = 0$ and 1 population attributed to ionic excitation was greatly enhanced relative to Condition II. This general pattern of results was reproduced in three other experiments for III. We attribute the difference in $N_2^+(B)$ populations found for Conditions II and III to the presence of He_2^+ in III. This conclusion is supported by the observation of a similar ionic enhancement of the $v' = 0$ and 1 populations for experiments at higher pressure, > 4 torr, in the cell used for I and II. The $N_2^+(B, v' \geq 3)$ populations excited by ions under Condition III was similar to that from He^+ alone, which suggests that He_2^+ does not yield significant amounts of $N_2^+(B)$ in high vibrational levels.

Carbon monoxide

The emission analogous to $N_2^+(C-X)$ is not known for CO^+ ; hence, an internal monitor of He^+ is not available. However, either an N_2 spectrum was run immediately after a CO experiment to obtain the ion collection efficiency or the average collection efficiency of several preceding experiments with N_2 was used for separation of metastable and ionic excitation yields. The $CO^+(A$ and $B)$ relative vibrational populations (see Tables III and IV) obtained from $He(2^3S)$ with no discernible contribution from He^+ or He_2^+ are in good agreement with our earlier results,³ if allowance is made for vibrational relaxation of the $CO^+(A)$.^{3,19} The $v' = 2$ and 3 populations must arise from $He(2^3S)$ or He_2^+ (see below) be-

cause $He(2^3S)$ can give only $CO^+(B, v \leq 1)$. The predicted Franck-Condon¹⁵ $CO(X, v = 0) - CO^+(B, v = 0-3)$ vibrational populations are 100:35:7.1:1.7, which do not decline with increasing v as rapidly as for $N_2^+(B)$. In analyzing the band areas of the $\Delta v = -2$ sequence, consideration must be given to the carbon $2p3s(1P^0) - 2p^2(1S)$ atomic line at 247.9 nm, which is excited by the $He(2^3S) + CO$ reaction.²⁰

Within the limits of our experimental uncertainty, He^+ made insignificant contribution to the $CO^+(B-X)$ and $CO^+(A-X)$ emission intensities. This conclusion was reached with difficulty because of the high propensity for He_2^+ to give $CO^+(B)$ as a product. Thus, slightly differing amounts of He_2^+ for the same apparent operating conditions would give nonreproducible results with respect to the dependence of $CO^+(B-X)$ emission upon ion collection as monitored by the $N_2^+(C-X)$ emission intensity. The results from experiments II-A and -B and II-C and -D, which are summarized in Table III, illustrate the problem. At 2.2 torr the contributions from ions to the $CO^+(B)$ emission was barely observable, but the "normal" He^+ effect was found for N_2 . Increasing the pressure to ~ 4 torr had the effect of making the $CO^+(B-X)$ emission markedly sensitive to the collector potential; the $CO^+(A-X)$ also was affected by the potential but to a lesser degree. These observations are consistent with the increase in $[He_2^+]$ with increasing pressure and with a branching ratio favoring $CO^+(B)$ rather than $CO^+(A)$ in the charge transfer reaction between He_2^+ and CO.

For Condition III there was a very strong ionic contribution to $CO^+(B)$ and $CO^+(A)$; scaling the data of Table III to total emission rates suggests that $CO^+(B)/CO^+(A)$ is ~ 5 . Although this ratio is based upon limited data, i. e., the $\Delta v = -2$ sequence for $CO^+(B)$ and the $v' = 0$ progression for $CO^+(A)$, without doubt the B state is highly favored by the $He_2^+ + CO$ reaction. The relative vibrational populations assigned to $He(2^3S)$ for III are consistent with I if allowance is made for the greater degree of vibrational relaxation¹⁹ of $CO^+(A)$. Although the experimental uncertainty associated with separating the metastable and ionic contributions, as well as the vibrational relaxation of $CO^+(A)$ make it difficult to assign initial vibrational populations¹ from He_2^+ reactions, the populations of both $CO^+(B)$ and $CO^+(A)$ are consistent with Franck-Condon type distributions.

No evidence could be found for the $CO^+(^2\Delta - ^2\Pi)$ emission system,²¹ which is not surprising since formation from $He^+ + CO$ is endoergic by 0.18 eV. Some unassigned emissions were observed for pressures > 4 torr under Condition II in the 200–300 nm region. The intensities of these bands, which are broad and featureless, were comparable to the $CO^+(B, v' = 3-X, v'' = 5)$ band. These bands were attenuated by the collector potential but not as strongly as for known ion excitation processes, which suggests the importance of secondary reactions.

DISCUSSION

Our results support and extend the earlier observations^{1a,2} with regard to formation of $N_2^+(B)$ and $CO^+(B)$

TABLE III. Intensity measurements^{a,b} for CO.

Experimental conditions	CO*(B-X), Δv = -2 sequence				CO*(A-X), v'' = 0 Progression								
	v' = 0	1	2	3	v' = 0	1	2	3	4	5	6	7	8
I ^c -He(2 ³ S) (1.0 torr)	6.4(3)	1.5(3)	1.2(1)	trace	2.0(2)	1.3(3)	2.4(3)	1.9(3)	1.6(3)	9.7(2)	4.0(2)	1.4(2)	1.1(2)
II ^c -A He(2 ³ S) + He*(2.2 torr)	1.3(5)	3.8(4)	6.9(2)	trace									
II ^c -B II-A with ion collection	1.2(5)	3.4(4)	1.5(2)	trace	The relative intensities of the CO* (A-X) bands were the same for both experiments.								
II ^c -C He(2 ³ S) + He* + He ₂ ⁺ (3.5 torr)	4.0(5)	1.7(5)	2.0(4)	1.6(3)	4.8(4)	1.1(5)	1.3(5)	7.2(4)	6.4(4)	3.6(4)	1.2(4)	5.5(3)	
II ^c -D II-C with ion collection	1.9(5)	5.8(4)	1.0(3)	1.1(2)	4.2(4)	0.96(5)	1.2(5)	6.6(4)	5.3(4)	3.1(4)	0.91(4)	3.8(3)	
III ^d -A He(2 ³ S) + He* + He ₂ ⁺ (3.6 torr)	1.5(3)	6.1(2)	1.7(2)	1.5(1)	5.1(1)	1.9(2)	2.2(2)	1.3(2)	1.2(2)	6.9(1)	2.4(1)	9.6	6.6
III ^d -B III-A with ion collection	4.4(2)	1.0(2)	1.5(1)	0.7	2.7(1)	1.1(2)	1.3(2)	6.2(1)	5.5(1)	2.9(1)	8.6	4.1	4.7

^aThe tabulated band areas have been corrected for monochromator-detector response. The relative intensities should not be compared from one set of conditions to another because viewing geometry, slit width, etc. are not necessarily the same. The number in parenthesis is the power of 10 to be associated with the preceding number.

^bThese band areas were converted to relative populations of Table IV using the Franck-Condon factors of Ref. 15(c). No corrections were made to CO*(A) populations for the small CO*(B-A) cascade.

^cThe operating conditions for I and II were the same as specified in Table I, except for the pressure, which is noted in the table. Experiment II-A was shown to have a significant [He*] by observation of emissions from N₂⁺(C) and N₂⁺(B, high v').

^dSee Table I for a description of Condition III; the data are for a 400 V discharge. An experiment with a 250 V discharge gave similar relative vibrational populations; however, the ratio of ionic to metastable emissions was reduced, i.e., the ratio of CO*(B-X) and CO*(A-X) excited by ions vs metastables was ~2 and ~0.5 respectively, as contrasted to ~5 and ~1 for the 400 V experiment.

and A) and assignment of vibrational populations from charge exchange with He* and He₂⁺ under thermal conditions. The yields of bound excited state appear to be quite substantial from the He₂⁺ reactions and suggest possibilities of excitation mechanisms for several diatomic laser systems. The rare gas atomic ions, molecular ions, and atomic metastable states²² offer useful ranges of energies for laser excitation purposes. The charge transfer reactions are more selective with respect to exit channels than are Penning ionization reactions, which usually yield products corresponding to all available ionization continua.

The recent suggestion⁵ that the interaction of He* with N₂ gives a Franck-Condon vibrational distribution for N₂⁺(B) appears to be incorrect; however, small concentrations of He* will have a minor effect upon the Penning method for measuring vibrational temperatures of N₂(X) providing that analysis is based on only N₂⁺(B, v=1, 0) bands. Since He₂⁺ excitation may enhance the v ≥ 1 levels of N₂⁺(B) relative to metastable excitation [Table II and Ref. 1(a)], He₂⁺ can add complications to the Penning determination of the vibrational temperature of N₂(X).

The CO*(B) populations from He(2³S) only approximately follow the Franck-Condon prediction due to the energy limitation; He₂⁺ excitation may increase the relative contribution to v = 1, which makes the overall result resemble the Franck-Condon predicted values. In our opinion the only safe course for measurement of N₂(X) or CO(X) vibrational temperature by the Penning method is to reduce the He* and He₂⁺ concentrations to such an extent that the N₂⁺(B) or CO*(B) vibrational populations are not affected by ionic processes.

Recent molecular beam investigations^{6,23,24} of charge exchange reactions between atomic ions and molecules have shown that the process is not necessarily simple at reduced kinetic energies. Energy resonance, Franck-Condon^{25,14c} or distorted Franck-Condon factors,^{6b} and the nature of the molecular orbitals^{23b} have been discussed. Although the He* reaction with N₂ has been intensively investigated, the distribution of primary product states still is not understood. Formation of N₂⁺(C) followed by predissociation and radiation is undoubtedly a significant product channel.¹² Bowers and co-workers¹⁴ have claimed that the pressure depen-

TABLE IV. Relative populations for CO*(A and B).

Helium species-condition	Relative populations ^a												
	CO*(B); v' =				CO*(A); v' =								
	0	1	2	3	0	1	2	3	4	5	6	7	8
He(2 ³ S)-I (1.0 torr)	100	12	0.5	...	40	86	100	67	56	41	22	12	12
He(2 ³ S)-II ^b (2.2 torr)	100	13	0.2	...									
He(2 ³ S)-II (3.5 torr)	85	13	0.1	0.1	100	77	61	27	23	15	6	3	...
He ₂ ⁺ -II (3.5 torr)	100	25	3.6	0.3	15	11	5	3	5	3	2	2	...
He(2 ³ S)-III (3.6 torr)	27	2	100	86	62	25	22	14	5	4	6
He ₂ ⁺ -III (3.6 torr)	100	22	5.7	0.6	86	83	55	33	32	24	12	6	3

^aThe relative populations of the B and A states are separately normalized to the highest populated level, because the measurements for the A and B states frequently were done in separate experiments. See text for discussion of relative rates of formation of CO*(A) and CO*(B) by He₂⁺ and He(2³S).

^bThe contribution to the emission from ions at 2.2 torr was too small to be distinguished from the metastable excitation.

dence of the N^+/N_2^+ ratio in the $0.1\text{--}6 \times 10^{-4}$ torr range, requires some role for a long lived N_2^+ state which can give N^+ . Govers *et al.*^{12b} also have emphasized that molecular N_2^+ states other than $N_2^+(C)$ must be products. Our work has demonstrated that $N_2^+(B)$ and $N_2^+(D)$ also are ionic²⁶ products. The latter appears to be of lesser importance; however, the total $N_2^+(B)$ yield is comparable to the fraction ($\sim 10\%$ for $^{14}N_2^+$) of $N_2^+(C)$ that decays by radiation. Following a suggestion made by Cartwright,²⁷ the radiative decay channel $N_2^+(D \rightarrow B)$ was investigated as a possible mechanism for production of $N_2^+(B)$. Extensive searches for $N_2^+(D, v' = 8\text{--}15\text{--}B, \text{ lower } v')$ bands, which are predicted to be strong and free of $N_2^+(B \rightarrow X)$ bands by the calculated²⁷ FC factors and band origins, were negative. The transitions to low v' levels of $N_2^+(B)$ may not be favored, in fact, because of the two-electron aspect of the process²⁷: $N_2^+(D)$ can be represented as $2\sigma_u^2 3\sigma_g^2 1\pi_u^2 1\pi_g^1$ whereas the lower part of the $N_2^+(B)$ potential curve is well represented as $2\sigma_u^1 3\sigma_g^2 1\pi_u^4$. On the other hand, the upper part of the $N_2^+(B)$ curve has a considerable contribution from $2\sigma_u^2 3\sigma_g^1 \pi_u^3 \pi_g^1$ and hence represents a more favorable radiative pathway from $N_2^+(D)$ levels. Transitions from $N_2^+(D)$ to the higher levels of $N_2^+(B)$ in the red region also are favored by the Franck-Condon factors. Nevertheless, based upon the observed intensity of the $N_2^+(B \rightarrow X)$ transitions, the complete absence of detectable $N_2^+(D \rightarrow B)$ emission, and the weak $N_2^+(D \rightarrow A)$ emission, which is an allowed transition, radiative cascade from $N_2^+(D)$ is not a likely mechanism for populating $N_2^+(B)$ in the $He^+ + N_2$ reaction. Since the $N_2^+(B)$ vibrational distribution is quite consistent with the populations obtained from extrapolation of the molecular beam data⁶ to lower energies, it can be argued that formation of $N_2^+(B)$ by charge exchange with He^+ does not require secondary collisions. The Lipeles^{8b} distortion model has been used^{8c} to explain shifts in vibrational populations relative to expected Franck-Condon distributions. However, the very recent finding²⁴ that collisional excitation of $N_2^+(B)$ by neutral hydrogen atoms gives vibrational population similar to charge exchange makes this explanation somewhat suspect for N_2 .

It is surprising that $N_2^+(B)$ competes as a product channel with $N_2^+(C)$, which satisfies both energy resonance and favorable FC factor criteria. However, in the *simpler*²⁷ description, formation of $N_2^+(C)$ requires both ionization *and* excitation of an electron, whereas $N_2^+(B)$ requires only ionization. The observed levels of $N_2^+(D)$ state are disfavored by Franck-Condon factors and by the two-electron consideration. Based upon the overall N^+/N_2^+ ratio^{11b} from He^+ interacting with N_2 , the need for a long lived N_2^+ state and the relatively small yields of $N_2^+(B)$ and $N_2^+(D)$, quartet states^{14c} or $^2\Sigma_u^-$ states²⁷ are likely possibilities as other product channels.

Formation of both $CO^+(A)$ and $CO^+(B)$ has been observed from charge exchange of CO and high velocity rare gas ions⁶ and the Lipeles^{8c} polarization model, at least, qualitatively fitted the $CO^+(A)$ vibrational distribution. However, under thermal conditions dissociative ionization is the only product channel.^{14c}

A striking difference between charge exchange of He^+ and He_2^+ with diatomic reagents is the favoring of bound

rather than dissociative ionic product states. For both N_2 and CO the B ionic state is the preferred channel, and we estimate that $CO^+(B)/CO^+(A) = 5$. This may be contrasted to a ratio of nearly unity from $He(2^3S)$ Penning ionization.^{3a,28} An experiment was done in which the relative intensities of $N_2^+(B \rightarrow X)$ and $CO^+(B \rightarrow X)$ excitations arising from the same concentration of He_2^+ were compared. Based upon the $\Delta v = -2$ sequence in both instances, the *total* emission rates favored $CO^+(B)$ by about a factor of 2. The wide range of product ion states, but with vibrational distributions resembling those expected from Franck-Condon considerations, appears to be characteristic of charge exchange reactions with He_2^+ . This must be a consequence of the dissociative molecular state for He_2 , which provides less stringent energy restrictions relative to charge transfer reactions yielding neutral products in bound states. The surprising absence of a polarization effect upon the vibrational population distributions from charge exchange between He_2^+ and N_2 and CO may be a consequence of the electron being transferred at a large distance.

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- ²⁸This ratio was remeasured in the current study and our previous value was confirmed. Although the monochromator is the same as that used previously, the calibration has been updated. Hurt and Grable²⁰ have reported a $CO^*(B)/CO^*(A)$ ratio of 3.1 from Penning ionization. One possible explanation of the different results from the two laboratories is the presence of a small concentration of He_2^* in the experiments of Hurt and Grable.