Mitigation of electron attachment to oxygen in high pressure air plasmas by vibrational excitation

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A series of time resolved microwave attenuation measurements are performed of the electron number density of an electron beam generated, CO laser excited nonequilibrium O$_2$/N$_2$ plasma. Resonant absorption of infrared radiation from the CO laser produces the nonequilibrium state, in which the heavy species vibrational modes are disproportionately excited, compared to the rotational and translational modes ($T_{\text{vib}}=2000–3000$ K vs $T_{\text{RT}}=300$ K). It is shown that this results in an increase in the plasma free electron lifetime by two orders of magnitude compared to the unexcited cold gas, an effect which is ascribed to complete mitigation of rapid three-body electron attachment to molecular oxygen. A series of heavy species filtered pure rotational Raman scattering measurements are also presented, which exhibit minimal temperature change ($\pm 50$ K), indicating that the observed lifetime increase cannot be due to heavy-species thermal effects. Finally, computational modeling results infer an increase in the rate of O$_2^-$ detachment by four to five orders of magnitude, compared to the equilibrium value. © 2007 American Institute of Physics. [DOI: 10.1063/1.2724796]

I. INTRODUCTION

Recently, there has been renewed interest in a variety of potential aerodynamic applications of high pressure (order 1 bar), low temperature (order of 298 K) air plasmas including supersonic flow control, magnetohydrodynamics (MHD) power extraction, ignition and flame holding in high speed reacting flows, and electric discharge gas dynamic lasers, to name only a few. In general, these applications require a stable, large volume nonequilibrium plasma with electron density of approximately $10^{10}–10^{11}$ m$^{-3}$, which is sustainable on the order of a few seconds or more, with maximum power expended of approximately 1–10 MW/m$^3$.

Meeting these stringent requirements is an extremely difficult challenge. It is well known that under these low temperature conditions the dominant mechanism for electron removal is direct three-body attachment to molecular oxygen,

$$O_2 + M + e^- \leftrightarrow O_2^- + M,$$

(1)

the forward rate of which is sufficiently fast that replacement of all lost electrons requires a minimum of $\approx 5–10$ GW/m$^3$, based on an electron impact ionization energy of 12 eV per electron-ion pair. In practice, due to inefficiencies inherent to the ionization process, the number can be substantially higher.

In this paper, experimental results are presented, obtained in a CO laser-electron beam crossed beam instrument in which air plasma lifetime is measured by means of microwave attenuation. It is demonstrated that vibrational excitation of all diatomic species, to vibrational temperatures of order 2000 K accomplished by resonant absorption of the CO laser radiation, results in an increase in the lifetime of the electron beam generated, nonequilibrium air plasma by more than two orders of magnitude. In addition, temperature measurements employing spectrally filtered pure rotational Raman spectroscopy definitively show that the observed effect is nonthermal in origin, with heavy-species rotational/translational temperature increasing only slightly, from 300 to $\sim 350\pm 10$ K, in the vibrationally excited medium.

Two potential mechanisms for the observed electron lifetime increase are examined, reduced attachment due to electron heating by superelastic collisions with vibrationally excited neutrals, and enhanced detachment of O$_2^-$ negative ions, due to collision with vibrationally excited, “rapid” detacher molecules. The second hypothesis is motivated by recent work in this laboratory which has shown substantial vibrational loading of all diatomic species by CO laser optical pumping, and by the rather small O$_2$ electron affinity of 0.43 eV, equivalent to approximately two O$_2$, N$_2$, or CO vibrational quanta. It is shown, based on a combination of experimental plasma decay data and kinetic modeling, that the second effect is the dominant one, with detachment in these nonequilibrium air plasmas accelerated by at least four to five orders of magnitude, compared to the equilibrium rate.

II. EXPERIMENT

A schematic of the experimental CO laser–electron beam crossed beam apparatus is shown in Figs. 1 and 2. A Kimball Physics EGH-8101 electron gun is used to generate a plasma of order several cm$^3$ volume in a variety of CO/O$_2$/N$_2$ mixtures, including pure N$_2$. The gun is operated in pulsed mode at 10 Hz with single pulse duration in the range of 5–40 $\mu$s and gun voltage of 80 kV. For all work to be presented here
the primary peak beam current is 1 mA, with rise time of approximately 150 ns. The beam passes through an aluminum foil window (thickness \( \approx 0.018 \) mm), to the high pressure measurement cell, with delivered primary beam energy, after foil losses, of \( \sim 40 \) kV. An unbiased Faraday cup is used to measure the delivered beam current. The mixture total pressure is 300 torr, and flow velocity is approximately 10 cm/s, conditions at which the plasma is predominantly convectively cooled.

A continuous wave (cw) CO laser beam is input normal to the electron beam axis and is focused (focal length \( =500 \) mm) to a diameter of approximately 0.1 cm. The CO laser beam vibrationally excites the gas medium, creating a highly nonequilibrium environment with approximate dimensions 1 cm (length) \( \times 0.1 \) cm (diameter), located a distance of approximately 1 cm from the foil window. Typical power output of the CO laser is 12 W, with a substantial fraction of the total output power resonant with the five or six lowest vibrational frequencies of CO.

A pair of microwave waveguides, with cross section of \( 1 \times 0.4 \) cm\(^2\), separated by a gap of 1 cm, are oriented orthogonal to both the electron beam and the CO laser propagation axes. A 40 GHz microwave system probes the temporal evolution of the electron density in the \( 1 \times 1 \times 0.4 \) cm\(^3\) region defined by the waveguides, which is centered on the CO laser excited volume. A Herotek tunnel diode detector with a time constant of approximately 2 ns is used to measure the transmitted microwave signal. A 300 MHz amplifier (Stanford Research Systems) and 400 MHz digital oscilloscope are used to capture the microwave signal.

Heavy-species temperature measurements were acquired using filtered rotational Raman spectroscopy. This system is described in detail in Refs. 9 and 13 and will only be reviewed here. The Raman pump is a single frequency, injection seeded-cavity stabilized Ti:sapphire laser. Raman scattering is collected at 90° and detected with a commercial optical multichannel analyzer (OMA) system, consisting of a 0.25 m grating spectrometer and an intensified charge-coupled device (CCD) camera. An optically thick rubidium vapor filter, placed between the scattering volume and the detector, attenuates molecular Rayleigh and elastically scattered interferences by approximately five to six orders of magnitude, while transmitting the entire pure rotational Raman spectrum. The volume element imaged by the rotational Raman system was approximately 1 cm (length) \( \times 0.01 \) cm (diameter). A translational stage was used to displace the Raman pump laser with respect to the CO laser, providing radial resolution of the optically pumped region.

III. BACKGROUND: ANHARMONIC VIBRATIONAL UP-TRANSFER

Vibrational nonequilibrium is created by a two-step process known as anharmonic collisional vibration-vibration (V-V) up-transfer, or Treanor pumping.\(^{14}\) The initial step, illustrated by (2), is resonant sequential single photon infrared absorption, which excites CO to vibrational levels as high as \( v \sim 10 \). In the second step, vibrational quanta are redistributed to higher levels by means of collisional V-V energy transfer, the rate for which exceeds that of vibration-translation (V-T) transfer, for levels less than \( v \sim 30 \).

\[
\text{CO}(v) + h\nu \rightarrow \text{CO}(v+1), \quad v = 0 \rightarrow 10, \tag{2}
\]

\[
\text{CO}(v) + \text{CO}(w) \rightarrow \text{CO}(v-1) + \text{CO}(w+1), \quad v < w. \tag{3}
\]

Additionally, vibrational quanta in CO are transferred to lower vibrational levels of \( \text{O}_2 \) and \( \text{N}_2 \) by interspecies V-V transfer. Sequential intraspecies V-V then populates higher levels. By such exchange processes, the vibrational mode of all diatomic species within the gas mixture is preferentially excited, while maintaining low translational/rotational temperature. For example, as recently reported by Lee \textit{et al.},\(^8\) CO laser pumping in CO seeded air mixtures at approximately 1 bar total pressure leads to vibrational temperatures, defined by the relative fractional populations of levels \( v=0 \) and 1, exceeding 2000 K for all diatomic species while maintaining a rotational/ translational temperature of \( \sim 350 \) K.
Finally, the electron temperature in vibrationally excited plasmas increases due to superelastic collisions between free electrons and vibrationally excited neutrals, as demonstrated by Adamovich and Rich.\textsuperscript{10}

\[
\text{CO}(\nu) + e^-(\varepsilon) \rightarrow \text{CO}(\nu - \Delta
\nu) + e^-(\varepsilon + \Delta
\varepsilon).
\]

IV. RESULTS AND DISCUSSION: DATA

As a base line case Fig. 3 shows the time-dependent electron number density in pure N\textsubscript{2} at 300 torr. Note that the initially formed N\textsubscript{2}\textsuperscript{+} is rapidly converted to N\textsubscript{4}\textsuperscript{+} by process (5) with rate coefficient \(k_{\text{com}} = 5 \times 10^{-31} \text{ (300}/T) \text{ m}^6/\text{s}^4\), which is near gas kinetic at 300 K.

\[
\text{N}_2^+ + \text{N}_2 + M \rightarrow \text{N}_4^+ + M.
\]

In pure N\textsubscript{2}, the plasma lifetime is determined by electron-ion recombination so that

\[
\frac{dn_e}{dt} = S - \beta_{eD}n_{eD}n_e = S - \beta_{eD}n_e^2,
\]

where \(S\) is the electron impact ionization rate and \(\beta_{eD}\) is the electron-ion recombination rate coefficient for N\textsubscript{4}\textsuperscript{+},

\[
\text{N}_4^+ + e^-(\text{secondary}) \rightarrow 2\text{N}_2,
\]

with reported value of \(2 \times 10^{-12} \text{ m}^3/\text{s}\).\textsuperscript{16} Equation (6) is an example of simple second order kinetics, with solution

\[
\frac{n_e(t)}{n_\infty} = \text{tanh}[n_\infty \beta_{eD}t] = \frac{\text{tanh}[\sqrt{S}\beta_{eD}]}{1 + n_\infty \beta_{eD}t},
\]

where \(n_\infty\) is the steady-state electron number density. Note that the solution for the decay results from setting \(S=0\) for times exceeding the electron beam pulse duration.

As can be seen from Eq. (8), the shape of the electron density rise and fall is determined completely by the product \(n_\infty \beta_{eD} = 1/\tau\).

The dashed curve in Fig. 3 is a least squares fit of the experimental data to Eq. (8), where \(\tau\) is an adjustable parameter and where the rise and fall portions of the curve were fit separately, which is necessary due to space charge interference during the rise portion of the measurement. The best fit value, \(1/\tau\), for electron decay is \((6.1 \pm 0.1) \times 10^4 \text{ s}^{-1}\). Using the known value for electron-ion recombination in N\textsubscript{2}, \(\beta_{eD} = 2 \times 10^{-12} \text{ m}^3/\text{s}\), the steady-state electron density, inferred from Eq. (9), is \(n_\infty = 3.1 \times 10^{16} \text{ m}^{-3}\). The ionization rate, \(S\), determined from Eq. (8c), is \(1.9 \times 10^{22} \text{ m}^{-3} \text{ s}^{-1}\).

With pure N\textsubscript{2} serving as a base line, a second set of measurements was performed in CO/O\textsubscript{2}/N\textsubscript{2} mixtures containing 5% CO and 10% or 20% O\textsubscript{2} at 300 torr total pressure. The electron beam was operated with current and voltage identical to that of the pure N\textsubscript{2} case. As can be seen in the lower trace of Fig. 4, which is the raw microwave voltage signal for the 20% O\textsubscript{2} mixture, the time dependence of the electron density of the cold (non-CO laser excited) gas mixture replicates the 10 \textmu s duration square pulse from the electron gun. The upper trace is the corresponding electron density trace when CO laser pumping vibrationally excites the gas mixture. It can be seen that both the rising and falling edges evolve with greatly reduced rate, indicating a substantial reduction in the net rate of O\textsubscript{2} attachment. From the approximately 100 ns equilibrium lifetime to an observed lifetime of approximately 10 \textmu s.

While O\textsubscript{2} attachment has clearly been mitigated by CO laser excitation, it is necessary to note that the net attachment rate is highly dependent upon the heavy species temperature. Specifically, while attachment is relatively temperature independent, the reverse, detachment process is highly sensitive to the heavy-species temperature, increasing by three orders of magnitude between 300 and 550 K.\textsuperscript{12} Therefore, it is imperative that temperature measurements be performed in order to determine whether the observed tail in Fig. 4 is due to vibrational loading of the diatomic gas, or to an increase in the rotational/translational temperature of the heavy species.
A series of spatially resolved rubidium vapor filtered pure rotational Raman measurements were performed, using the instrument described in detail in Refs. 9 and 13. The centerline rotational temperature, determined by least squares fitting to a standard spectral model, was observed to increase, but only slightly, from 303±10 K (2σ) to 350±10 K (2σ) when the gas is vibrationally pumped. In addition, radially resolved temperature measurements, results of which are shown in Fig. 5, were performed by translating the Raman probe laser with respect to the fixed CO excitation laser. It can be seen that the radius of the cylindrical excited region, defined as the distance from centerline where the rotational/translational temperature has dropped by ~25 K from the centerline value, is approximately 0.05 cm.

We conclude that the observed two order of magnitude increase in the plasma lifetime cannot be due to equilibrium thermal heating of the gas mixture and must, therefore, be a nonequilibrium effect.

Least squares fitting was performed on the O$_2$/N$_2$ mixtures using two limiting models, reduced attachment and accelerated detachment. In either case, there must be a correction for the disparity between the cold and pumped plasma volumes. This is accomplished by fitting a square wave form to the cold trace, which is then subtracted from the CO laser pumped microwave trace. This removes the contribution to the observed microwave absorption due to the nonpumped (cold) region of the vibrationally excited plasma. This simple subtraction is justified because the pumped region is quite small and the percent attenuation from the cold gas is more than an order of magnitude less than that from the vibrationally excited region.

The reduced attachment limiting case, which assumes that detachment is sufficiently slow that it can be ignored, predicts simple first order exponential decay of the electron density. While it was found that such a model can reproduce the observed data with reasonable accuracy, it required a reduction in the attachment rate coefficient by a factor of 200, compared to the equilibrium rate. Extrapolation of experimental electron temperature-dependent attachment rate data\textsuperscript{11} results in a physically unrealistic value of ~20 eV for the electron temperature, a factor of ~100 greater than the measured first level vibrational temperature. Additionally, it is recognized that the rate of attachment can, at least in principle, be reduced due to vibrational excitation of the attaching oxygen molecule or of the third collision partner. However, since the majority of the attaching species at the present conditions (~66%) remain in the ground vibrational state, the upper bound reduction of the attachment rate by this mechanism would be by a factor of less than 2, even if it is assumed that vibrationally excited molecules do not participate in the attachment process at all. It is concluded, therefore, that while first order kinetics can produce a fit to the experimental data, the required parameters are nonphysical.

As an alternative to reduced attachment, the second limiting case considered is one in which three-body electron attachment is balanced by rapid detachment.\textsuperscript{15} In this case, it is assumed that vibrational excitation creates a pool of “rapid” detachers, with number density $n_d$. The corresponding time-dependent electron and negative ion densities are described by the coupled rate equations

\begin{equation}
\frac{dn_e}{dt} = S - \beta_{ei} n_e n_i - \nu_A n_e + k_d n_d, \quad (10a)
\end{equation}

\begin{equation}
\frac{dn_i}{dt} = \nu_A n_e - k_d n_d - \beta_{ei} n_i n_e, \quad (10b)
\end{equation}

where $n_e$ and $n_i$ are the number densities of cations and anions, respectively. It is necessary to include ion-ion recombination ($\beta_{ii}$), as well as electron-ion recombination ($\beta_{ei}$) in this model. If detachment is assumed to be rapid, then the steady-state approximation becomes valid for the time-dependent anion number density.

\begin{equation}
[n_i]_{ss} = \left( \frac{\nu_A}{\nu_d + \beta_{ii}} \right) n_e. \quad (11)
\end{equation}

Upon substitution of (11) into (10), and assuming that $\nu_d \gg \beta_{ii} n_e$ and $n_i = n_e$, Eq. (10) simplifies to

\begin{equation}
\frac{dn_e}{dt} = S - \beta_{ei} n_e^2, \quad (12)
\end{equation}

where the following definitions have been made:

\begin{equation}
\beta_{ei} = \beta_{ei}^0 \frac{\nu_A}{\nu_d}, \quad (13a)
\end{equation}

\begin{equation}
\nu_d = k_d n_d. \quad (13b)
\end{equation}

More details on this model may be found in Ref. 15. The form of Eq. (12) is identical to that of Eq. (8), with identical solution except that $\beta_{ei}$, the rate coefficient for electron-ion recombination, is replaced by $\beta_{ei}^0$, defined by Eq. (13a).

The balanced attachment/detachment model is motivated by the fact that the electron affinity of O$_2$ is relatively low, ~0.43 eV.\textsuperscript{15} From a purely energetic perspective, three-body collision partners, O$_3$, N$_2$, or CO, with two or more vibrational quanta have internal energies very near (0.38 eV for O$_2$) or exceeding (0.57/0.52 eV for N$_2$/CO, respectively) this amount. It is reasonable, therefore, that collisions between O$_2^-$ and a vibrationally excited third body with two or more quanta could result in a high probability of detachment.
\[ O_2^- + M_2(v \geq 2) \rightarrow e + O_2 + M_2. \]  

(14)

Figure 6 shows the microwave attenuation data for a 20% O\(_2\)/N\(_2\) gas mixture, and the least squares fit to the balanced attachment/detachment model, Eq. (8), where the product \( n_d \beta_{\text{eff}} \) is treated as an adjustable parameter. It can be seen that the fit to both the rise and fall is excellent. If it is assumed that the electron ionization rate, \( S \), is constant for constant total pressure and beam current, then combining Eqs. (8b) and (8c) gives

\[ \beta_{\text{eff}} = \frac{1}{S \tau^2}, \]  

(15)

where \( \tau \), defined analogously to Eq. (9), is equal to \( 1/n_d \beta_{\text{eff}} \). Best fit values of \( \beta_{\text{eff}} \) inferred in this manner, along with reported equilibrium values for \( \beta_{\text{eq}} \) (Ref. 16) and \( \beta_{\text{eff}} \) are given in Table I. It can be seen that this procedure yields values of \( \beta_{\text{eff}} \) that are of the same order of magnitude as the literature values for both electron-ion recombination, \( \beta_{ei} \) and ion-ion recombination, \( \beta_{ii} \).

A simple estimate of the minimum vibrational excitation required to sufficiently increase the detachment rate in a manner consistent with the above result can be made by assuming that the detachment rate is approximately gas kinetic, with \( k_d \approx 2.5 \times 10^{-10} \text{ m}^3/\text{s} \), so that every collision between a suitably excited “rapid” detacher and an O\(_2^-\) anion results in electron detachment. If it is assumed that for the 20% O\(_2\) mixture \( v_d = \nu_A = 1.1 \times 10^7 \text{ s}^{-1} \), then the minimum required fraction of rapid detachers, \( n_d/N \), is \( \sim 0.005 \). Summing the vibrational populations in Fig. 7, taken from the Raman scattering data of Ref. 8, shows that the fraction of molecules with \( v \geq 2 \) is approximately 0.08, more than a factor of 10 greater than the minimum required. A similar analysis can be made for the 10% O\(_2\) mixture. In this case, again assuming \( v_d = \nu_A \) where \( \nu_A \) is now equal to \( 3.5 \times 10^6 \text{ s}^{-1} \), the minimum required rapid detacher fraction is even lower, \( n_d/N \sim 0.001 \).

V. RESULTS AND DISCUSSION: NUMERICAL MODELING

The above two limiting case models were explored because they provide physical insight, and the resulting analytical solutions are readily amenable to least squares curve fitting. They have the inherent disadvantage, however, of representing ideal limiting cases. As a complement to the previous analysis, numerical solutions to Eq. (10) have also been obtained. A parametric study was performed, a few results of which are given in Fig. 8. The parameters used to create the “best-fit” modeled curves for the decay portion of the data are found in Table II.

These simulations require absolute electron number density data since the relative contribution of attachment/detachment (first order kinetics) and recombination (second order kinetics) is dependent upon this. The relative to absolute electron density calibration was performed by combining Eqs. (8c) and (15), to yield

\[ n_{\alpha} = S \tau. \]  

(16)

Using the value of \( S \) from the pure N\(_2\) data, along with the value of \( \tau \) from the balanced attachment/detachment limiting case, the steady-state electron density is estimated to be \( n_{\alpha} = 1.4 \times 10^{16} \text{ m}^{-3} \) for the 10% O\(_2\)/N\(_2\) mixture, which is approximately 50% of that inferred for the pure N\(_2\) case.

It is also necessary to provide an initial condition for the anion number density. This estimate is obtained by assuming that a rapid equilibrium is established for process (1) within the vibrationally excited region. It immediately follows that if \( t = 0 \) is defined as the time when the electron beam is turned off, then

\[ \left[ n_{O_2^-} \right]_0 = n_{\alpha} \left( \frac{\nu_A}{\nu_d} \right). \]  

(17)
The modeling results are summarized in Fig. 8, which shows a comparison of the 10% O2/N2 data with predictions based on a “best” value of $\beta_{ei}$ equal to $1.1 \times 10^{-11}$ m$^3$/s, and several values of the ratio $V_e/V_d$, between 0.1 and 100. $\beta_{ei}$ is assumed equal to the equilibrium N$_2$ value. It can be seen that the calculation replicates the data well only when $V_e/V_d \approx 1$. Additional simulations, performed with other values of $\beta_{ei}$, confirmed this result.

It is concluded that under nonequilibrium conditions produced by CO laser pumping, attachment is mitigated and the plasma decay is controlled by recombination. Specifically, the results above indicate that the detachment rate must be equal to or exceed the equilibrium attachment rate to replicate the experimental data. Additionally, the numerical modeling indicates that the increase in plasma lifetime is not due to a reduction in electron-ion recombination (which is dependent on electron temperature) coupled with an increase in detachment, but solely to an increase in the detachment rate. Assuming $V_e/V_d = 1$, the results indicate that at room temperature and 300 torr total pressure CO laser pumping results in a nonequilibrium detachment rate which is at least four to five orders of magnitude greater than equilibrium value of $\sim 45$ s$^{-1}$.

Finally, the discrepancy between the inferred recombination rates from this work and previously reported equilibrium values is briefly discussed. While this work was not intended to quantitatively determine these rates, it is nonetheless expected that the inferred values would approximately equal those previously reported. A possible explanation for the observed discrepancy is the effect of electron diffusion on the observed plasma lifetime. For sufficiently small vibrationally excited regions, the rate of diffusion of electrons out of the excited volume, which would subsequently experience rapid attachment, could in principle exceed the rate of decay due to recombination. To provide an estimate of this effect, it is noted that the ambipolar diffusion coefficient for $\sim 1$ eV electrons in air at $P \sim 0.5$ atm is approximately 2 cm$^2$/s. As shown in Fig. 5, the radius of the rotationally hot region is approximately 0.05 cm and, while not measured explicitly for the exact conditions of this work, previous work under very similar conditions of CO laser pumping has shown that the radius of vibrationally excited air is even larger ($\sim 0.1$ cm) than the measured radius (again $\sim 0.05$ cm) as determined by the rotational/translational temperature. A simple estimate for the time scale for plasma decay due to ambipolar diffusion is given by, $\tau_a \sim R^2/D_a \sim 1.25$ ms, which is nearly two orders of magnitude slower than the 10–20 $\mu$s observed in this study.

VI. CONCLUSIONS

A series of time-resolved measurements have been performed of the electron density in electron beam generated, high pressure molecular plasmas. Electron density traces in equilibrium airlike O$_2$/N$_2$ gas mixtures confirm rapid electron removal due to three-body electron attachment to O$_2$. Vibrational excitation of all diatomics to vibrational temperatures of approximately 2000 K or greater causes an increase in the plasma lifetime of more than two orders of magnitude. Spatially resolved spectrally filtered pure rotational Raman measurements indicate that the rise in heavy-species rotational/translational temperature due to the laser excitation process is small, rising to approximately 350±10 K. Under equilibrium conditions attachment mitigation would require a temperature increase to approximately 650–700 K, conclusively showing that the observed increase in plasma lifetime is not a thermal effect.

The experiment and results indicate that, while one limiting kinetic case is studied, each resulting in simple analytical solutions amenable to least squares curve fitting. While both cases exhibit good agreement with the experimental data, analysis of these two limiting cases shows that vibrationally activated detachment is the mechanism responsible for the increase in the plasma lifetime. This limit is motivated by the low ($\sim 0.43$ eV) electron affinity of O$_2$, $\epsilon_i$. Additional simulations, performed with other values of $\beta_{ei}$, confirmed this result.

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However, the effect of spatial nonuniformity of the vibrationally excited region needs to be considered in some additional detail. Within the CO laser defined volume where the vibrational loading is maximized, it is clear that three-body attachment is completely mitigated so that the effective electron loss rate is determined by recombination. It is also clear that at some distance from the CO laser centerline the vibrational loading becomes negligible and rapid attachment again dominates. It is this region that the subtraction procedure is intended to correct for. However, in the intermediate region, where vibrational loading is not maximized but still significant, the effective electron loss rate will be intermediate between that dominated by attachment and recombination. It is plausible that such nonuniformity will result in a path averaged electron loss rate that is greater than that predicted using equilibrium recombination rates, resulting in a least squares inferred value of $\beta_{ei}$ which is greater than the equilibrium recombination rate, $\beta_{ei}$. Further experiments using an unfocused CO laser beam with a large aperture ($\sim 1$ cm) may provide insight into this issue.

VI. CONCLUSIONS

A series of time-resolved measurements have been performed of the electron density in electron beam generated, high pressure molecular plasmas. Electron density traces in equilibrium airlike O$_2$/N$_2$ gas mixtures confirm rapid electron removal due to three-body electron attachment to O$_2$. Vibrational excitation of all diatomics to vibrational temperatures of approximately 2000 K or greater causes an increase in the plasma lifetime of more than two orders of magnitude. Spatially resolved spectrally filtered pure rotational Raman measurements indicate that the rise in heavy-species rotational/translational temperature due to the laser excitation process is small, rising to approximately 350±10 K. Under equilibrium conditions attachment mitigation would require a temperature increase to approximately 650–700 K, conclusively showing that the observed increase in plasma lifetime is not a thermal effect.

To explore the mechanism of the observed effect, two limiting kinetic cases are studied, each resulting in simple analytical solutions amenable to least squares curve fitting. While both cases exhibit good agreement with the experimental data, analysis of these two limiting cases shows that vibrationally activated detachment is the mechanism responsible for the increase in the plasma lifetime. This limit is motivated by the low ($\sim 0.43$ eV) electron affinity of O$_2$, $\epsilon_i$. Additional simulations, performed with other values of $\beta_{ei}$, confirmed this result.
equivalent to approximately two vibrational quanta. Previously reported measurements of vibrational distribution functions in identical CO laser excited gas mixtures have shown that the pool of “rapid detaching” species exceeds the minimum number required by more than a factor of 10, assuming a near gas kinetic detachment cross section.

Numerical modeling confirms the validity of the assumptions used in the least squares model and indicates that the increase in plasma lifetime is due solely to an increase in the detachment rate and not to a coupled reduced recombination/enhanced detachment effect. Compared to equilibrium detachment, vibrational excitation results in an effective detachment rate which is increased by at least four to five orders of magnitude. Under such conditions, attachment is completely mitigated by detachment and the plasma decay is dictated by the rate of electron-ion and ion-ion recombination.

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