Excitation of nitrogen and carbon monoxide ionic emissions by He(2\(^3\)S), He\(^+\), and He\(_2\)^+ 

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(Received 11 October 1974) 

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

INTRODUCTION 

Results from several laboratories\(^1\)-\(^3\) are in general agreement regarding the optical emission spectra from thermal reactions between He(2\(^3\)S) with N\(_2\) and CO. The N\(_2\)^+(B) and 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 results are inconsistent and/or in partial conflict. A recent claim\(^4\) that the N\(_2\)^+(B) vibrational populations from thermal charge exchange between He\(^+\) and N\(_2\) were similar to those from He(2\(^3\)S)+N\(_2\) disagreed with our own experience and with prior published suggestions.\(^1\),\(^2\) An understanding of the N\(_2\)^+(B) vibrational populations is important for utilization of the He(2\(^3\)S) Penning ionization method for measurement of vibrational temperatures of N\(_2\) because He\(^+\) and He\(^+_2\) are often impurities with the He(2\(^3\)S). The discrepancy\(^7\) of the 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 [helium ions]/[He(2\(^3\)S)] in our cold hollow-cathode discharge flow apparatus\(^8\) prompted the present investigation of the optical emission spectra excited by He(2\(^3\)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 N\(_2\)^+(B-X) laser system\(^9\) 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\(^10\) faster than that for He(2\(^3\)S) at room temperature\(^11\); the energies (eV) provided by the species are 19.818(He\(^+\), \(^3\)S), \(<22(\text{He}_2\), \(^1\) and \(24.58(\text{He}^+_2\)). The He(2\(^3\)S) limit is not quite sufficient to produce N\(_2\)^+(B) \(v'=4(19.90 \text{ eV})\) or CO\(^+\)(B)\(v'=1(19.879 \text{ eV})\) without utilization of some thermal energy of the collision.\(^12\),\(^13\) The N\(_2\)^+(C-X) emission can be used as a diagnostic\(^15\) indication of He\(^+\) in the presence of He(2\(^3\)S) and He\(^+_2\) because 23.6 eV are required to form N\(_2\)^+(C). The competition between emission and predissociation\(^13\) for N\(_2\)^+(C) has been characterized\(^16\) and for \(^14\)N\(_2\) the ratio of predissociation to emission is 9.8, but for \(^15\)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 \(^14\)N\(_2\) case\(^17\); N\(_2\) must arise from states other than N\(_2\)^+(C). However, a satisfactory mechanism for describing the N\(_2\) product states has yet to be formulated.\(^13\),\(^14\) 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 He(2\(^3\)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 He(2\(^3\)S). Spectra with varying concentrations of ions, monitored by the N\(_2\)^+(C-X) emission intensity, were then contrasted to the He(2\(^3\)S) reference spectra in order to deduce the role played by the He\(^+\) and He\(^+_2\) reactions. Our spectral range was \(\sim 190-800 \text{ nm}\); since the 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\(^16\) for study of He(2\(^3\)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.\(^18\) 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 \(\text{ m}^3\) \(\text{min}^{-1}\) 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 CO₂ 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 He(²S) and Ne. Under conditions such that the [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 N₂(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 [He⁺]/[He(²S)] relative to Condition I, but the low signal from He(²S) 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 [He⁺] and [He⁺]. 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 end 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 He₂, 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 [He(²S)] was monitored by observing the Ne 703.2 nm line and, later in the work, the N₂(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 N₂(B, v' = 0–X) emission intensity. However, the data for this report are based on experiments for which the diagnostic emissions from [He(²S)] were unchanged (±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 NO(A, v' = 0, 1–X) transitions 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 CO(a, v' = 0, 1–X) transitions were used to extend the calibration to 198 nm. The branching ratios of the CO(B, v' = 0, 1–X) transitions were used to confirm the calibration curve based on the CO(a) and NO(A) transitions; agreement to within ±15% was obtained for strong bands. The Δv = ±8, ±7, and ±6 sequences of N₂(C–X), which comprise 65% of the emission intensity, are at 206, 198.5, and 191.3 nm, respectively; the calibration curve was extrapolated to obtain the relative response for the Δv = ±6 bands. The corrected band areas of the N₂(B–X), CO(C–X), and CO(B–A) transitions were converted to relative vibrational populations using the Franck-Condon factors of Ref. 15(c).

RESULTS

Nitrogen

The results from N₂ are summarized in Tables I and II; for the first entry the N₂(C–X) emission was either very weak or not observable and the N₂(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 He(²S) excitation. Although the N₂(B) vibrational populations are based only on the Δv = 2 sequence and, hence, are not as reliable as a summation over all bands, the N₂(B) v' = 0 and 1 populations from He(²S) 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, N₂(X, v = 0) ~ N₂(B, v = 0–4), values56 (1000:134: 2.4: 0.03; 0.002). The excess population for v' ≥ 3 (a trace of v' = 6 also was noted in the spectrum) probably reflects the presence of residual concentrations of He⁺ or He(²S). No rotational intensity anomalies were found to suggest that the populations of the N₂(B, v' = 0–4) levels were being affected by perturbations48 from high vibrational levels of N₂(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 we previously have observed intensity anomalies for CN(B–X) at similar pressures, rotational relaxation would not have obscured such effects if they were present.

For Conditions II and III the N₂(C–X) intensity was monitored and the ratio of this signal with (I_C²) and without (I_C¹) a potential applied to the collector electrodes was used to separate the other emission intensities into contributions from metastables and from ions, i.e.,

\[ I_B(\text{He}^+ + \text{He}_2^+) = I_C^2 - I_C^1 / F \]

\[ I_B(\text{He}^+) = I_C^2 - I_B(\text{He}^+ + \text{He}_2^+) \]

\[ F = (I_C^1 - I_C^2) / I_C^1 \]

The relative contributions from He⁺ and He₂⁺ can be qualitatively identified by comparing results from II, for which the ion species is largely He⁺, and III, for which
TABLE I. Results* for \( \text{N}_2 \).

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Relative intensities&lt;sup&gt;b&lt;/sup&gt; ( \text{N}_2^0(\text{B}-\text{X}), \Delta v = -2 )</th>
<th>Relative intensity&lt;sup&gt;b&lt;/sup&gt;</th>
<th>( \text{N}_2^1(\text{C}-\text{X}) ) ( \Delta v = -6, -7 ) and 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>I ( \text{He}^5(\text{S}) ); 1.2 torr</td>
<td>( 7.1(4) ) ( 1.2(4) ) ( 4.2(2) ) ( 8.5(1) ) ( 3.8 ) ( 4.2 ) ( *** ) ( 2.73(3) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II-( \text{He}^5(\text{S}) )+( \text{He}^5 ); 2.7 torr</td>
<td>( 3.1(5) ) ( 6.2(4) ) ( 8.3(4) ) ( 1.1(4) ) ( 8.0(3) ) ( 4.4(3) ) ( 1.7(3) ) ( 9.7(3) )</td>
<td></td>
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</tr>
<tr>
<td>II-B-( \text{II}-\text{A} ) with ion collision</td>
<td>( 3.2(5) ) ( 5.7(4) ) ( 5.7(3) ) ( 4.1(3) ) ( 2.9(3) ) ( 1.9(3) ) ( 5.1(2) ) ( 3.4(3) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III-( \text{A} ) ( \text{He}^5(\text{S}) )+( \text{He}^5 )+( \text{He}^5 ); 3.6 torr</td>
<td>( 6.4(3) ) ( 1.1(3) ) ( 1.0(2) ) ( 9.1(1) ) ( 6.4(1) ) ( 2.3(1) ) ( 2.6(1) ) ( 5.1(3) )</td>
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<tr>
<td>III-B-( \text{II}-\text{A} ) with ion collision</td>
<td>( 4.5(3) ) ( 7.4(2) ) ( 4.0(1) ) ( 1.1(1) ) ( 7.1 ) ( 2.1 ) ( 1.5 ) ( 4.5(2) )</td>
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</table>

<sup>a</sup>Conversion of the total relative emission intensities assigned to ionic and metastable excitation into a \( \text{He}^5(\text{S})/\text{ions} \) ratio is not straightforward because of the uncertainty in branching ratios for \( \text{He}^5 \) and \( \text{He}^5 \) reactions. It should be remembered that the product ratios must be inversely weighted by the total rate constants to obtain reactant ratios.

<sup>b</sup>The intensities of the \( \Delta v = -2 \) 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.

<sup>c</sup>Integrated band areas have been corrected for monochromator-detector response; the \( \text{N}_2^1(\text{C}-\text{X}) \) 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.

<sup>d</sup>See text for description of Condition I.

<sup>e</sup>The 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.

<sup>f</sup>The 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 500 V and 15 mA; a potential difference of 40 V was used on the second set to collect ions.

He\(^5\)/He\(^5\) has been enhanced. Presumably the metastable He\(^{25S^5}\) 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 \( \text{N}_2 \): (1) Application of the collector voltage hardly altered the \( \text{N}_2(\text{B}, \Delta v = 0, 1) \) band intensities; however, all other \( \text{N}_2(\text{B}) \) bands are strongly attenuated and, except for \( \Delta v = 2 \), by roughly the same factor as for the \( \text{N}_2^1(\text{C}) \) emission. (2) Separating the contributions from ions and metastables as just described gives \( \text{N}_2(\text{B}, \Delta v) \) populations from He\(^{25S}\) in close accord with the results of the first entry of Table II. (3) The populations assigned to He\(^\ast\) excitation extend to higher vibrational levels than for He\(^5\). In addition to the systematic study of the \( \Delta v = -2 \) 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 \( \text{N}_2^1(\text{C}-\text{X}) \) and they can be attributed to excitation by He\(^\ast\). The bands which were not overlapped by other emissions were used to obtain the relative populations of \( \Delta v = 11, 12, 14, 16, 17, \) and 19 shown in Table II. Unfortunately no information could be obtained for the \( \Delta v = 7-10 \) levels because of the headless nature of the majority of these transitions. It is evident that the thermal He\(^\ast\) reaction gives a broad vibrational excitation in the \( \text{N}_2^0(\text{B}) \) state.

The photon emission rate from the \( \text{N}_2^0(\text{B}) \) \( \Delta v = -2 \) sequence, which was assigned to He\(^\ast\) excitation, was scaled to represent the total \( \text{N}_2^1(\text{B}) \) emission rate from \( \Delta v = 0-5 \) and 13 and this was compared to the \( \text{N}_2^1(\text{C}-\text{X}) \) emission intensity; the average \( \text{N}_2(\text{B})/\text{N}_2(\text{C}) \) ratio from several experiments was \( -0.4 \). Correcting this for the higher vibrational levels of \( \text{N}_2(\text{B}) \) and for the unobserved \( \text{N}_2(\text{C}-\text{X}) \) emission intensity suggests that the ratio of photon emission rates from \( \text{N}_2^1(\text{B}) \) and \( \text{N}_2(\text{C}) \) is \( \approx 0.2-0.5 \) from the thermal charge exchange reaction between He\(^\ast\) and \( \text{N}_2 \). 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 \( \text{N}_2^1(\text{B}) \). |
|-----------------|----------------|----------------|----------------|----------------|
| He\(^{25S}\)-I  | 1000           | 93             | 2.8            | 0.5            | 0.3            | 0.3            |
| He\(^{25S}\)-II | 1000           | 82             | 5.9            | 0.01           | 0.02           | 0.03           |
| He\(^{25S}\)-III| 1000           | 88             | 3.5            | 0.3            | 0.2            | 0.2            |
| He\(^{25S}\) and He\(^{25S}\)-III | 488           | 51             | 6.6            | 8.7            | 6.9            | 3.0            |

<sup>a</sup>Vibrational levels 0–5 and 13 are based upon the \( \Delta v = -2 \) sequence. Levels 11, 12, 14, 16, 17, and 19 are based upon the levels 1–10, 12–11, 14–12, 17–12, 16–14, and 19–13 bands which were normalized to the population of \( \Delta v = 13 \) (using the 13–11 band). The populations in the second set of levels are the average results of several experiments.

<sup>b</sup>The populations from the metastables and ions are normalized to the level with the largest population, which was the \( \Delta v = 0 \) level from He\(^{25S}\) excitation in all experiments.

<sup>c</sup>Since the \( \text{N}_2(\text{B}, \Delta v = 0, 1) \) populations are large from He\(^5\) excitation, assignment of excitation to these levels from He\(^\ast\) excitation is uncertain.

<sup>d</sup>The 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 \( \Delta v = 13 \).
\( \frac{N_2^0(B)}{N_2^0(C)} \) ratio.

Searches were made for the \( N_2^0(D-A) \) and \( N_2^0(A-X) \) emissions. Very weak bands in the 200–320 nm region were found which corresponded to transitions of \( v' = 2-10 \) of the \( N_2^0(D-A) \) system.\(^{18} \) These band intensities correlated with the \( N_2^0(C-X) \) intensity and were reduced by application of voltage to the collector electrodes; thus, \( N_2^0(D) \) appears to be produced by charge exchange between \( N_2 \) and \( He^+ \). It is difficult to estimate the relative importance of \( N_2^0(D) \) 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 \( N_2^0(B) \) emission intensity. Qualitative observations of the 5–1, 6–2, 3–0, and 4–1 bands of the \( N_2^0(A-X) \) 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 \( N_2^0(A) \) excitation from \( He(2^3S) \). High pressure experiments in the apparatus used for II, which enhance the \( He^+/He \) ratio, strongly suggested that the \( N_2^0(A-X) \) bands were reduced by ion collection. Thus charge exchange between \( He^+ \) and \( N_2 \) apparently yields \( N_2^0(A) \) as a product. Unfortunately no observations of the \( N_2^0(A-X) \) 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 \( N_2^0(B, v' = 0, 1) \) 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 \( N_2^0(B) \) populations found for Conditions II and III to the presence of \( He^+ \) 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 \( N_2^0(B, v' = 3) \) populations excited by ions under Condition III was similar to that from \( He^+ \) alone, which suggests that \( He^+ \) does not yield significant amounts of \( N_2^0(B) \) in high vibrational levels.

Carbon monoxide

The emission analogous to \( N_2^0(C-X) \) is not known for \( CO_2 \); hence, an internal monitor of \( He^+ \) is not available. However, either an \( N_3 \) 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 \( CO^+(A \text{ and } B) \) 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,\(^{18} \) if allowance is made for vibrational relaxation of the \( CO^+(A) \).\(^{5,19} \) The \( v' = 2 \) and 3 populations must arise from \( He(2^3S) \) or \( He_2^+ \) (see below) because \( He(2^3S) \) can give only \( CO^+(B, v \leq 1) \). The predicted Franck–Condon\(^{15} \) \( CO_2, v = 0 \text{– } CO^+(B, v = 0-3) \) 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 \( 2p5s(1^3P^0)-2p5p(1^3P) \) 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 \( He^+ \) to give \( CO^+(B) \) as a product. Thus, slightly differing amounts of \( He^+ \) 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 \( N_2^0(C-X) \) emission intensity. The results from experiments II–A and II–B and III–C and III–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 \( [He^+] \) with increasing pressure and with a branching ratio favoring \( CO^+(B) \) rather than \( CO^+(A) \) in the charge transfer reaction between \( He^+ \) 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 relaxation\(^{19} \) 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 populations\(^{1} \) 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 \( CO^+(2^3\Delta^2-H) \) emission system,\(^{14} \) 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\(^{1,14,5} \) with regard to formation of \( N_2^0(B) \) and \( CO^+(B) \)

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

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>(\text{CO}^\text{(B-X), } \Delta v = -2) sequence</th>
<th>(\text{CO}^\text{(A-X), } \Delta v' = 0) Progression</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{I}^\text{I} = \text{He}^\text{2S}) (1.0 torr)</td>
<td>6.4(2) (0.5(3)) (1.2(1)) trace (2(2)) (1.3(3)) (2.4(3)) (1.9(2)) (1.6(3)) (9.7(2)) (4.0(2)) (1.4(2)) (1.1(2))</td>
<td>(\text{I}^\text{I} = \text{He}^\text{2S} + \text{He}^\text{2S}) (2.2 torr)</td>
</tr>
<tr>
<td>(\text{I}^\text{I} = \text{He}^\text{2S} + \text{He}^\text{2S}) (2.2 torr)</td>
<td>1.3(5) (3.8(4)) (6.9(2)) trace</td>
<td>4.8(4) (1.1(2)) (1.3(2)) (7.2(2)) (6.4(4)) (3.6(6)) (1.2(4)) (5.5(3))</td>
</tr>
<tr>
<td>(\text{I}^\text{I} = \text{He}^\text{2S} + \text{He}^\text{2S}) with ion collection</td>
<td>1.3(5) (3.4(4)) (1.3(2)) trace</td>
<td>(\text{I}^\text{I} = \text{He}^\text{2S} + \text{He}^\text{2S}) (3.5 torr)</td>
</tr>
<tr>
<td>(\text{I}^\text{I} = \text{He}^\text{2S} + \text{He}^\text{2S}) with ion collection</td>
<td>4.0(5) (1.7(3)) (2.9(4)) (1.6(3)) (4.8(4)) (1.1(2)) (1.3(2)) (7.2(2)) (6.4(4)) (3.6(6)) (1.2(4)) (5.5(3))</td>
<td>(\text{I}^\text{I} = \text{He}^\text{2S} + \text{He}^\text{2S}) (3.5 torr)</td>
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</table>

\*The 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.

\*These bands areas were converted to relative populations of Table IV using the Franck–Condon factors of Ref. 15(c). No corrections were made to \(\text{CO}^\text{(A)}\) populations for the small \(\text{CO}^\text{(B-A)}\) cascade.

\*The 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\textsuperscript{2}S] by observation of emissions from \(\text{N}_2\text{(C)}\) and \(\text{N}_2\text{(B), high } v'\).

\*See 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 \(\text{CO}^\text{(B-A)}\) and \(\text{CO}^\text{(A-X)}\) 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 \(\text{He}^\text{2S}\) and \(\text{He}^\text{2S}\) under thermal conditions. The yields of bound excited state appear to be quite substantial from the \(\text{He}^\text{2S}\) reactions and suggest possibilities of excitation mechanisms for several diatomic laser systems. The rare gas atomic ions, molecular ions, and atomic metastable states\textsuperscript{25} 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 suggestion\textsuperscript{26} that the interaction of \(\text{He}^\text{2S}\) with \(\text{N}_2\) gives a Franck–Condon vibrational distribution for \(\text{N}_2\text{(B)}\) appears to be incorrect; however, small concentrations of \(\text{He}^\text{2S}\) will have a minor effect upon the Penning method for measuring vibrational temperatures of \(\text{N}_2\text{(X)}\) providing that analysis is based on only \(\text{N}_2\text{(B, } v=1, 0)\) bands. Since \(\text{He}^\text{2S}\) excitation may enhance the \(v \geq 1\) levels of \(\text{N}_2\text{(B)}\) relative to metastable excitation [Table II and Ref. 1(a)], \(\text{He}^\text{2S}\) can add complications to the Penning determination of the vibrational temperature of \(\text{N}_2\text{(X)}\).

The \(\text{CO}^\text{(B)}\) populations from \(\text{He}^\text{2S}\) only approximately follow the Franck–Condon prediction due to the energy limitation; \(\text{He}^\text{2S}\) 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 \(\text{N}_2\text{(X)}\) or \(\text{CO(X)}\) vibrational temperature by the Penning method is to reduce the \(\text{He}^\text{2S}\) and \(\text{He}^\text{2S}\) concentrations to such an extent that the \(\text{N}_2\text{(B)}\) or \(\text{CO}^\text{(B)}\) vibrational populations are not affected by ionic processes.

Recent molecular beam investigations\textsuperscript{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\textsuperscript{25,26} or distorted Franck–Condon factors,\textsuperscript{16} and the nature of the molecular orbitals\textsuperscript{26} have been discussed. Although the \(\text{He}^\text{2S}\) reaction with \(\text{N}_2\) has been intensively investigated, the distribution of primary product states still is not understood. Formation of \(\text{N}_2\text{(C)}\) followed by predissociation and radiation is undoubtedly a significant product channel.\textsuperscript{12} Bowers and co-workers\textsuperscript{25} have claimed that the pressure depen-

<table>
<thead>
<tr>
<th>Relative populations\textsuperscript{a}</th>
<th>(\text{CO}^\text{(B)}; \Delta v'' = 0)</th>
<th>(\text{CO}^\text{(A)}; \Delta v'' = 0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{He}^\text{2S(I)} = 1.0 \text{ torr} )</td>
<td>100</td>
<td>12</td>
</tr>
<tr>
<td>(\text{He}^\text{2S(I)} = 2.2 \text{ torr} )</td>
<td>100</td>
<td>13</td>
</tr>
<tr>
<td>(\text{He}^\text{2S(I)} = 3.5 \text{ torr} )</td>
<td>85</td>
<td>13</td>
</tr>
<tr>
<td>(\text{He}^\text{2S(I)} = 3.5 \text{ torr} )</td>
<td>100</td>
<td>25</td>
</tr>
<tr>
<td>(\text{He}^\text{2S(I)} = 3.5 \text{ torr} )</td>
<td>27</td>
<td>2</td>
</tr>
<tr>
<td>(\text{He}^\text{2S(I)} = 3.5 \text{ torr} )</td>
<td>100</td>
<td>22</td>
</tr>
</tbody>
</table>

\*The 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 \(\text{CO}^\text{(A)}\) and \(\text{CO}^\text{(B)}\) by \(\text{He}^\text{2S}\) and \(\text{He}^\text{2S}\).

\*The contribution to the emission from ions at 2.2 torr was too small to be distinguished from the metastable excitation.

dence of the N⁺/Nₐ ratio in the 0.1–8×10⁻⁴ torr range, requires some role for a long lived N₂ state which can give N⁺. Govers et al.¹² have also emphasized that molecular N₂ states other than N₂(C) must be products. Our work has demonstrated that N₂(B) and N₂(D) also are ionic⁵⁸ products. The latter appears to be of lesser importance; however, the total N₂(B) yield is comparable to the fraction (~10% for [¹⁴N₂] of N₂(C) that decays by radiation. Following a suggestion made by Cartwright,⁴⁷ the radiative decay channel N₂(D–B) was investigated as a possible mechanism for production of N₂(B). Extensive searches for N₂(D, v=8–15=B, lower v’) bands, which are predicted to be strong and free of N₂(B-X) bands by the calculated⁷² FC factors and band origins, were negative. The transitions to low v’ levels of N₂(B) may not be favored, in fact, because of the two-electron aspect of the process⁷¹: N₂(D) can be represented as 2σ⁺ 2σ⁺ 1π⁺ 1π⁺ whereas the lower part of the N₂(D) potential curve is well represented as 2σ⁺ 3σ⁺ 1π⁺ 1π⁺. On the other hand, the upper part of the N₂(B) curve has a considerable contribution from 2σ⁺ 2σ⁺ 1π⁺ 1π⁺ and hence represents a more favorable radiative pathway from N₂(D) levels. Transitions from N₂(D) to the higher levels of N₂(B) in the red region also are favored by the Franck–Condon factors. Nevertheless, based upon the observed intensity of the N₂(B→X) transitions, the complete absence of detectable N₂(D→B) emission, and the weak N₂(D→A) emission, which is an allowed transition, radiative cascade from N₂(D) is not a likely mechanism for populating N₂(B) in the He⁺+N₂ reaction. Since the N₂(B) vibrational distribution is quite consistent with the populations obtained from extrapolation of the molecule beam data⁶ to lower energies, it can be argued that formation of N₂(B) by charge exchange with He⁺ does not require secondary collisions. The Lipeles⁵⁷ distortion model has been used⁶⁸ to explain shifts in vibrational populations relative to expected Franck–Condon distributions. However, the very recent finding⁶⁹ that collisional excitation of N₂(B) by neutral hydrogen atoms gives vibrational population similar to charge exchange makes this explanation somewhat suspect for N₂.

It is surprising that N₂(B) competes as a product channel with N₂(C), which satisfies both energy resonance and favorable FC factor criteria. However, in the simple⁵⁷ description, formation of N₂(C) requires both ionization and excitation of an electron, whereas N₂(B) requires only ionization. The observed levels of N₂(D) state are disfavored by Franck–Condon factors and by the two-electron consideration. Based upon the overall N⁺/Nₐ ratio¹¹ from He⁺ interacting with N₂, the need for a long lived N₂ state and the relatively small yields of N₂(B) and N₂(D), quartet states⁶⁴ or ²Π₅/₂⁵ states⁷⁷ 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 ions⁵ and the Lipeles⁶⁸ polarization model, at least, qualitatively fitted the CO(A) vibrational distribution. However, under thermal conditions dissociative ionization is the only product channel.¹⁶

A striking difference between charge exchange of He⁺ and He²⁺ with diatomic reagents is the favoring of bound rather than dissociative ionic product states. For both N₂ and CO the B ionic state is the preferred channel, and we estimate that CO(A)/CO(B)=5. This may be contrasted to a ratio of nearly unity from He(2S) Penning ionization.⁴³ An experiment was done in which the relative intensities of N₂(B=X) and CO(B=X) excitations arising from the same concentration of He²⁺ were compared. Based upon the Δv = -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 He²⁺. This must be a consequence of the dissociative molecular state for He₂⁺, 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 He²⁺ and N₂ and CO may be a consequence of the electron being transferred at a large distance.

ACKNOWLEDGMENTS

This work was supported by the U.S. Army Research Office–Durham (DA-ARO-D-31-124-71-G127 and DAHC04–75–G0018) and the Petroleum Research Fund (administered by the American Chemical Society). We wish to thank Dr. Abritton and Dr. Haugh for critically reading a preliminary draft of the manuscript and Dr. Ottinger and Dr. Cartwright for helpful discussions.

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(3) W. C. Richardson and D. W. Setser, J. Chem. Phys. 58, 1809 (1973). For this work discharge conditions were similar to Condition I, but with lower current. (b) D. W. Setser, Int. J. Mass Spectrom. Ion Phys. 11, 301 (1973). Excitation by He⁺ may augment some of the processes assigned to He(2S) in this work. The Δv² value in Table 2 for SCO was incorrectly listed as 18.2 eV; the correct value is 18.9 eV; thus, part of the CO(A) formed from SCO may involve a higher energy source than He(2S). These considerations do not affect the conclusions of the paper.


(5) S. J. Young and K. P. Horn, J. Chem. Phys. 57, 4835 (1972); (b) S. J. Young, ibid. 58, 1603 (1973).


17(a) P. R. Kemper and M. T. Bowers, J. Chem. Phys. 59, 4915 (1973); (b) M. T. Bowers, P. R. Kemper, and J. B. Landenlager, ibid. 61, 4394 (1974); (c) J. B. Landenlager, W. T. Huntress, Jr., and M. T. Bowers, ibid. 61, 4600 (1974).
29For very high concentrations of added N₂, strong neutral emission, N₂(B→A), appears in either the He∞ or He∞(S) flowing afterglow [M. S. Manatis and H. P. Broida. Mol. Phys. 20, 947 (1971) and G. W. Taylor and D. W. Setser, unpublished results]. We also observed weak N₂(C→B) emissions in the current work under Condition II.
30D. C. Cartwright and T. H. Dunning, Jr. (private communication, 1974). These authors point out the strong mixing between the N₂(C) state and the upper vibrational levels of N₂(B), which modifies the simplest molecular orbital description of these excited states.
31This ratio was re-measured 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 Grable have reported a CO(3)/CO(1) 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 in the experiments of Hurt and Grable.