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Sub-excitation Electron Interactions in Rare Gases:

I. Evidence for the Time Evolution of the Sub-excitation Spectrum*

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ABSTRACT

The production of the '2p' electronic excited states of the rare gases neon, argon, krypton and xenon has been studied using picosecond pulse radiolysis techniques. At pressures below about 5 torr, the emission from these excited states shows a pressure dependent growth-decay pattern. Kinetic analysis of the growth-decay curves reveal formation rate constants which are all greater than $10^{12} \text{M}^{-1} \text{sec}^{-1}$. These observations preclude atom-atom collisional processes and support an excitation mechanism involving collisional energy loss from electrons.

It is thus concluded that the secondary electron spectrum in pure rare gases at pressures below a few torr takes a few nanoseconds to degrade to energies below that of the lowest excited state. This time scale therefore (by definition) corresponds to the time needed to form subexcitation electrons. In 1 atmosphere of rare gas the time taken would be of the order of 20-30 picoseconds.

INTRODUCTION

In earlier studies^(1,2), we have shown that pulse radiolysis techniques can be successfully used to study the formation of electronic excited states of traces of luminescent probes in bulk rare gases. The results for nitrogen in helium or neon showed that the $C^3\Pi_u$ state of nitrogen was generated too rapidly to be a collisional process involving excited atoms or molecules. The interpretation was that the process responsible for the formation of the excited states was a sub-excitation electron interaction with the probe gas N_2 . Theoretical calculations⁽³⁾ using Monte-Carlo methods with available elastic and inelastic cross-section data for He and H_2 show that such a mechanism can satisfactorily explain the observations. Further experiments,⁽²⁾ using polycyclic aromatic hydrocarbons as luminescent probes in all five of the rare gases, revealed similar types of behavior as in the rare gas-nitrogen system. Calculations for these systems (aromatic hydrocarbon-rare gas) are impossible to carry out due to a virtual dearth of electron excitation cross section data for these molecules.

These earlier studies relied on the sub-excitation spectrum of the bulk rare gas interacting with an added fluorescent probe. An interesting question to ask is how long does it take for the electrons to reach sub-excitation energies at typical bulk gas pressures?

This study examines the emission from the 2p excited states of neon, argon, krypton and xenon at low pressures of pure rare gases and seeks a definitive answer (maybe!).

EXPERIMENTAL

The pulse radiolysis facility used for this study was that associated with the Argonne National Laboratory Chemistry Division Linac. This system

was used with only minor changes from what has been described in detail in earlier publications.^(2,4)

A short (<40 ps) pulse of 20 MeV electrons - ~7nC per pulse - was used to initiate the excitation processes in sample gases. The samples were contained in cylindrical quartz vessels (12cm x 3cm diameter) with Suprasil windows. The cells were irradiated with the long axis perpendicular to the electron beam. The kinetics of light emission were observed by focussing emitted light from an axis at right angles to the electron beam onto the slits of a Bausch and Lomb monochromator. An Electro-Optical Products micro-channel plate (MCP) photomultiplier tube (type FA128fQ/520) was used to monitor the output of the monochromator, and the rise time of this system was found to be ~200 ps.

A Tektronix 7904 oscilloscope with a 7S11 sampling unit was used to analyze the signal from the photomultiplier tube using electron pulse frequencies in the range 30-120 sec⁻¹. The output of the sampling unit was fed into an A to D converter, and thence into an LSI-11 computer. Data files from the LSI-11 were transferred to a VAX computer for analysis by non-linear least squares fitting to an exponential formation and decay mechanism.

Materials and Procedures

Neon (Matheson, Research Grade) was purified immediately prior to use by slow passage through a copper U-tube packed with activated molecular sieve (type 5A) maintained at liquid nitrogen temperatures. This procedure removed traces of water, nitrogen and oxygen from the bulk neon. Argon (Matheson) was condensed into a storage bulb on the vacuum line, and degassed several times before storage at liquid nitrogen temperatures; samples of up to 5 torr were taken off this stored sample (equilibrium pressures at ~77 K, ~150 torr). Krypton and Xenon (Matheson Research Grade) were further purified by several freeze-pump-thaw cycles.

All samples were prepared on a conventional greaseless, mercury-free metal-glass vacuum line. Connections to the vacuum line were made using Cajon "ultra-torr" fittings and pressure measurements were made with an M.K.S. Baratron (type 77) pressure gauge.

RESULTS AND DISCUSSION

The emissions from small pressures of the rare gases Ne, Ar, Kr of Xe, were examined over a low but extensive pressure range - typically 0.3 to 5.0 torr. The emissions from these samples were weak but with sampling times of 5 to 15 minutes, a rigorously optimized optical system, and maximum beam current from the Argonne National Laboratory Linac, a good signal-to-noise ratio was obtained. The background and/or Cerenkov radiation was recorded at a wavelength a few nanometers away from the main emission wavelength. This was then subtracted, by computer, from the emission vs. time data recorded at the wavelength of maximum emission. Typical raw and background data are shown in Figure 1, which is for a sample of 3 torr of xenon observed at 840 nm, which is the emission maximum of the $2p_6$ state of xenon. The subtracted data is shown in Figure 2.

As can be seen, the emission from this sample grows in for a few nanoseconds, then decays slowly over the rest of the observation time (~ 2 nsec). The decay of the excited state was generally followed for longer periods (up to 50 nsec) in order to determine the exact decay characteristics of the excited state. The data for these determinations was acquired exactly as for the growth-decay curves. These observations were usually taken at pressures of 0.3, 1, 2, 3, and 5 torr of each of the rare gases. The emission wavelengths used were 585 nm, $2p_1$, neon; 750 nm, $2p_1$ argon; 762.5 nm, $2p_6$

krypton; and 840 nm, 2p₅, xenon. In all cases, the emission was observed to grow in and decay more slowly as the pressure was reduced.

The growth decay curves were analyzed for all pressures and systems in terms of the following mechanism:

The mechanism requires that energetic secondary electrons ($e^-(T)$), react with a rare gas atom, R , to produce an electronic excited state R^* and a sub-excitation electron, $e^-(s.e.)$, which cannot further excite a rare gas atom. The excited state, R^* , may then decay by emission or be quenched by rare gas atoms. In this mechanism, pseudo first order conditions apply, i.e., $[e^-(s.e.)]$ and $[R^*]$ are both $\ll [R]$. These equations and these conditions lead to the expression

$$[R^*]_t = \frac{e^-(T)_0 k_g R}{k_e + k_q R - k_g R} \left[e^{-(k_g R)t} - e^{-(k_e + k_q R)t} \right], \quad (I)$$

where R represents the concentration of the rare gas.

The experimental curves were analyzed in terms of this exponential formation-decay function using a nonlinear least squares method. A typical fit to experimental data for xenon is shown in Figure 2. The experimental data were generally found to adequately fit this exponential growth decay function, which supports the above mechanism. The fitting program produces

values for the pseudo first order constants for formation, k_f and decay, k_d . Clearly, k_f may be identified with $k_g R$ and k_d with $k_e + k_q R$. The variation in these parameters with pressure was determined for all the systems studied. In order to increase the accuracy of the analysis, the data obtained from the emission curves taken over longer sweep times - mainly decay - was included in the double-exponential analysis, either as a fixed parameter or as an initial guess. (The decay curves were generally good exponential decays over at least two half lives.)

The values of k_f and k_d obtained from this analysis were plotted as a function of the pressure of rare gas. From k_f ($k_g R$) versus R plots, values of k_g for each system were determined and are shown in Table 1. From the k_d data, values for k_e - the zero pressure decay constant and k_q - the self quenching constant were determined. Typical plots of k_f for xenon and k_d for neon versus R are shown in Figures 3 and 4. The data obtained for all the gases studied are shown in Table 1.

DISCUSSION

1. The observation of a pressure dependent delayed formation of emission indicates a two body collisional formation process.
2. The two body rate constants for this formation process range from $\sim 2 \times 10^{12} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ for neon to $\sim 7 \times 10^{12} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ for xenon. These rate constants are similar in magnitude to those determined by us for sub-excitation electron interactions with nitrogen⁽¹⁾ and aromatics.⁽²⁾ They are also too large for atom-atom collisions to be responsible for the formation process of R^* , e.g., by collision of a higher excited state with R to produce R^* .

3. The self quenching rate constants, k_q , for these excited states are of the order of 10^{10} - 10^{11} dm³ mole⁻¹ sec⁻¹. This is typical of the rate constant expected for a collisional process whereby an electronic excited state is quenched by its own ground state atomic species. The process is similar to reaction (4), but is 20 to 100 times slower than the observed formation rate constants. These results strongly negate the idea of atom-atom collisional processes being responsible for the formation of the observed emission in these systems and thereby support an electron-atom interaction.
4. The electronic excited states observed in these systems are the so-called '2p' levels. These are a series of 10 closely spaced electronic levels which decay by radiative means down to the lowest electronic excited states (1s). The 2p levels are generally 1-2 eV above the lowest electronic level of the rare gas atom and about 3 eV below the ionization threshold - see Table 2.
5. No initial step in $[R^*]$ is observed, which means that the states observed here are not produced in observable amounts by any faster excitation process involving higher energy electrons.

TABLE 2

Gas	E(s.e.) eV	E(2p _n) eV	I _p eV
Ne	16.6	18.96 (2p ₁)	21.56
Ar	11.6	13.2 (2p ₁)	15.76
Kr	9.6	11.2 (2p ₆)	13.996
Xe	8.6	10.1 (2p ₅)	12.127

6. The conclusions to be drawn from the formation rate constant data in these systems are:

(a) the excited states are formed by the interaction of energetic electrons with ground state rare gas atoms, $E(e^-) > E(s.e.) + \sim 1-2$ eV, i.e., the electrons are secondary electrons with energies significantly greater than the lowest excitation level of the gas.

(b) the time scale of the formation process is pressure dependent, but over the range 5 torr to 0.5 torr, occurs in the time domain of ca. 0-5 ns. Assuming that the kinetic parameters determined here are reasonable, this would translate to a time of the order of 20 picoseconds in 1 atmosphere of rare gas.

(c) recently⁽⁵⁾ we have obtained data for the formation constants for these same rare gases in an excess of lighter rare gas. The results are similar in magnitude to those obtained in the pure rare gases. This indicates that the electrons responsible have a similar energy distribution in both types of system.

CONCLUSION

The 'rule of thumb' idea that the sub-excitation electron spectrum is formed "instantly" is now observably incorrect. The secondary electron energy spectrum in a pure gas takes a finite time to evolve and the rates of secondary electron interactions can be observed in low pressure gases. As a result of these interactions, the secondary and subsequent generations of electrons produced from primary ionization events are degraded by inelastic processes until they become sub-excitation electrons. Further energy loss by momentum transfer (elastic collisions) processes results in thermalization of the electrons.

These experiments have clearly shown the time scale for the degradation of epithermal electron to sub-excitation energies in pure rare gases. If sufficient excitation cross-section data is available, then these data will provide a new opportunity for comparison with theoretical calculations.

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TABLE 1: Summary of Pure Rare Gas Emission Data

Formation Constants

Gas	Atomic Level	k_g ($10^{12} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)
Neon	($2p_1$, 585 nm)	2.08
Argon	($2p_1$, 750 nm)	5.74
Krypton	($2p_6$, 762.5 nm)	4.77
Xenon	($2p_5$, 840 nm)	6.89

Decay Data

Gas	Zero Pressure Natural Lifetime (ns)	k_{dec} [10^7 s^{-1}]	k_q (self quenching) [$10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$]
Neon	19.0	5.25	9.09
Argon	40.0	2.50	1.21
Krypton	43.4	2.30	2.72
Xenon	46.6	2.14	3.89

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FIGURE CAPTIONS

- Figure 1 Emission: time curves for xenon-3 torr. Curve A: raw data from $2p_5$
 at 840 nm; Curve B: background at 810 nm.
 Ordinate: emission intensity
 Abscissa: time ns.
- Figure 2 Emission: time curve with computer subtracted background
 Solid curve: curve from least squares fit
 Dots: experimental data
- Figure 3 Pseudo first order formation constants versus xenon pressure
 Ordinate: growth constant (10^9s^{-1})
 Abscissa: xenon pressure (torr)
- Figure 4 First order decay constants for argon ($2p_1$) at various argon
 pressures
 Ordinate: decay constant (10^7s^{-1})
 Abscissa: argon pressure (torr)

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Figure 3

Figure 4