Determination of non-Boltzmann vibrational distributions of $N_2(X,v'')$ in He/N₂ microwave-discharge afterglows

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We have extended a technique for studying the vibrational distributions of ground-electronic-state, molecular nitrogen in the afterglow of a microwave discharge through mixtures of helium and nitrogen. The technique is based upon adding metastable helium atoms to the afterglow. The He*($2\,^3S$) excites the $N_2(X,v)$ to N_2^+ ($B\,^2\Sigma_u^+$) in a Penning-ionization reaction. Since Penning ionization is a Franck–Condon process, the vibrational distribution of the N_2^+ (B) product is determined by that of the N_2 (X,v) from which it was produced. The measurements show that the ground-state nitrogen distribution is highly non-Boltzmann, with vibrationally hotter distributions being produced with lower mole fractions of nitrogen in the discharge. We have also observed the production of N_2^+ ($C\,^2\Sigma_u^+$) from He* Penning ionization of molecular nitrogen. This process is energetically allowed only if the vibrational energy in the ground-electronic-state nitrogen exceeds 3.8 eV or 15 vibrational quanta.

I. INTRODUCTION

Our recent observations in discharged nitrogen afterglows showed that $IF(B\,^3\Pi_{0^+})$[1] and $N_2(B\,^3\Pi_g)$[1,2] excitation appeared to result from V–E transfer rather than the more conventional E–E transfer from one electronically excited species to another. To investigate these processes more fully, we needed to develop a diagnostic for $N_2(v)$. This report details our development of an N_2 (X,v) diagnostic based upon Penning ionization by metastable helium atoms.

Vibration-to-electronic transfer processes, if efficient, could have important implications for chemical laser development as well as for the modeling of disturbed atmospheres because, unlike the lowest electronically excited nitrogen metastable, $N_2(A^3\Sigma_u^+)$,[3] $N_2(v)$ does not destroy itself efficiently in collisions. Indeed, quite high levels of vibrational excitation can be achieved by V–V up-pumping.[4-7] Thus $N_2(v)$ might act as an energy storage medium in a laser system, and $N_2(v)$ created in an atmospheric disturbance could cool only by collisions with unlike species. We note that Starr observed V–E excitation of Na and K by N_2 (v),[8,9] and the work of Rich and co-workers provides evidence of efficient V–E transfer in systems involving $CO(v)$[10] and $NO(v)$.[11]

A number of previous studies of the effluents of active-nitrogen discharge afterglows have shown qualitatively the presence of vibrationally excited nitrogen. Quantitative assessment of the degree of ground-state vibrational excitation, however, generally has proved difficult. Because N_2 is not an infrared active molecule, the degree of vibrational excitation in the active nitrogen has been probed primarily by indirect methods. Kaufman and Kelso[12] remarked on the heated walls of their flow reactor downstream from their discharge and attributed the source of this heat to deactivation of vibrationally excited nitrogen molecules in collisions with the walls. Morgan, Phillips, and Schiff[13,14] noted an excess temperature given to the catalytic probe placed in their flow reactor which could not be attributed N-atom re-combination. Again they suggested that the source of this excess heat was vibrationally excited nitrogen molecules. Starr[8] and Starr and Shaw[9] observed excitation of sodium and potassium electronic transitions when they introduced sodium or potassium atoms to the afterglow of a nitrogen discharge. They suggested that the excitation resulted from a vibrational-to-electronic (V–E) excitation from $N_2(v)$ to Na or K. Bass[15] and Tanaka *et al.*[16] used vacuum ultraviolet (VUV) absorption spectroscopy, employing the partially forbidden Lyman–Birge–Hopfield bands, to show that $N_2(v)$ was indeed present in nitrogen-discharge afterglows. A number of other diagnostics have been developed in more recent years including photoionization,[17] photoelectron spectroscopy,[18,19] electron energy loss,[20] Penning ionization,[21-24] Raman,[25-27] CARS,[28,29] and multiphoton ionization,[30,31] among others. Caledonia *et al.* have reviewed much of this work in a recent report.[32]

Our diagnostic for vibrationally excited nitrogen in discharge afterglows extends the pioneering work of Schmeltekopf *et al.*[21] and Young and Horn.[22,23] They relied on the vertical nature of Penning-ionization transitions from ground-electronic-state, neutral nitrogen to produce N_2^+ ($B\,^2\Sigma_u^+,v$) distributions characteristic of the ground-state distributions. Mixing metastable helium atoms with a flow of molecular nitrogen results in strong emission of the nitrogen first-negative system, N_2^+ ($B\,^2\Sigma_u^+ - X\,^2\Sigma_g^+$). Since the Penning-ionization process follows a Franck–Condon excitation pathway, the vibrational distribution in the neutral, ground state will determine the distribution observed in the upper, ionic state. One problem with this approach is that care must be taken not to have any He$^+$ or He$_2^+$ in the flow of metastable helium. Both of those species also excite N_2^+ (B) quite strongly in charge–transfer reactions, but with an N_2^+ (B) vibrational distribution that is decidedly non-Franck–Condon.[33] This diagnostic is most sensitive to vibrational excitation of the first six vibrational levels in the ground electronic state. Our goal is to be able to estimate the

overall vibrational distribution of the ground-state nitrogen by combining our experimental determination of the vibrational distribution in the lower levels with modeling calculations on the temporal development of the fully coupled vibrational-state manifold.[4,5] Jolly et al.[24] have also re-investigated the Penning-ionization technique.

II. EXPERIMENTAL

The discharge-flow apparatus used in these experiments has been described in most respects previously.[34–39] We summarize briefly the modifications required for the measurements related to $N_2(v)$. Figure 1 shows the configuration of the flow reactor. A microwave discharge at the upstream end of the flow reactor, through a flow of helium and nitrogen, creates the active nitrogen. It enters a section of 2 in. diameter Pyrex® containing three sidearms. Small amounts of SF_6 flow through the first sidearm to attach electrons created in the Penning-ionization reactions and the metastable helium atoms enter through the third sidearm to produce the Penning-ionization spectrum. A 0.5 m monochromator, mounted on rails, views the region of the flow reactor just downstream from the He* injector to observe the fluorescence created in the Penning-ionization reaction.

A hollow-cathode, dc discharge through a flow of purified helium creates the metastable helium atoms. Flowing the helium through a molecular-sieve trap at liquid nitrogen temperature, upstream from the discharge, removes most of the impurities in the helium, including nitrogen and oxygen. Small amounts of residual neon in the helium ($\leqslant 10$ ppm) have no effect on our observations. The discharge operates at 350 V with a current, limited by a 200 kΩ resistor, below a milliamp.

We showed previously[33] that operating the hollow-cathode discharge at high voltage and high current tended to produce significant number densities of atomic and molecular helium ions. These ions are an anathema to the Penning-ionization measurements because they produce highly non-Franck–Condon distributions in the N_2^+ (B). Thus one could be led to false conclusions regarding the extent of ground-state vibrational excitation. The absence of significant number densities of helium ions was confirmed by failing to observe N_2^+ ($B, v' > 2$) when the active-nitrogen discharge was off.
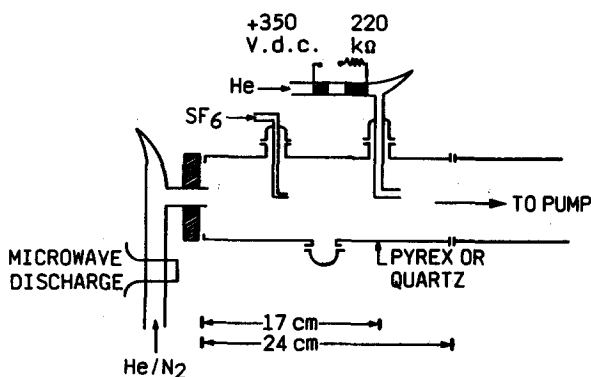

FIG. 1. Flow reactor for studies on the vibrational energy content of active nitrogen.

Typical conditions comprised flow rates of helium through the microwave discharge and the metastable-producing dc discharge of 3600 and 1200 μmol s^{-1}, respectively, nitrogen flow rates between 25 and 250 μmol s^{-1}, SF_6 flow rate of 4 μmol s^{-1}, total pressure of 1.5 Torr, and transit time between the microwave discharge and observation region of ~ 11 ms. Generally, the microwave power, which was coupled through a McCarroll cavity, was 75 W.

A least-squares fitting procedure[35] analyzes the Penning-ionization spectra. We generate basis functions consisting of a synthetic electronic spectrum for a unit population in each vibrational level of each electronic state appearing in the spectral region of interest. A linear least-squares routine then finds the populations of each vibronic band which, when multiplied by the appropriate basis function and summed with overlapping bands, gives a composite spectrum most nearly matching the experimental spectrum.

III. THEORY BEHIND THE PENNING-IONIZATION MEASUREMENTS

The Penning ionization between metastable helium atoms and molecular nitrogen is a vertical process. One can calculate the vibrational distribution in the final state, therefore, knowing only the vibrational distribution in the lower state and the Franck–Condon factors that couple the two states together. Thus

$$N_{v'} \propto \sum_{v''} N_{v''} \, q_{v'v''}, \tag{1}$$

where v' and v'' represent the vibrational levels of the upper and lower states, respectively, and $q_{v'v''}$ is the Franck–Condon factor coupling them.

We calculated a set of Franck–Condon factors over the range of ground-electronic-state vibrational levels of 0–18, and N_2^+ (B)-state vibrational levels of 0–9 using a calculational procedure previously described.[40] Table I contains the results of these calculations.

In theory, if one measures the vibrational distribution in the upper state, that in the ground state can be determined simply by inverting the Franck–Condon matrix, and multiplying this inverse matrix on both sides of Eq. (1). This procedure did not work for us because the measurements of the upper-state populations have some uncertainty associated with them, and the uncertainties become greatly magnified by the matrix multiplication. Jolly et al.[24] apparently succeeded in using this approach to analyze N_2 (v) distributions created in a glow discharge. We do not understand their success in light of our lack of it. Our spectral fitting approach for determining N_2^+ (B) number densities ought to be more accurate than their graphical integration of one branch from each band. We analyzed our data, therefore, using a model to describe the $N_2(X)$ vibrational distributions which we then used to predict N_2^+ (B) vibrational distributions. We then compared these predictions with observation.

Using the Franck–Condon factors in Table I, we computed the N_2^+ (B)-state vibrational populations relative to that in N_2^+ ($B, v' = 0$) expected for a number of values of

TABLE I. Franck–Condon factors of N_2^+ $(B\,^2\Sigma_u^+,v')$–$N_2(X\,^1\Sigma_g^+,v'')$.

$v'\backslash v''$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0	0.8836	0.1034	0.0117	0.0012												
1	0.1141	0.6917	0.1611	0.0285	0.0039											
2	0.0023	0.2000	0.5572	0.1854	0.0458	0.0078	0.0012									
3		0.0048	0.2633	0.4694	0.1864	0.0611	0.0122	0.0023								
4			0.0060	0.3087	0.4192	0.1711	0.0736	0.0165	0.0037							
5			0.0006	0.0049	0.3382	0.4008	0.1444	0.0841	0.0199	0.0054	0.0012					
6				0.0018	0.0019	0.3506	0.4098	0.1099	0.0940	0.0217	0.0075	0.0018				
7					0.0043	···	0.3405	0.4422	0.0711	0.1065	0.0211	0.0100	0.0025			
8						0.0079	0.0056	0.2994	0.4904	0.0339	0.1256	0.0171	0.0138	0.0029	0.0017	
9							0.0113	0.0300	0.2198	0.5355	0.0072	0.1580	0.0094	0.0206	0.0027	0.0030

vibrational temperature of ground-state nitrogen between 300 and 30 000 K, assuming a Boltzmann distribution among the levels. Figure 2 displays the results of these calculations. If the ground-state vibrational level populations follow a Boltzmann distribution, one can use experimentally derived N_2^+ (B) population ratios and Fig. 2 to find the vibrational temperatures of ground-state nitrogen which corresponds to those excited-state population ratios.

If the ground-electronic-state vibrational levels do not follow a Boltzmann distribution, one can still compute expected excited-state populations from Eq. (1), if the ground-state distribution is known. Effluents from nitrogen discharges generally have nonequilibrium vibrational distributions, with the higher vibrational levels more strongly populated than would be predicted on the basis of a Boltzmann distribution. Caledonia and Center[4] and Capitelli and Dilonardo[7] have shown that for low vibrational levels the analytical distribution given by Treanor *et al.*[6] holds:

$$\frac{N_{v''}}{N_{v''=0}} = \exp\left\{ -v''\left[\frac{1.4388(\omega_e - 2\omega_e x_e)}{\theta_1} \right. \right.$$
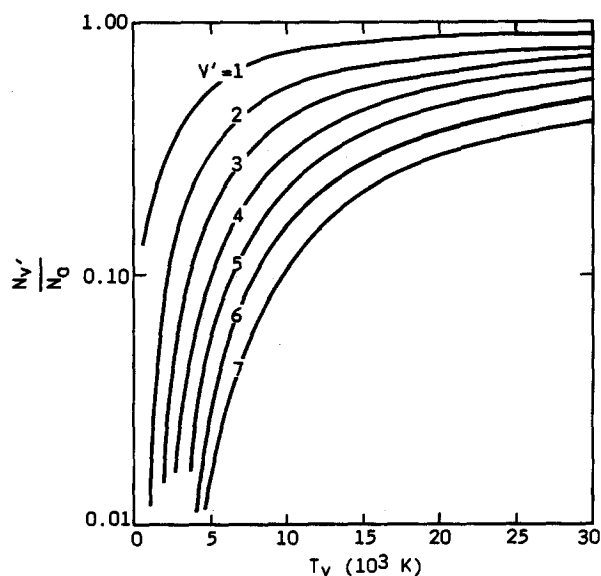$$\left. \left. - (v''-1)\frac{1.4388\omega_e x_e}{T} \right] \right\}, \tag{2}$$

FIG. 2. Ratio of the populations of N_2^+ (B,v') to N_2^+ ($B,v''=0$) created in He* Penning ionization of $N_2(X,v')$ as a function of the vibrational temperature of the ground-state nitrogen.

where θ_1 is the Boltzmann vibrational temperature referenced to $v'' = 1$, T is the ambient gas temperature, and ω_e and $\omega_e x_e$ are spectroscopic constants in units of cm^{-1}. The Boltzmann vibrational temperature is given by

$$\theta_1 = -\frac{\omega_e - 2\omega_e x_e}{k\ln(N_{v''=1}/N_{v''=0})}. \tag{3}$$

This distribution goes through a minimum, generally referred to as the Treanor minimum, at vibrational level v^*, given by

$$v^* = \frac{T(\omega_e - 2\omega_e x_e)}{2\omega_e x_e \theta_1} + 0.5. \tag{4}$$

For vibrational levels greater than the Treanor minimum, the product $v''N_{v''}$ is essentially constant. The resulting distribution for $v'' > v^*$, therefore, is

$$\frac{N_{v''}}{N_{v''=0}} = \frac{v^* - 1}{v''}\exp\left\{ \frac{-1.4388(v^{*2} - 1)\omega_e x_e}{T} \right\}, \tag{5}$$

where the various parameters in Eq. (5) are determined by requiring that the two distributions be equal at $v'' = v^* - 1$.

The Penning-ionization spectrum calculated from a non-Boltzmann, ground-state distribution based upon Eqs. (2), (4), and (5) is significantly different from what one would calculate from a Boltzmann ground-state distribution. The Penning-ionization technique, therefore ought to differentiate between the two ground-state distributions rather easily.

IV. RESULTS OF THE PENNING-IONIZATION MEASUREMENTS

Figures 3 and 4 show a portion of the nitrogen first-negative spectrum with the active-nitrogen discharge off and on, respectively. Clearly, the vibrational development of the emission is greatly enhanced by discharging the gas. We determined vibrational populations in the upper state by fitting the spectrum in the manner described previously.[35,38] While the fits included upper-state vibrational levels 0–8, for the most part, only vibrational levels 0–7 contributed any significant intensity to the spectra.

A number of different and conflicting sets of Einstein coefficients for the N_2^+ ($B\,^2\Sigma_u^+$–$X\,^2\Sigma_g^+$) transition fill the literature.[41–44] In particular, the constancy of the electronic transition moment with r centroid is unsettled.[45,46] To analyze our data, we calculated a set of Einstein coefficients based upon the relative electronic transition moment vari-
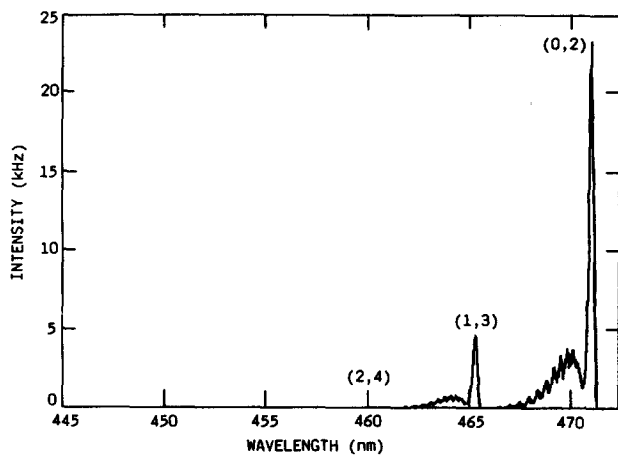
FIG. 3. Spectrum of the $\Delta v = -2$ sequence of the N_2^+ ($B\,^2\Sigma_u^+ - X\,^2\Sigma_g^+$) system excited in the Penning ionization of vibrationally cold nitrogen by He*($2\,^3S$). The light line is the experimental spectrum; the heavy line shows the best-fit synthetic spectrum.

ation given by Brown and Landshoff,[46] which has received some support by Comes and Speier[47] and by Chang *et al.*,[48] the Franck–Condon factors of Albritton *et al.*,[49] and a radiative lifetime of N_2^+ ($B,v' = 0$) of 62.5 ns.[41] They are tabulated elsewhere.[1(a),24] We are currently investigating this issue of transition-moment variation. The molecular potential constants given in Lofthus and Krupenie[41] were found to be inadequate for predicting band positions accurately. Our fitting program uses the recent potential constants determined by Gottscho *et al.*[50]

Early in this measurement program, we discovered that moving the monochromator slightly downstream from the injector, through which the He* entered the reactor, resulted in a much different vibrational distribution in the upper state. There appeared to be no reason why the vibrational distribution in the active nitrogen should change over short distances. A diffuse emission could be seen extending somewhat downstream from the well-defined flame created by the Penning ionization. Several centimeters downstream from
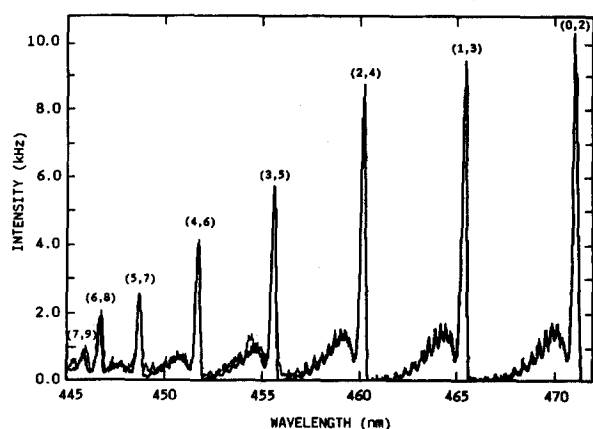

FIG. 4. Spectrum of the $\Delta v = -2$ sequence of the N_2^+ ($B\,^2\Sigma_u^+ - X\,^2\Sigma_g^+$) system excited in the Penning ionization of active nitrogen by He*($2\,^3S$). The light line is the experimental spectrum; the heavy line shows the best-fit synthetic spectrum.
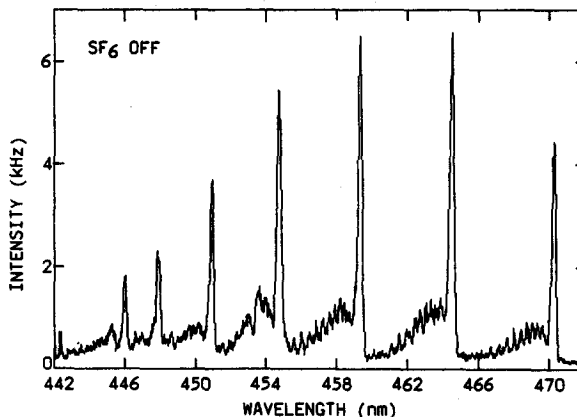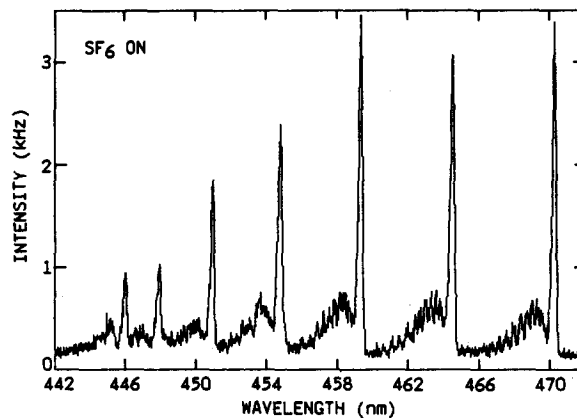

FIG. 5. Spectra of the $\Delta v = -2$ sequence of the N_2^+ ($B\,^2\Sigma_u^+ - X\,^2\Sigma_g^+$) system excited in the Penning ionization of active nitrogen by He*($2\,^3S$) in the presence and absence of SF_6.

the injector, the Penning-ionization flame disappeared, and only the diffuse emission remained. Figure 5 shows the diffuse-emission spectrum.

On the assumption that the emission was caused by energetic electrons exciting N_2^+ (X), a trace of SF_6 was added to act as a scavenger for the electrons. This addition eliminated the diffuse flame, and also resulted in N_2^+ (B) vibrational distributions which did not change with the location of the monochromator relative to the He* injector. Presumably, the electrons created in the Penning-ionization reaction pick up some extra kinetic energy either from stray microwave fields which have penetrated downstream, or else from collisions with energetic species in the active nitrogen. The amount of energy must be fairly considerable, because exciting N_2^+ (B) from N_2^+ (X) requires more than 3 eV. All the results given below were obtained in the presence of small traces of SF_6.

Analyzing the N_2^+ (B,v') vibrational distributions with the help of Fig. 2 gave different ground-state vibrational temperatures depending upon which upper-state vibrational level was considered. The data fell into three groups. The temperature determined from $v' = 1$ was only 63% of that determined from $v' = 2$ and 3, which were themselves reasonably consistent. Vibrational temperatures determined from $v' = 4$–7 also were reasonably consistent with each other, but were 30% larger than temperatures determined from vibrational levels 2 and 3. Clearly, a Boltzmann model for
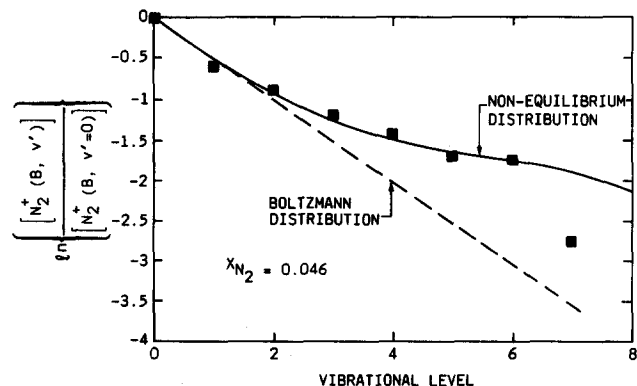
FIG. 6. Comparison between experimental and calculated vibrational distributions of N_2^+ (B) created in the Penning ionization of active nitrogen by metastable helium atoms for a nitrogen mole fraction of 0.011 ($p = 1.5$ Torr, transit time from discharge $= 11$ ms).

the ground-state vibrational distribution is inadequate.

Fitting our distributions to the analytical model described by Eqs. (2), (4), and (5) was more successful. Figures 6 and 7 show two examples. Clearly, the nonequilibrium model does a reasonable job of fitting observations out through $v' = 6$. We do not understand the sudden discrepancy at $v' = 7$. The dashed lines in Fig. 6 and 7 show the distribution which would be predicted were the ground state to be determined by a Boltzmann distribution. This shows graphically the inadequacy of that model for the ground-state levels. In the future we plan to use an improved model to predict the population distribution up to higher vibrational levels.

Our observations show that effective vibrational temperatures, θ_1, as determined from fits of the data to Eqs. (2) and (5) rather than what one would calculate from Eq. (3), tended to be smaller with larger nitrogen mole fractions flowing through the discharge (Fig. 8) and also at higher total pressures. Placing a nickel screen in the reactor, downstream from the discharge, only slightly reduced the effective vibrational temperature of the nitrogen (about 5%). The nickel screen, however, reduced atomic nitrogen number densities by more than an order of magnitude. Placing a screen in the afterglow, therefore, is a means to produce a
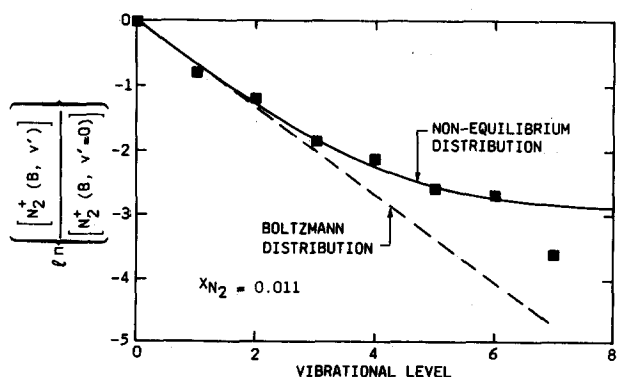

FIG. 7. Comparison between experimental and calculated vibrational distributions of N_2^+ (B) created in the Penning ionization of active nitrogen by metastable helium atoms for a nitrogen mole fraction of 0.046 ($p = 1.5$ Torr, transit time from discharge $= 11$ ms).
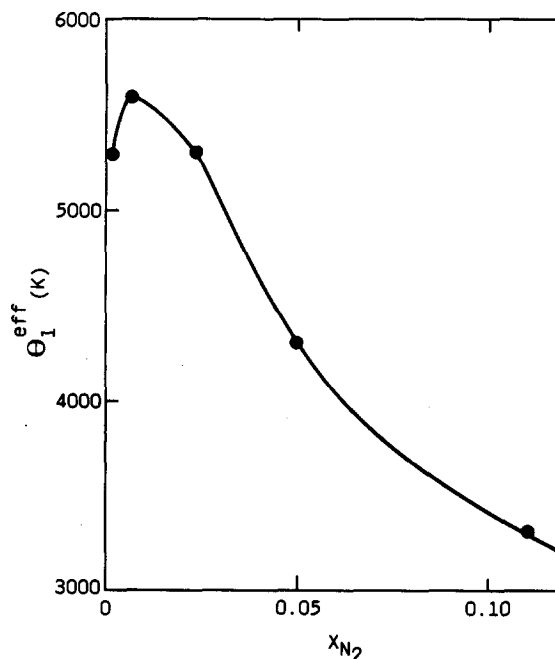

FIG. 8. Effective vibrational temperature from the nonequilibrium model vs nitrogen mole fraction through the discharge.

somewhat cleaner flow of N_2 (v) in a discharge-flow system. The Penning-ionization technique appears to provide a reasonably accurate monitor of the vibrational distribution of ground-electronic-state nitrogen, at least for the lower vibrational levels. Extending the model to include higher vibrational levels would need experimental confirmation.

To extend the Penning-ionization technique as a diagnostic for N_2 (v) containing energies of several eV, we investigated excitation of the nitrogen second-negative system, N_2^+ ($C\,^2\Sigma_u^+ - X\,^2\Sigma_g^+$). This system can be excited by collisions between metastable helium and molecular nitrogen only if the nitrogen has at least 3.8 eV of internal energy. Because the N_2^+ (C) potential curve is somewhat offset from that of $N_2(X)$, vertical transitions connecting the two states would arise from highly excited ground-state vibrational levels. Observing the second-negative system, therefore, would provide unequivocal evidence of highly excited ground-state nitrogen in the reactor.

Using a quartz flow reactor we observed the second-negative system in the ultraviolet between 185 and 210 nm. Figure 9 shows the spectral region between 188 and 208 nm with the metastable helium off and on. In both cases, the active-nitrogen discharge is on. The two features appearing at 191 and 199 nm are the $\Delta v = -6$ and -7 sequences, respectively, of the nitrogen second-negative system. The $\Delta v = -8$ sequence at 206 nm is masked by the 2,0 band of the $NO(A\,^2\Sigma^+ - X\,^2\Pi)$ system. This system is excited by interactions between $N_2(A\,^3\Sigma_u^+)$, created in the active-nitrogen discharge, and some impurity NO also created in the discharge.[38]

Scans with the active nitrogen discharge off, but the metastable-helium discharge on, resulted in no observed emissions. This latter observation is important because it establishes the absence of He^+ from the metastable helium
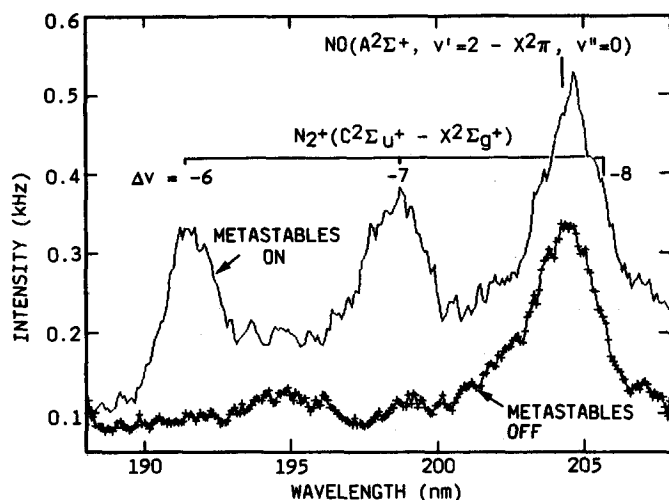
FIG. 9. Spectra from active nitrogen between 184 and 208 nm in the absence and presence of metastable helium atoms.

flow. Charge–transfer between He^+ and $N_2(X)$ is a well-known source of the second-negative system.[33,51]

Observing the nitrogen second-negative system from the interaction between metastable helium atoms and active nitrogen demonstrates the presence of metastable nitrogen in the afterglow containing at least 3.8 eV. In addition to $N_2(X,v)$, the electronic metastables $N_2(A\,^3\Sigma_u^+)$ or $N_2(a'\,^1\Sigma_u^-)$ are significantly populated in active nitrogen afterglows. Using alternative sources to generate the electronic metastables, we observed the resulting spectra when they were mixed with helium metastables.

The $N_2(A\,^3\Sigma_u^+)$ is produced cleanly by adding N_2 downstream from a hollow-cathode, dc discharge through a mixture of helium and argon.[52,53] Scans of the Vegard–Kaplan bands between 220 and 400 nm established that the $N_2(A)$ number densities from this source were of comparable magnitude to those obtained from the active-nitrogen discharge. Turning the metastable nitrogen on and off in the presence of metastable helium showed no detectable change in the emissions in the region between 185 and 210 nm.

$N_2(a')$ is made along with slightly enhanced number densities of $N_2(A)$—about a factor of 3—when the molecular nitrogen flows through the dc discharge with the He/Ar mixture.[39,54] Again, turning the metastable nitrogen on and off indicated no emissions between 185 and 210 nm. We conclude therefore that interactions between metastable helium and $N_2(A)$ and $N_2(a')$ do not produce $N_2^+(C)$.

The appearance of $N_2^+(C)$ from the interaction between metastable helium and active nitrogen, therefore, appears to be the result of Penning ionization of ground-electronic-state nitrogen containing at least 3.8 eV of vibrational energy. This corresponds to ground-electronic-state vibrational levels of $v'' \geqslant 15$.

V. SUMMARY

In summary, Penning ionization of $N_2(v)$ by metastable helium atoms excites $N_2^+(B)$ up to at least $v' = 8$. Analysis indicates the ground-state nitrogen vibrational distribution

follows a Treanor rather than Boltzmann distribution, with effective vibrational temperatures of up to 6 000 K at times up to 30 ms downstream from the active-nitrogen discharge.

The diagnostic is complicated by the presence of free electrons created in the Penning ionization. These free electrons absorb energy from the active-nitrogen medium and produce further excitation of $N_2^+(B)$. Adding traces of SF_6 removes the free electrons from the reactor, and thereby eliminates their interfering effects.

Observing emission from $N_2^+(C)$, excited by Penning-ionization reactions in the afterglow, demonstrates the presence of $N_2(v)$ containing at least 3.8 eV internal energy. Future efforts will be directed towards a more quantitative assessment of the $N_2^+(C)$ observations to identify the range of $N_2(v)$ levels responsible for this excitation.

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