

Light Sources using Energy Transfer from Excimer to Line Radiation

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ABSTRACT

Efficient energy transfer between neon excimer molecules and hydrogen has been found. A small, high gas density light source has been developed, emitting entirely on the hydrogen 2p-1s transition at 121.567nm (Lyman- α). Light output densities of $10\text{W}/\text{cm}^2$ are obtained. Electron beam energy conversion efficiencies of $\approx 10\%$ have been measured.

Keywords: Neon excimer, Lyman- α radiation, excimer lamp

1. INTRODUCTION

In this article the development of a bright, efficient light source, emitting hydrogen H (2p-1s) line radiation in the vacuum ultraviolet spectral region is described.

Qualities important in such a light source include spectral output and power, brilliance and efficiency. The spectral composition is most significant for many applications. Lasers, of course, have high brilliance but for many applications such as photolithography coherence and interference effects can be a problem. To circumvent the interference problem, bright high power spontaneously emitting light sources are desirable. In this class of light sources, high efficiency, high specific power deposition, short and/or tunable wavelength, and small emitting bandwidth usually cannot be met with one device.

Due to their relative high power efficiency and wide selection of the emission spectra by choosing the appropriate phosphor material, fluorescence lamps have found wide application for lighting devices. Emitting mainly the mercury resonance lines these lamps also are used in photolithography steppers in semiconductor industry. To achieve high resolution in photolithography applications, monochromatic, short wavelength light has to be used. One access to shorter wavelengths is exciting the resonance lines of rare gases¹, resulting in very high efficiencies². The disadvantage, however, is the low pressure, required for efficient production of resonance line radiation, and thus a quite low specific output power. As bright, point like light sources high pressure arc discharges are widely used e.g. in xenon arc lamps. Arc lamps, however, have the disadvantage of a relative low efficiency and broad spectral bandwidth, due to high temperatures and large optical densities in the arc zone³. A recent approach combining high pressure, and thus high power densities, with high efficiency and short wavelengths of resonance lines, is using the formation and radiative decay of excimer molecules. Excimers, here mainly rare gas or rare gas halide excimers, are weakly bound molecules⁴ formed by an excited rare gas atom together with a ground state atom. Due to the low binding energy of typically less than one eV, and the relatively high potential energy of the rare gas resonance levels, special excitation schemes, providing high excitation energy in a low temperature, high pressure gas have to be used. Since the first excimer laser⁵, excitation schemes, using high voltage, high current pulsed beam facilities have been used to produce pure rare gas excimer laser radiation. For lower excitation power, as necessary in rare gas halide lasers or excimer lamps, the afterglow regime of pulsed discharges is used, providing the conditions necessary for excimer formation. Recent commercial excimer lamps are barrier discharge lamps⁶⁻⁸ or devices using special glow discharges⁹. Pulsed x-ray beams¹⁰, synchrotron¹¹ and laser radiation¹², as well as heavy ion beams¹³ or supersonic cooling¹⁴ have also been used for excimer research.

Here a novel type of a small, versatile excimer lamp, using low energy (15keV) electron beams, sent through a thin, strong and vacuum tight ceramic foil into a gas target is described¹⁵. The technology is described in detail in ref. 16.

For broad band vacuum ultraviolet (VUV) lamps, as well as for excimer lasers of pure rare gases, the emission on the so called 'second continuum' is used. This continuum is due to an optical transition of excited diatomic molecules from vibrationally relaxed $^1\Sigma_u$ and $^3\Sigma_u$ states to the repulsive ground state of the pure rare gases. It is well known that, due to the

high potential energy of the rare gas ions and atomic resonance levels, as well as the long lifetime and slow kinetics, leading to the formation of the molecules¹⁷, the efficiency of light output is extremely sensitive to impurities, acting as quenching species. For maximum energy efficiencies, reaching a theoretical limit near 50%, extremely pure rare gases have to be used^{2,16}. On the other hand, some of these quenching species also emit optical radiation and may be used as wavelength shifters, when longer wavelengths than the excimer second continuum are needed.

The 121.567nm 2p-1s transition in atomic hydrogen (Lyman- α) may be of particular interest for imaging systems. Due to an absorption minimum in oxygen¹⁸ this line can be transmitted in dry air, opening a wide field for applications. Practical use of Lyman- α radiation has so far been in hygrometers¹⁹ and for VUV intensity calibration light sources²⁰. Application studies for thin film processing²¹ and surface treatment²² have been performed. However, these light sources usually use the Lyman- α emission of standard deuterium arc lamps or discharges in He-H₂ mixtures with low efficiency on the Lyman- α line. In any light source, emitting on the H (2p-1s) transition, hydrogen molecules have to be dissociated and hydrogen atoms must be excited. Photodissociation and -excitation of molecular hydrogen gas has been extensively studied with different broad band light sources, using emission from He or air capillary discharges²³, and a dissociation probability of unity has been found for wavelengths between 80nm and 85nm. Furthermore the quantum efficiency for emitting a Lyman- α photon has been found to be one.

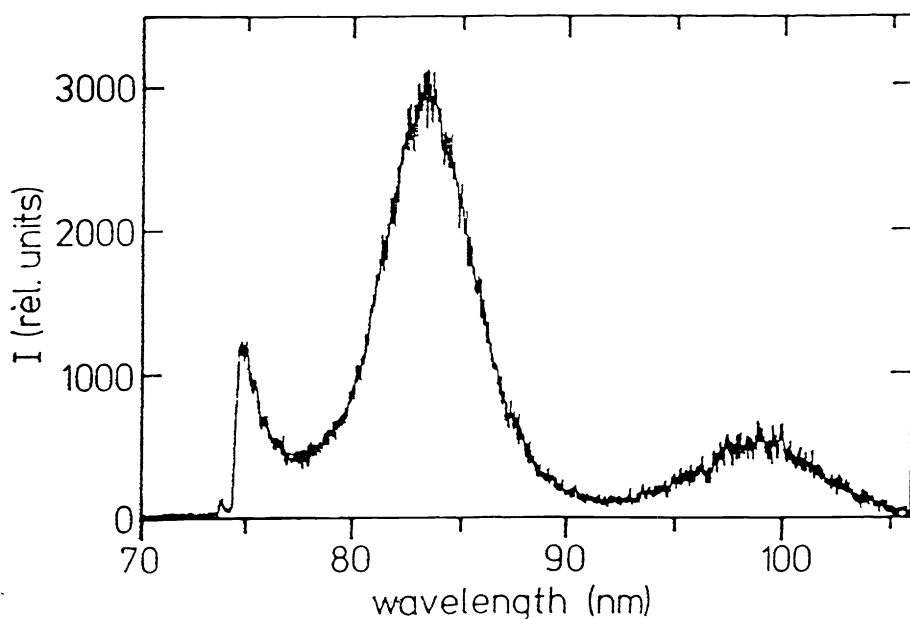


Fig. 1: Emission Spectrum of 385mbar neon, excited by an 85MeV ²³S-beam

Here a new mechanism, the quasi resonant energy transfer from neon excimers to hydrogen molecules is described. It is known that the neon excimer second continuum emits in the wavelength range between 80nm and 85nm²⁴ (Fig.1). The decay energy of neon excimer molecules coincides exactly with the sum of dissociation energy of the hydrogen molecule plus the excitation energy for one of the hydrogen atoms. Energy transfer can take place by direct collisions between neon excimer and hydrogen molecules or via excimer photoemission and absorption.

2. EXPERIMENTAL SETUP

Using the process, described above, a light source has been developed, which combines small emitting volumes and high specific power of excimer lamps with the small bandwidth of line radiation in the far ultraviolet spectral region. Rare gas atoms are excited by an externally produced electron beam of 15keV particle energy. The electron beam is produced in a vacuum tube, using a commercially available electron gun. The beam is sent into a gas filled target cell through a $1 \times 1 \text{mm}^2$ aperture, sealed by a 300nm thick silicon nitride foil, readily mounted on a $5 \times 5 \text{mm}^2$ silicon frame. The target cell can be evacuated by a turbo molecular pump to a pressure below 10^{-4} mbar, prior to filling with research grade rare gases of 99.998% purity. To further purify the gas, an electrically heated titanium wire has been installed. Gas pressure is measured, using a capacitive manometer (MKS Baratron). Optical radiation is observed through a VUV grade MgF_2 window, using a $f=30\text{cm}$ VUV monochromator (McPherson 218). This setup is described in detail in ref.15,16. Two slightly different systems have been built so far. One, a pure dc-excimer lamp, was equipped with a VUV optical multichannel analyser (OMA), consisting of a multi channel plate detector with a MgF_2 entrance window and a diode array as readout detector for the emitted radiation, attached to the monochromator. Another setup, shown in Fig.2. was modified for pulsing the electron beam for time resolved optical spectroscopy. Here the detector is a solar blind photomultiplier tube (Hamamatsu R1080), operated in the counting mode. For pulsing the electron beam, a pulsed voltage was applied to the extractor of the electron gun as shown in Fig.2. To achieve maximum pulse intensity, the following procedure is performed: Beam intensity, measured by a cylindrical cup inside the target cell as well as by light intensity, is first maximized by adjusting the voltages applied to the extraction electrodes G1 (and G2, not shown in Fig.2.), and on the focussing element F. Then the voltage on the extraction electrode G1 is reduced, so that no beam intensity is measured inside the target cell. By applying a positive pulse which reestablishes the optimum voltages in the electron gun (in this case 22.5V) the beam is switched on and focussed again into the target cell. Since, unlike in a TV tube, the cathode and focussing elements are on high potential, the extraction pulse had to be applied via a high voltage capacitor.

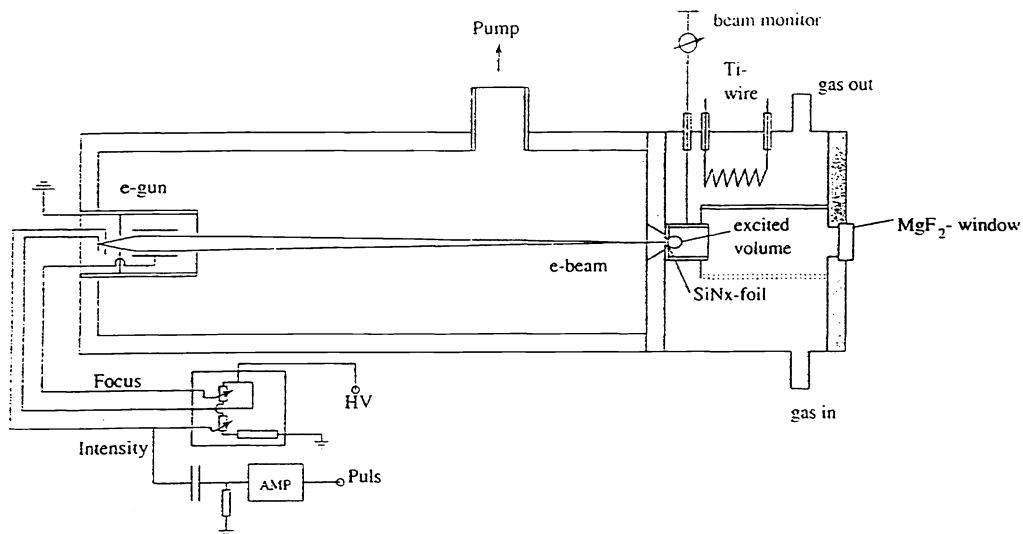


Fig.2: Experimental setup for time resolved measurements. An electron beam is sent through a thin SiN_x ceramic window into the target cell. Beam spot size and intensity can be adjusted by variable resistors. The electron beam can be pulsed, using a pulse generator, pulse amplifier and a high voltage capacitor for high frequency input coupling. Beam intensity can be measured, using a cylindrical faraday cup and a beam monitor. Light emitted from the excited volume can be observed through a MgF_2 window.

Only a simple pulsing system could be used so far. For pulsing the electron beam, a pulse generator, connected to a 15MHz adjustable amplifier (amplifier research, model 50A15) was used to provide 22.5V pulses for beam extraction. A 500pF capacitor was used to separate the high voltage part from the pulse generating electronics. A minimum pulse width of about

800ns has been achieved in these experiment. This was sufficient for the experiments, presented here, since the time constants to be measured are on the order of 10 μ s. It should be noted that by using better electronics, comparable to TV sets, time constants in the 10ns range should be possible with the e-gun, used. Time spectra have been measured, using the time to amplitude converter technique. The start signal was provided by the pulse generator, the stop signal by the photomultiplier pulse. To prevent pile up, a countrate of less than 5% of the pulsing rate was used. Time spectra have been recorded, using a PC based multi channel analyser.

3. The Ne₂^{*} - H₂ system: Efficient Energy Transfer from Excimer to Line Radiation

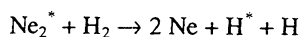
3.1 Observation and interpretation of the effect

Intense Lyman- α radiation has been observed in nominally pure neon gas, excited by a 15keV electron beam. Efficient energy transfer from excited neon excimers to hydrogen molecules has been found.

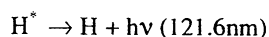
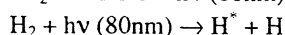
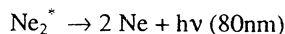
Since hydrogen is present only in traces in the target volume, the intense Lyman- α radiation cannot be due to direct excitation of the hydrogen molecules by the electron beam, leading to molecule dissociation and simultaneous excitation of the hydrogen atoms. Actually, by exciting low pressure, pure hydrogen gas, no emission of the 121.5nm 2p-1s line could be observed. Therefore, effective energy transfer from excited neon species to hydrogen molecules has to be considered. In the experimental setup, described above, an electrically heated Ti-wire is used as a rare gas purifier. Among the few active gases not removed by hot titanium is hydrogen, which can be stored on interlattice places in cold titanium, but will be released at elevated temperatures. Hydrogen gas will therefore always be present, at least in traces, in the target cell.

Comparing the energies involved, an energy resonance between the neon excimer radiation with wavelengths between 80 and 85nm, and thus energies between 14.5 and 15.5 eV and the sum of the binding energy of the hydrogen molecule (4.3eV) and excitation energy of one remaining hydrogen atom (10.2eV) can be found. Energy can be transferred from neon excimer molecules to hydrogen either by collisional processes, thereby reducing the Ne₂^{*} excimer lifetime in a quenching process, or by photoexcitation, both leading to a strong emission of the H (2p-1s) transition. Another indication of increased Lyman- α emission by a resonance energy transfer effect is given by the large difference in Lyman- α intensities when comparing Ne-H₂ and He-H₂ spectra. Excited He atoms, as well as He excimer molecules have sufficient energy to dissociate and excite hydrogen molecules. Nevertheless, He-H₂ spectra measured under same conditions (with respect to stopping power and thus electron range and solid angle in the excited target volume) show a factor of 100 lower H (2p-1s) light intensity than those observed in the Ne-H₂ mixture.

As pointed out in ref.²³, quantum efficiencies for dissociation of hydrogen by photons in the wavelength range of the second neon excimer continuum reach unity. It has been shown that absorption of photons close to the dissociation edge populates B¹ Σ^+ states, at shorter wavelengths also the C¹ Π_u and B¹ Σ^+ states, leading to a production of both 2s and 2p states²³. Following reaction schemes may therefore be assumed:



and/or



Estimations of the cross sections involved indicate that both processes, collisional- and photoexcitation may be of comparable probability. A spectrum of 1bar Ne, excited by a 15keV electron beam is shown in Fig.3. The neon gas has been purified by a hot Ti wire and 2mbar hydrogen gas has been deliberately added. Data were recorded using a 600lines/mm grating and the OMA system. The spectrum shows only the Lyman- α (2p-1s) resonance line at 121.567nm of atomic hydrogen.

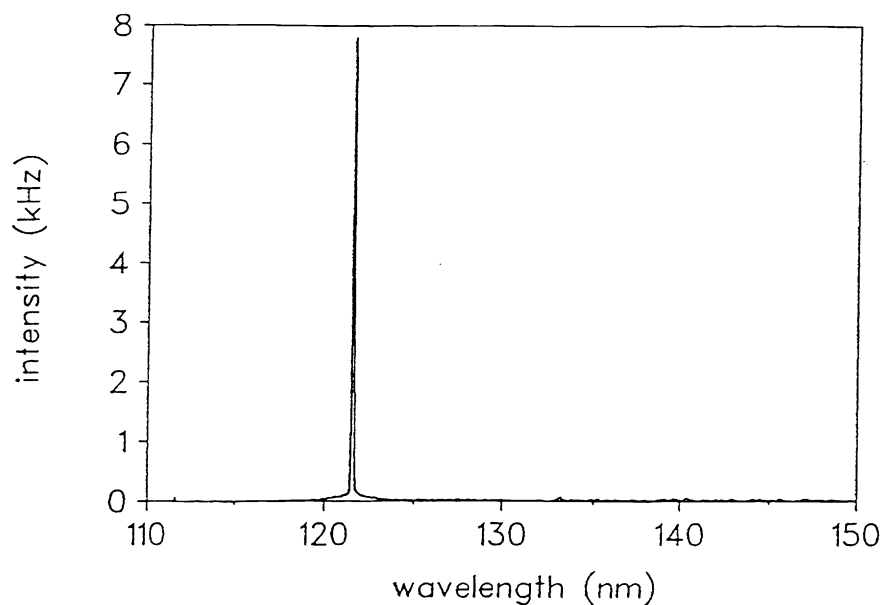


Fig. 3: Spectrum of a mixture of 2mbar H₂ in 400 mbar Ne, excited by a 15keV electron beam. No other line except the Lyman- α H(2p-1s) transition at 121.567nm could be observed in the wavelength range between 110 and 150 nm. Radiation below 100nm could not be observed, due to the MgF₂ window, used.

According to ref.23, approximately 85% of the preliminary formed photoexcited hydrogen states are in the metastable 2s state. They can decay only after collisional or electric field quenching via the p states, leading to thermalization and a small emission linewidth. A few percent of the hydrogen atoms are excited directly into the 2p state and can decay immediately after the excitation, carrying kinetic energy which will lead to a Doppler line broadening.

The spectrometer was intensity calibrated²⁵. By measuring the absolute light intensity and the electron beam current inside the target cell, an efficiency for Lyman- α emission of about 10% was calculated. Another, independent, estimate of the efficiency can be obtained from a comparison of the integrated line intensity with known spectral structures in the same wavelength region. Therefore, an argon spectrum has been measured using the same beam parameters. The efficiency for the second excimer continuum in 1bar argon was determined to be about 35%¹⁶. The integrated line intensity of the 121.5nm hydrogen line in Fig.3 is about 1/6 of the integrated argon excimer intensity, leading to an efficiency for the hydrogen line of about 6%. Due to the large errors in the intensity calibration at wavelengths below 125nm, resulting from the use of a commercial deuterium lamp as intensity transfer standard, this result is consistent with the previous one within the experimental errors.

3.2 Energy transfer rate constant

A first experiment to determine the collisional energy transfer rate constant from Ne excimers to hydrogen molecules was performed, using the apparatus described above. The lifetime of the neon excimer is measured for various hydrogen concentrations. Time spectra were recorded on the 121.6nm H (2p-1s) transition, using this radiation as an indicator for the neon excimer population.

The target volume was evacuated by a turbomolecular pump with the Ti-filament switched off for not releasing outgassing hydrogen. Hydrogen gas at various pressures, as measured using a sensitive capacitive manometer, was filled into the target cell. Then the target cell was filled with neon gas to a pressure of 500mbar. The cell was evacuated after each spectrum to be refilled with a new gas mixture. Time spectra on the 121.5nm H (2p-1s) transition with hydrogen pressures of 0.08mbar, 0.53mbar, 1.05mbar and 2.6mbar, respectively are shown in Fig.4a.

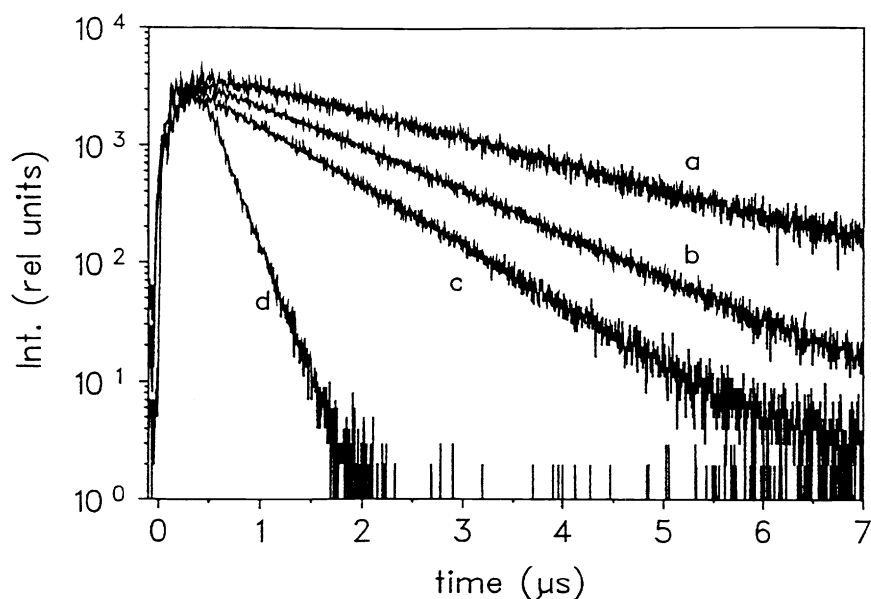


Fig. 4a: Time spectra of the 121.6nm H (2p-1s) transition in a neon hydrogen mixture with different hydrogen pressures. The neon pressure was fixed at 500mbar. Hydrogen pressures were: a) 0.08mbar, b) 0.53mbar, c) 1.05mbar, and d) 2.6mbar.

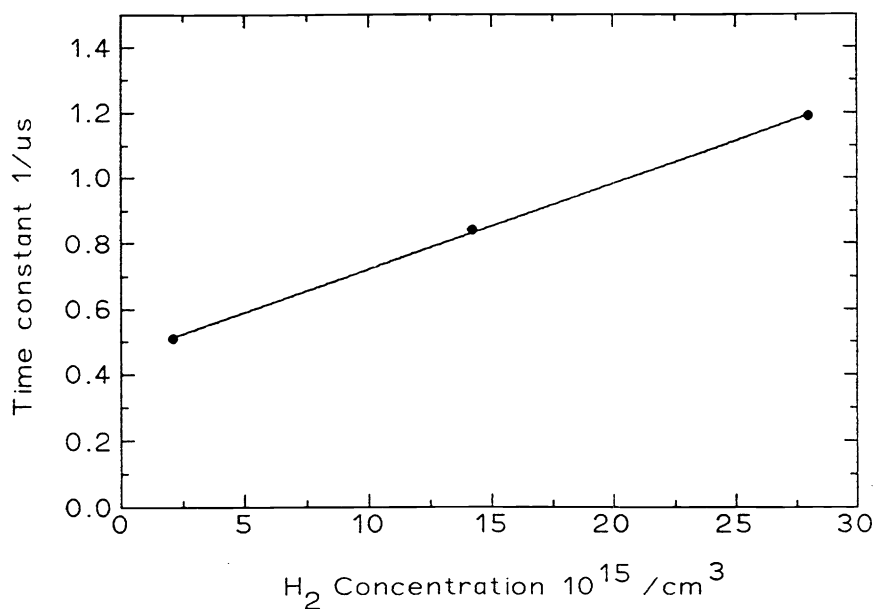


Fig. 4b: Time constant of the 121nm H (2p-1s) transition versus hydrogen concentration. The slope of the curve is the transfer rate constant, the time constant value at hydrogen concentration $[H]=0$ is the neon excimer lifetime. Note that other quenching species might be present.

It is assumed that the formation of neon excimer molecules is fast with respect to the decay time, observed. This assumption is supported by the observation that the leading edge of the pulse is fast, compared to the decay rate, and no changes in the leading edge time constant of the different spectra can be observed. Radiation of the 121.567nm line should essentially occur instantaneously after excitation²⁶. This means that the 121.5nm H (2p-1s) line than can be used as a monitor of the neon excimer density. Using the reaction scheme, described above, following differential equation then can be used for analyzing the data:

$$d[\text{Ne}_2^*]/dt = -(A_{ik} + k_q[\text{Q}]) [\text{Ne}_2^*] - k_t [\text{Ne}_2^*] [\text{H}_2]$$

with A_{ik} being the natural lifetime of the neon excimer molecule Ne_2^* , $k_q [Q]$ the sum over all other quenching rates, assumed to be constant in all experiments, and k_t the energy transfer rate constant to be measured. This leads to a simple exponential decay of light intensity : $I = I_0 \exp (t/\tau)$ with $1/\tau = (A_{ik} + k_q [Q]) + k_t [H_2]$. A plot of $1/\tau$ versus hydrogen concentration $[H_2]$ is show in Fig 4b. Using the model described above, the value at $[H_2] = 0$ is equal to the natural lifetime of the neon excimer, reduced by a constant quenching time constant $k_q [Q]$, the slope of the curve plotted in Fig. 4b is the rate constant k_t . A rate constant of $3 \times 10^{11} \text{cm}^3/\text{s}$ was determined. A neon excimer lifetime of $2.2 \mu\text{s}$ was measured, while the longest lifetime, given in the literature is $12 \mu\text{s}$ ¹⁷, indicating that quenching processes with a rate of $k_q [Q] \approx 4 \times 10^5 \text{ s}^{-1}$, induced by species other than hydrogen occurs in the target gas.

Due to the simple model used and possible systematic errors, an approximate 30% uncertainty in the rate constant is estimated.

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