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TECHNICAL PROGRESS REPORT

Kinetics of Growth and Decay of Excited Rare-Gas Atoms and Molecules in the Pulse Radiolysis of Pure Rare Gases and of Mixtures of Rare Gases with Molecular Quenching Agents

PROJECT TITLE

KINETICS OF FAST REACTIONS OF EXCITED SPECIES

U.S.D.O.E. CONTRACT NO. DE-AC02-76ER01116.A008

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Abstract

The temporal behavior of vibrationally relaxed first triplet Kr_2 in the presence of N_2 has been examined, and the rate constant for destructive quenching by N_2 has been evaluated at 298K. Its value is of the same order of magnitude as that for quenching of first triplet Ar_2, but is somewhat smaller. This suggests that the krypton and argon excimers excite different electronic states of N_2, the former leading to $N_2(A)$ and $N_2(B)$ and the latter principally to $N_2(C)$, in accord with the general rule that near-resonant energy transfer tends to be favored over events which form products bearing significant translational energy. A new value for the spontaneous radiative decay constant of vibrationally relaxed first triplet Kr_2 has also been determined.

A generalized mechanism for decay of Paschen(1s) atoms and for concomitant growth and decay of bound-state excimer molecules has been developed. Modelling calculations have shown that decay constants for $Ar(^3P_2)$ measured at low(1-20 torr) and high(100-700 torr) pressures are not discrepant with respect to one another and can be precisely fitted with the generalized mechanism. Implications regarding the temporal behavior of vibrationally relaxed Ed_2 excimers are also discussed.

Data obtained by single frequency laser probe monitoring of $Ar(^3P_2)$ suggests that, although the 1s-2p absorption lines are of Lorentzian form at 700 torr, as expected, the apparent line width narrows with increasing time. The cause of this phenomenon has not yet been identified.

I. Spontaneous Radiative Decay and Quenching of $Kr_2(^3\Sigma_u^+)(v=0)$ by N_2.

We have completed an investigation of effects of the presence of N_2 on the rate of decay of the vibrationally relaxed first triplet excimer of Kr_2 at 298K and a krypton pressure of 800 torr. This work has been done in partial fulfillment of requirements for the M.Sc. degree by William E. Selander. As we have shown previously[1], the temporal dependence of the optical absorbance of this species can be acceptably fitted by least squares methods by the expression, $\ln(I_o/I) = A_1e^{-A_2t} - A_3e^{-A_4t}$, at all pressures in the 250 - 850 torr region. For each of the rare gas first triplet excimers there is a critical pressure above which the smaller of the exponential parameters, A_2 and A_4, becomes independent of pressure and assumes the value of the spontaneous radiative decay constant of the vibrationally relaxed triplet excimer. The open data points of Figure 1 in the 600 - 800 torr range represent, accordingly, experimental values of $k_R(v=0)$ measured during the current contract year. The $1/\sigma^2$ weighted mean of these six values is $2.48(\pm0.07)10^6s^{-1}$. This is, we believe, a more reliable value than that which we reported earlier[1], because it is smaller and probably reflects a lower level of impurities. A summary of reported values is presented in Table I.

Table I

Reported Values of the Spontaneous Radiative Decay Constant of $Kr_2(^3\Sigma_u^+)(v=0)$

Investigators	$10^{-6}k_R$, s^{-1}	Reference
Oka, Rama Rao, Redpath and Firestone	2.83(±0.08)	1
Leichner and Ericson	3.3	2
Salamero	4.0	3
Haaks and Becker	2.9	4
Selander and Firestone	2.48(±0.07)	This work

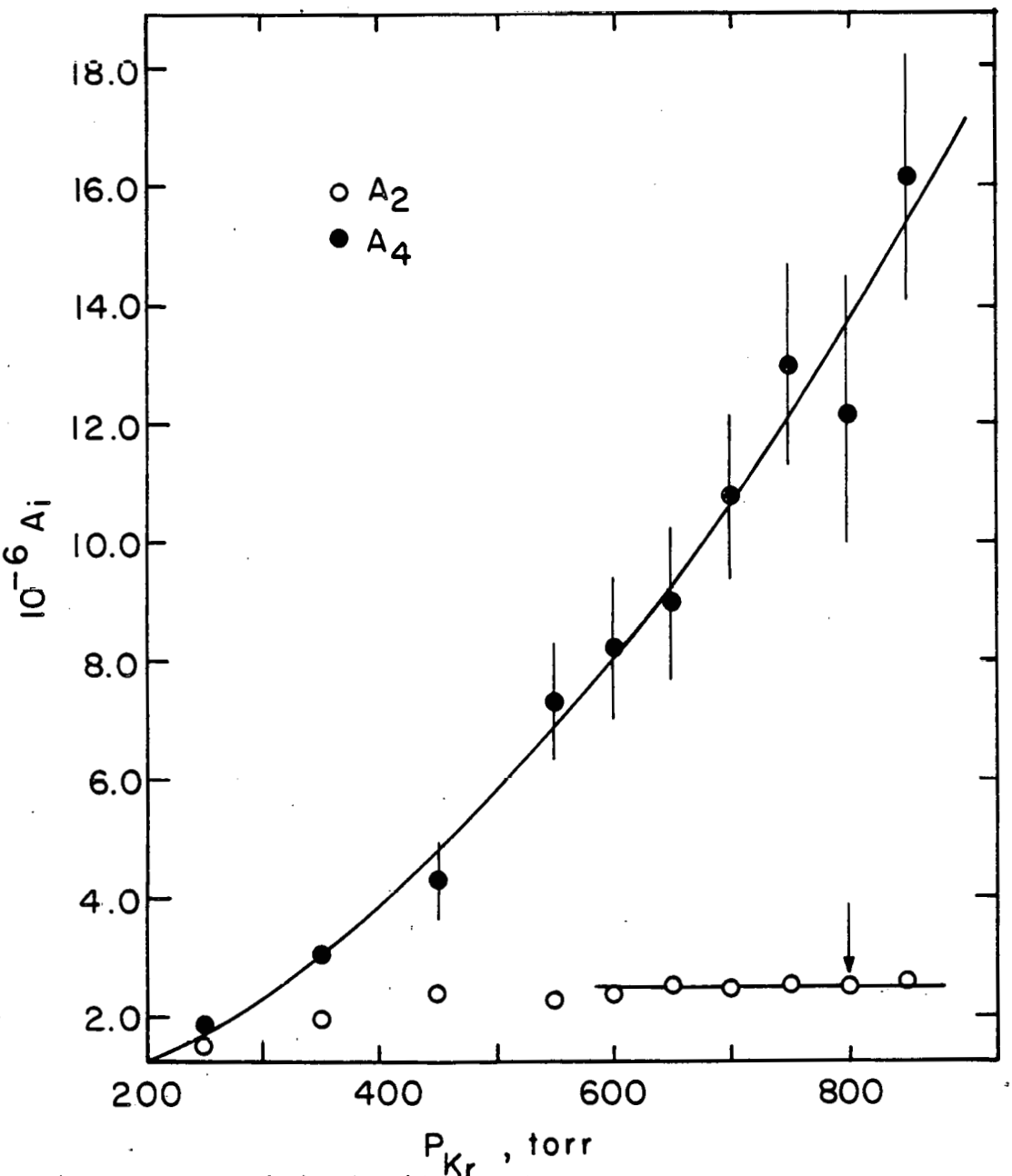

Figure 1. Empirical Fitting Parameters, A_2 and A_4, for the Expression Describing the Temporal Behavior of First Triplet(v=0) Kr_2 at 298K.

In the presence of a quenching agent, Q, the excimer decay constant is given by $k = k_R + k_Q(Q)$, as illustrated in Figure 2. The solid line of Figure 2 is the $1/\sigma^2$ weighted least squares best fitting line and is given by $10^{-6}k = 2.45(\pm0.06) + 0.243(\pm0.011)P_{N_2}$. We note that the value of the intercept is in excellent agreement with the mean value of k_R determined in pure krypton and may also be identified with k_R. The rate constant for quenching of the first triplet of Kr_2 is therefore found to be equal to $7.50(\pm0.34)10^{-12}$ cm^3 $molec^{-1}s^{-1}$ at 298K. This is the first reported value of a rate constant for quenching of the first triplet Kr_2 excimer species.

The products of quenching of the krypton excimer by N_2 have not been determined. The A and B triplet electronic states are the most likely products. Figure 3 implies that $N_2(A^3\Sigma_u^+)$ and $N_2(B^3\pi_g)$ are likely to be formed with considerable amounts of vibrational energy, but it is clear that nitrogen atoms cannot be formed by energy transfer from the Kr_2 excimer, because the dissociation energy of ground state N_2 exceeds that of all of the bound vibrational levels of $Kr_2(^3\Sigma_u^+)$. It cannot be predicted by analogy or otherwise which of the N_2 species is more likely to be formed or which v states are more probable, except to note that there is generally a propensity in favor of energy transfer events in which product translational energies are relatively small. The v=0 level of $Kr_2(^3\Sigma_u^+)$ is not well determined.

The general rule that $k_{Q,excimer} > k_{Q,1s_5}$ is seen to be valid for krypton species quenched by N_2; Setser's value for the latter is only half that for $k_{Q,excimer}$(Cf., Reference 5). We also note that N_2 is a much <u>more</u> efficient quencher of the krypton excimer than of the argon excimer, although $Ar_2(^3\Sigma_u^+)$-(v=0) lies approx. 1.5 eV <u>higher</u> in energy.[6] This suggests that, because the Ar_2 species lies just below the $N_2(C^3\pi_u)$(v=0) level and is near resonant with very high v states of $N_2(B)$ or $N_2(A)$, there must be a generally lessened

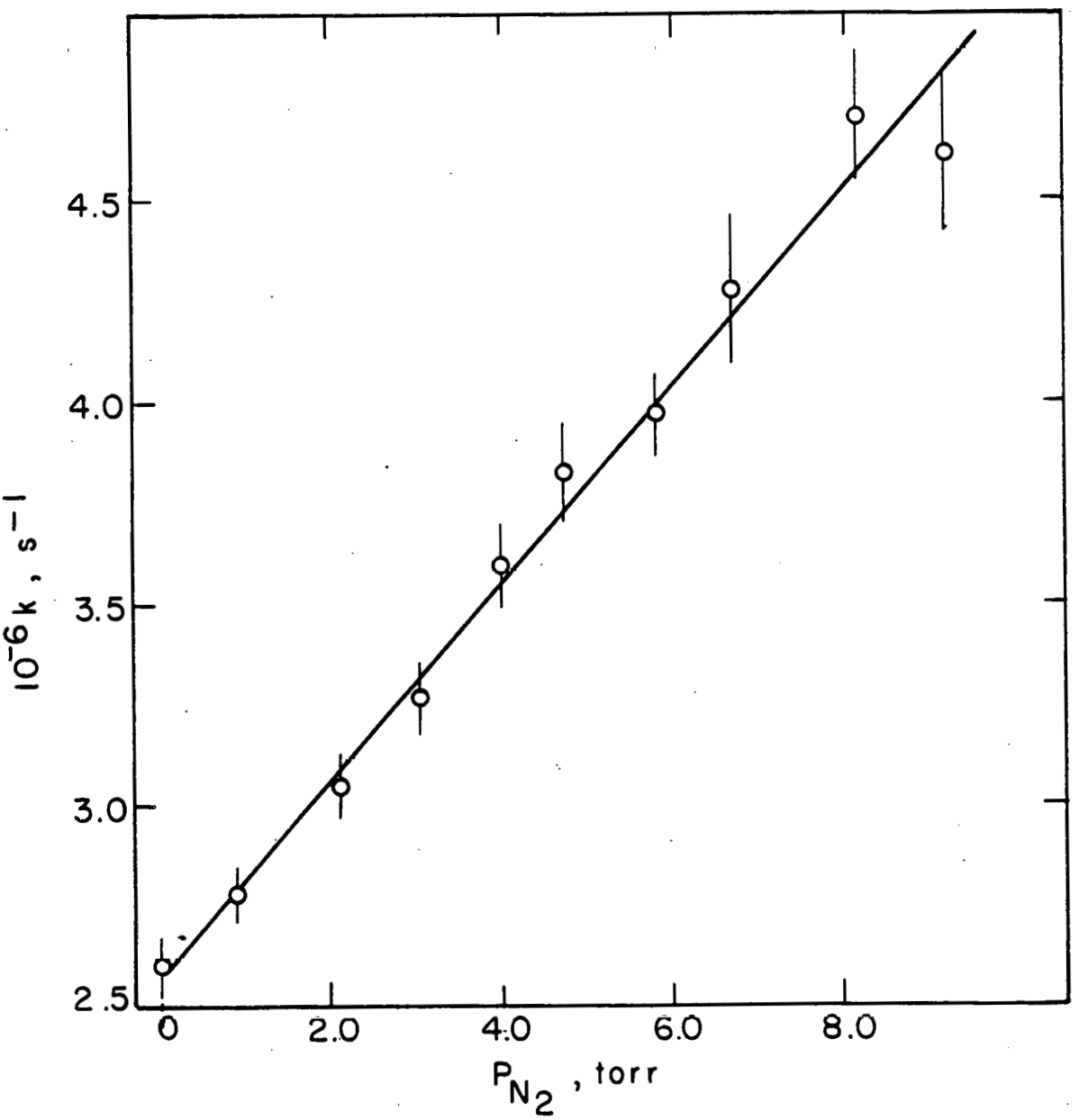

Figure 2. Decay Constant of First Triplet Kr_2 as a Function of the Partial Pressure of Ground State N_2 Molecules in Kr Gas at 800 torr. and 298K.

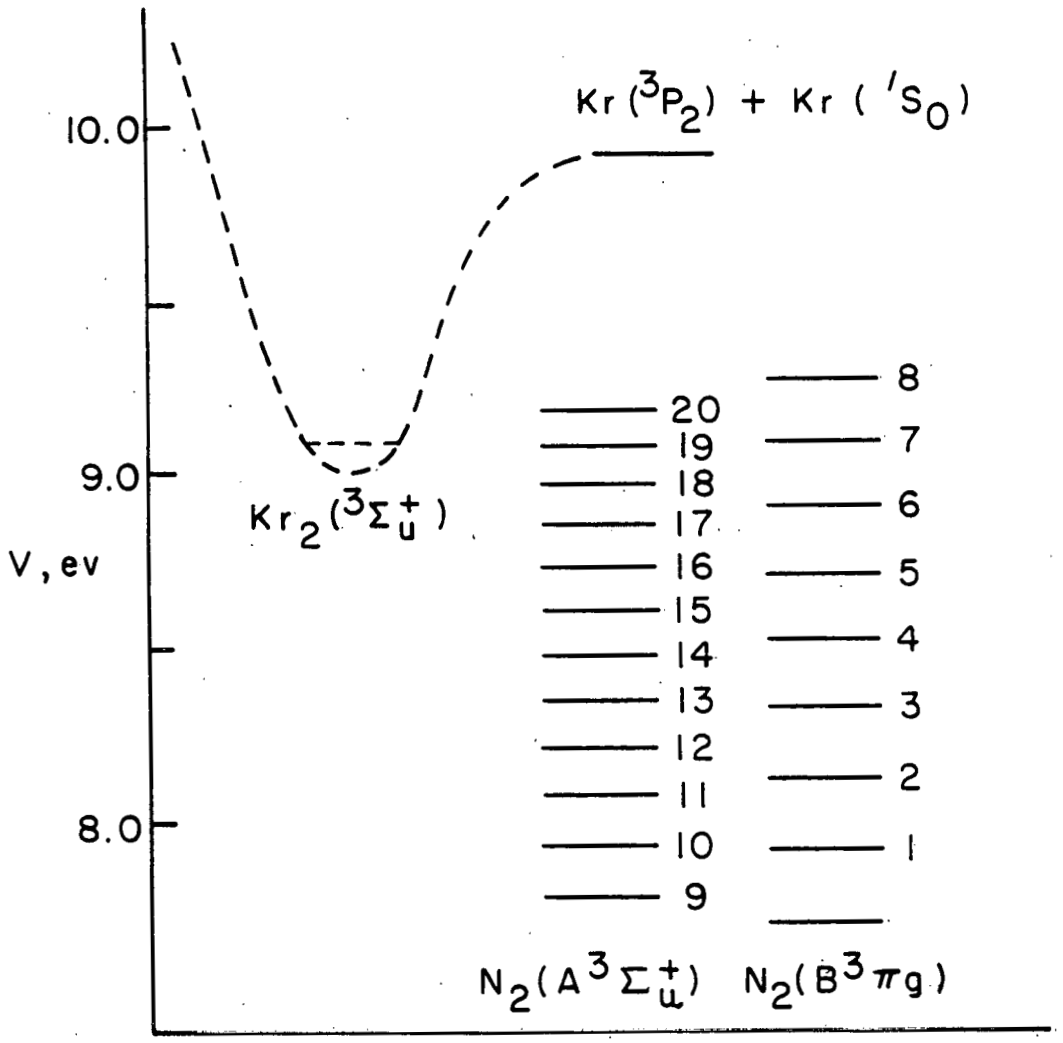

Figure 3. Approximate Potential Curve for First Triplet Kr_2 and Vibrational Levels for $N_2(A)$ and $N_2(B)$ States.

probability for large changes in vibrational energy of the system. Too few quenching data for rare gas excimers are available to establish this as a rule.

The filled data points of Figure 1 represent values of A_4, the larger of the exponential parameters, A_2 and A_4, as a function of krypton pressure. The significance of the A_4 values is obscure. If the mechanism for growth and decay of the excimer were a simple irreversible first order sequence of steps proceeding from the atomic precursor without provision for radiative decay of successive partially relaxed excimer states, the larger of the exponential parameters below 600 torr would be identifiable as k_R, and the smaller one would be identifiable as k_R above 600 torr. Conversely, the smaller one would possibly be identifiable as the precursor decay constant below 600 torr and the larger one would possibly represent the precursor decay constant above 600 torr. In such a case the adherence of the parameter representing the precursor decay constant to the form $AP^2 + BP$ might be mechanistically significant. Such is clearly not the case however. Careful analysis of the pressure dependence of the $Ar(^3P_2)$ decay constant and of the pressure dependence of the growth and decay parameters of $Ar_2(^3\Sigma_u^+)(v=0)$ indicates that the mechanism for decay of $Ar(^3P_2)$ and for concomitant growth and decay of the vibrationally relaxed first triplet Ar_2 species necessarily includes a sequence of reversible relaxation steps and that radiative decay of partially vibrationally relaxed states of the excimer plays an important part in the mechanism which culminates in the v=0 state. Thus, adherence of A_4 to the form $AP^2 + BP$ is essentially fortuitous; neither A nor B has any meaning except as an empirical fitting constant in the case of the argon system. We believe that the excimer forming mechanisms must be essentially similar in all of the rare gases and that it is a futile exercise to attempt to obtain any mechanistical-

ly useful information by analysis of the A and B parameters.

II. Generalized Mechanism for Decay of Ed(1s) Atoms in Pure Rare Gases.

An article entitled, "Mechanism for the Decay of $Ar(^3P_2)$ Atoms in Pure Argon. Reconciliation of Low Pressure and High Pressure Values for the Decay Constant." is scheduled for publication in the Journal of Chemical Physics in August 1983. A copy of this article accompanies this report. This article provides a comprehensive basis for interpretation of the dependence of Ed(1s) atom decay constants on pressure and temperature. In addition, it provides a rationale for the pressure dependence of the A_2 and A_4 parameters of the empirical fitting expression, $\ln(I_o/I) = A_1e^{-A_2t} - A_3e^{-A_4t}$, for excimer data. In brief summary, the Ed(1s) atom decay mechanism is linked with the mechanism for growth of vibrationally relaxed bound excimer states by a sequence of reversible collisional relaxation steps. This sequence is initiated by a reversible termolecular step,

$$Ed(1s) + 2Ed(^1S_o) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ed_2^*(I) + Ed(^1S_o),$$

where $Ed_2^*(I)$ represents one of many bound states of the excimer and the Roman I indicates that it lies very close to the Ed_2^* dissociation limit. The mechanism is carried forward by successive reversible stages of collisional relaxation, e.g.,

$$Ed_2^*(I) + Ed(^1S_o) \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Ed_2^*(II) + Ed(^1S_o),$$

and may eventually culminate in formation of $Ed_2^*(v=0)$. However, at each rovibrational level, $Ed_2^*(I, II, III, \text{etc.})$ may alternatively radiate spontaneously to the excimer ground state. Thus, a principal and probably the

most important effect of variations in rare gas pressure is seen to be alteration of the ratio of collisional relaxation to radiative decay at each of many rovibrational states of the excimer. Modelling calculations show that competition between collisional and radiative channels sharply limits the number of relaxation stages which are significant in determining the net rate of removal of Ed(1s) atoms. Thus, we find that the decay constant for $Ar(^3P_2)$ is completely determined by the parameters of only the eight uppermost relaxation stages of the Ar_2 triplet excimer at 700 torr of argon and only by those of the two uppermost stages at 2 torr. Consistently, the number of uppermost stages which determine the value of the excited atom decay constant increases monotonically from two to eight in the 2 - 700 torr range. These modelling calculations are an outgrowth of work reported in our July 1982 report (U.S.D.O.E. Document No. DOE/ER/01116-35) which was based on a much simpler three-step single-reversible-stage mechanism.

In contrast, it is clear that all of the rovibrational levels may be significant at all pressures in determining the temporal profile of the $Ed_2^*(v=0)$ species. The number of possibly significant relaxation stages in this context is nearly unlimited, if allowance is made for rotational as well as vibrational relaxation and if collision induced multiple quantum jumps are permitted. Therefore, the model used in our calculations is necessarily oversimplified, because it permits only single quantum jumps in the collisional steps and is restricted to vibrational relaxation. Calculations based on this simplified model, assumption of an exponential gap expression, $k_{ij} = ae^{-b\Delta\varepsilon/kT}$, for exoergic steps and $k_{ji}/k_{ij} = e^{-\Delta\varepsilon/kT}$ for endoergic steps demonstrate that when b is relatively large the modelling procedure produces $Ar_2(^3\Sigma_u^+)(v=0)$ vs. t data sets which lead to A_2 and A_4 parameters in good agreement with values in the $\ln(I_o/I) = A_1e^{-A_2t}\ A_3e^{-A_4t}$ expression determined experimentally for the

vibrationally relaxed Ar_2 excimer at 700 torr. To date it appears that $k_r(v=0)$ is recoverable without regard for the magnitude of b, but that markedly exoergic quantum jumps are proscribed in the real system.

III. Single Frequency Laser Probe Monitoring of Ar(1s) Atoms.

Monitoring of Ar(1s) atoms via fast single frequency laser probe spectrophotometry using a ring dye laser probing beam pumped by a high power krypton ion laser have been continued during the current contract year. We have continued to experience severe technical difficulties with the lasers, i.e., persistent high frequency noise and far too frequent plasma tube failure in the ion laser and low output power from the dye laser. The manufacturer, Spectra-Physics, has replaced, to date, four plasma tubes. Spectra-Physics also replaced the original power supply for the ion laser with a new unit in May of 1983. Delivery and installation of a new resonator assembly for the dye laser is promised for the summer of 1983. At present the ion laser does not meet power or noise level specifications. We trust that acceptable performance of the lasers will be attained in the near future.

Interpretation of the time and laser frequency dependence of excited atom absorbance values is not simple and straightforward, even with a properly functioning single frequency monitoring system. As discussed in our July 1981 report (U.S.D.O.E. Report No. DOE/ER/01116-34) front-to-back power density variations in a sample of gas containing absorbing species must be carefully considered and properly integrated at high power densities. Significant variations of power density across the face of the laser beam must be scrupulously avoided at high power densities, because only absorbance values measured at constant power density have interpretable significance when temporal coupling (bleaching) of the states linked by the laser induced transitions occurs. Radial variations in power density can be minimized by accepting only a small

portion of the laser beam at the detector, but at the cost of severely reduced signal amplitudes. At presently attainable power levels we are restricted to power densities which are not great enough to induce temporal coupling of most 1s - 2p pairs.

At low power densities at which front-to-back and radial variations in power density are not troublesome, we have recently observed an unexpected and troublesome phenomenon which we cannot as yet explain satisfactorily. This occurs when a single Ar(1s) species is monitored at different laser frequencies within a single 1s - 2p absorption line profile. In principle one expects the effect of probing at a number of different frequencies within a given absorption line to be a simple translation upward of the absorbance at any given time without change in any of the line shape parameters as one moves from the wings of the line toward line center. Figure 4 presents, in descending order, absorbance values recorded at 0.3, 0.4, 0.5 and 0.9 microseconds following the electron beam pulse as functions of laser frequency - all within the profile of the $1s_5 - 2p_3(^3P_2 - {}^3P_2)$ line at 700 torr of argon. Each set of values has been fitted with the Lorentzian expression for a collision broadened line; the solid lines are least squares best fit Lorentzian profiles at each time point. The quality of fitting is consistent with experimental uncertainties.

The analytic expression for a Lorentzian collision broadened line is $\ln(I_o/I) = A(1)/[(\nu - \nu_o)^2 + \delta_\nu^2]$, where A(1), ν_o and δ_ν are fitting parameters; ν_o and δ_ν are the frequency at line center and the line width (HWHM); A(1) is defined below for an electron dipole oscillator transition. As anticipated, ν_o is found to be strictly independent of time and in excellent agreement with values reported by the NBS/NSRDS tabulations for each of the 1s - 2p lines examined. The line width, however, is observed to decrease with

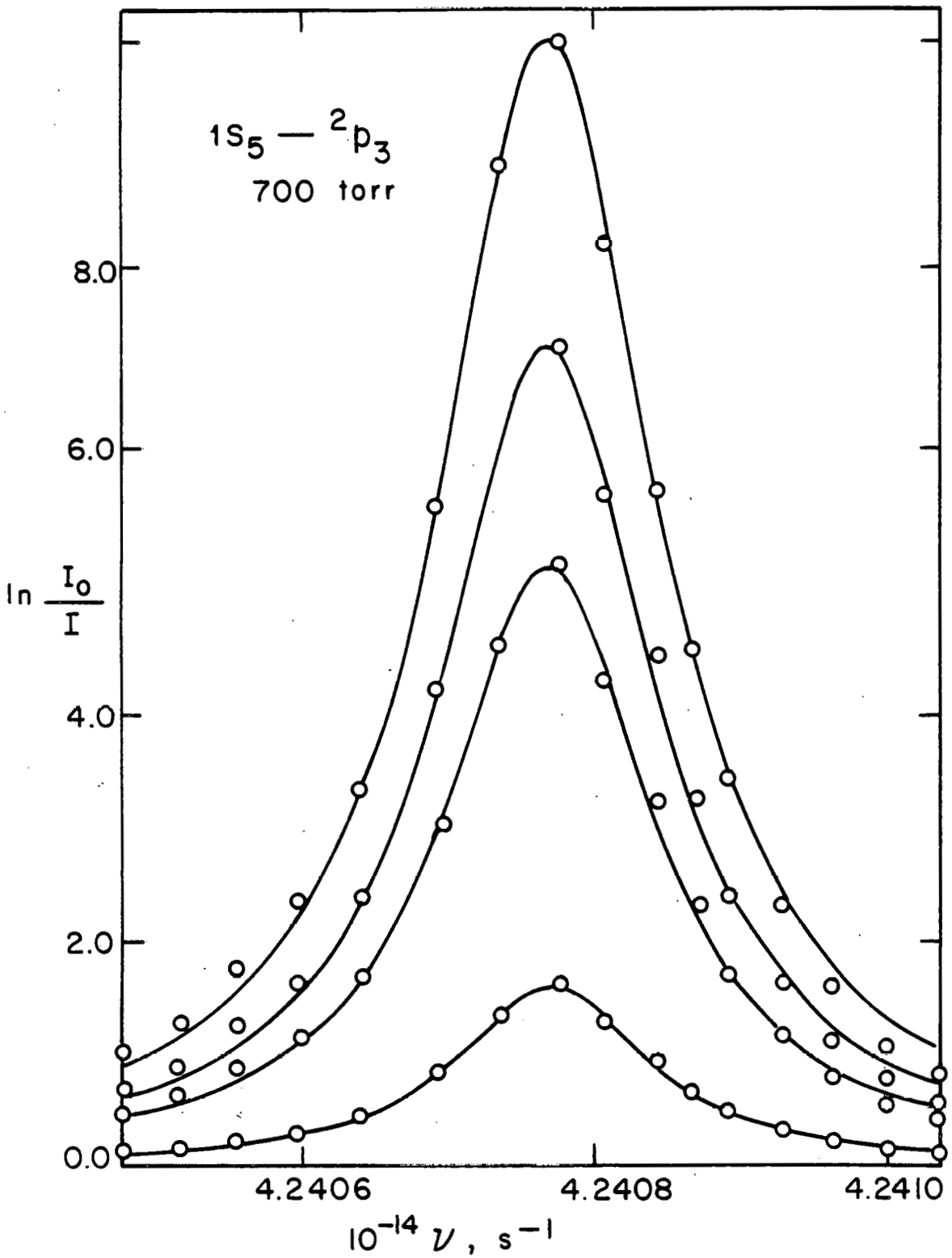

Figure 4. Absorbance as a Function of Laser Frequency for the $1s_5$ - $2p_3$ Transition. Solid Curves are Least Squares Best Fit Lorentzian Profiles. Uppermost Curve is for 0.3 microsecond.

time. This behavior is entirely unexpected and is troublesome, because it has the effect of changing the extinction coefficient with respect to time at each laser frequency. Figure 5 illustrates the apparent time dependence of line width for the $1s_5 - 2p_6$ line at 700 torr of argon(7637.37Å). The terminal value of the line width is in good agreement with that extrapolated by means of the pressure broadening coefficient measured at very low argon pressures.[7] Since the ground state atom concentration remains constant during the course of each experiment, one expects the width of a collision broadened line to remain constant. The possibility that the electric field induced by the electron beam pulse might persist longer than a few nanoseconds can be dismissed. We must look to other possible causes of the line narrowing phenomenon.

It is possible that the 1s - 2p lines may be significantly broadened by collisions with 1s atoms as well as with ground state atoms. If so, the line width at any time t should be given by $\delta_\nu = \theta C + \theta^* C^* e^{-kt}$ when the 1s atoms decay via first order processes, where θ and θ^* represent coefficients for collision broadening by ground state and 1s atoms, resp., and C and C_o^* represent the ground state atom concentration and the apparent initial concentration of 1s atoms, resp. The solid curve of Figure 5 is the least squares best fit line of this expression. The fitting procedure equates θ^* to $6.92 \times 10^{15}/C^*$, Å/torr. Now, $A(1)/\delta_\nu$ is a direct measure of the concentration of absorbing species, n, in the expression for a classical electron dipole oscillator transition; i.e., $A(1)/\delta_\nu = \pi e^2 f l n/m_o c$, where e and m_o are the charge and rest mass of the electron, f is the oscillator strength and c is the speed of light in vacuo. Since the oscillator strength is known and the path length, l, can be estimated at ca. 2 cm. we can calculate n at any time t. Assuming that each of the four 1s states is populated roughly in proportion to 2J + 1, we estimate that the maximum concentration of 1s atoms is of the order

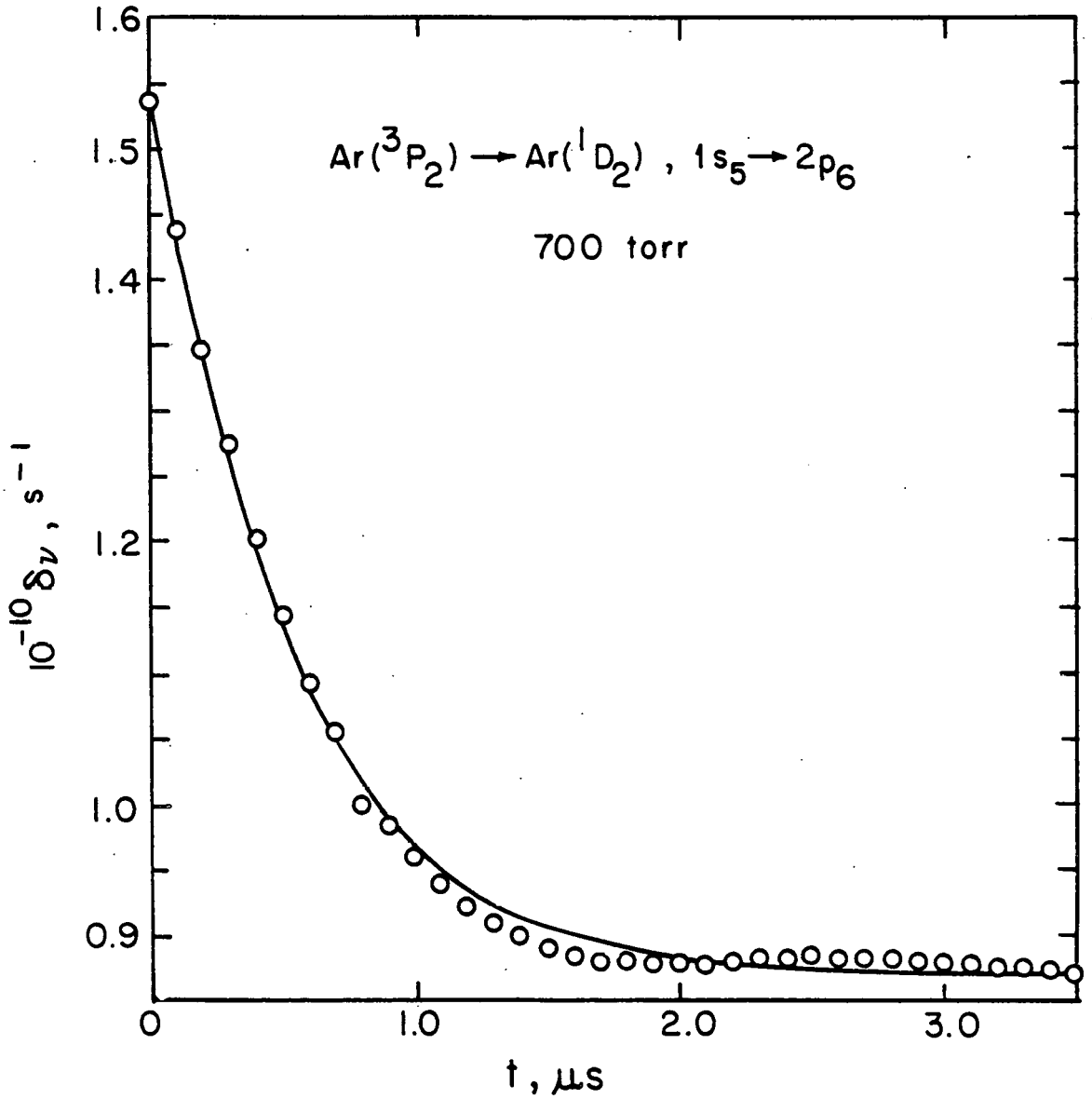

Figure 5. Lorentzian Absorption Linewidth(HWHM) as a Function of Time for the $1s_5$ - $2p_6$ Line

of 10^{15} atoms/cm^3, which is in good agreement with an estimate based on N_2O dosimetry.[8] This indicates that θ^* must be of the order of unity in Å/torr, or 10^4 times the value of the coefficient for line broadening by ground state atoms. This is, in our judgment, not a credible possibility. We are also skeptical of this treatment because $\ln[A(1)/\delta_\nu]$ vs. t plots yield quite different $Ar(^3P_2)$ decay constants when data for different $Ar(^3P_2)$ absorption lines are used, whereas all should be identical. It is also observed that $A(1)/\delta_\nu$ values for different absorption lines do not scale correctly with respect to the well determined oscillator strengths. Thus, we tend to doubt the possibility that line broadening by 1s atoms can be significant under the conditions of our experiments.

Since the dye laser beam is polarized, 2p atoms formed in the laser induced transition have their m vectors preferentially oriented with respect to the direction of polarization. Thus, since a portion of the 2p atoms radiate back to the original 1s state, these produce 1s atoms with selectively oriented m vectors. Thus, as time proceeds the fraction of 1s atoms whose m vectors are relatively favorably oriented for the laser induced transition might be expected to increase steadily, if nothing occurs simultaneously to disorient the m vectors. This hypothesis therefore requires that the frequency of disorienting collisions be lower than the frequency of destructive collisions which remove 2p and 1s atoms. This is hardly credible, because the ratio of frequencies of disorienting collisions to destructive collisions is of the order of 10^2 for 2p atoms.[9] We, therefore, believe that the cause of the line narrowing phenomenon lies elsewhere, but can test this hypothesis by depolarizing the laser beam.

An alternative possibility is that the line narrowing phenomenon is an experimental artifact associated with noise fluctuations in the laser power or

caused by malfunctioning of the recording and detection system. We have shown that a slight shift in the signal levels corresponding to 100% and 0% transmittance triggered by the electron beam pulse will produce absorbance vs. time data which share some, but not all, of the anomalous characteristics of the experimental data. Tests of the Biomation 8100 recording system indicate that it performs within specifications at signal frequencies in the megahertz region. Static tests of the silicon photodiode and power supply indicate that this system responds linearly to steady power levels in the appropriate range. We are presently setting up dynamic tests of this system which will help us to identify causes of possible signal distortion or absolve the recording and detection systems of blame. It is our present belief that the line narrowing phenomenon is probably at least partly caused by signal distortion.

IV. Effects of the Presence of H_2 and O_2 on the Decay of Ne(1s) Atoms.

A copy of a manuscript entitled "Bimolecular and Three-Body Quenching of Paschen(1s) Neon Atoms by H_2 and O_2 "based on work performed by Mary Frances Beno in partial fulfillment of requirements for the Ph.D. degree accompanies this report. A preliminary report of this work appears in our July 1981 report (U.S.D.O.E. Document No. DOE/ER/01116-34).

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Personnel Engaged on the Project During the Current Year

1. Richard F. Firestone, Professor of Chemistry and Principal Investigator, half-time (1 December, 1982 - 30 June, 1983, and 1 October, 1983 - 30 November, 1983); full-time (1 July, 1983 - 31 August, 1983).

2. Elizabeth R. Manzanares, Visiting Postdoctoral Research Associate; full-time (30 November, 1982, - 15 October, 1983).

3. Krishna P. Chakravorty, Visiting Postdoctoral Research Associate; full-time (1 August, 1983 - 30 November 1983).

4. William E. Selander, Graduate Teaching Associate; half-time (1 December, 1982 - 30 November, 1983).