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Citation: *The Journal of Chemical Physics* **64**, 2605 (1976); doi: 10.1063/1.432513

View online: <http://dx.doi.org/10.1063/1.432513>

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# Study of excitation transfer in a flowing helium afterglow pumped with a tuneable dye laser. III. Transfer and quenching reactions of the $\text{He}_2(3p^3\Pi)$ molecule\*

C. B. Collins and B. W. Johnson

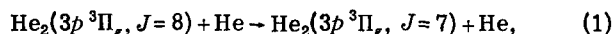
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(Received 12 September 1975)

The collisional transfer of excitation from the  $\text{He}_2(3p^3\Pi_g)$  state to other electronically excited states energetically lying within a few  $KT$  is examined by optically pumping a flowing helium afterglow with a tuneable dye laser. Rate coefficients for the transfer of excitation to states conserving spin, particularly  $3d^3\Pi_u$  and  $3d^3\Delta_u$ , are found to be greater than  $10^{-10}$   $\text{cm}^3/\text{sec}$ , resulting in a rapid thermalization of electronic and rotational energy. Relative probabilities of spontaneous radiation for transitions in the visible wavelength range from the product states are found to be 1 and  $1/3$  for the  $3\Pi_u$  and  $3\Delta_u$  states, respectively, relative to that from the initial  $3\Pi_g$  state. The absence of significant fluorescence from singlet states tends to confirm the conservation of spin during such reactions.

## I. INTRODUCTION

In Part I of this series<sup>1</sup> a general technique for the determination of excited state lifetimes as functions of colliding particle densities was described. In principle, from such data the rate coefficients for the collisional reactions quenching the excitation of atomic or molecular systems can be determined.

The particular experimental system discussed employed a pulsed tuneable dye laser to optically pump nonequilibrium populations of excited states of free radicals and other short-lived species produced in a high-pressure flowing afterglow of the type first described by Collins and Robertson.<sup>2</sup> From the decay of the populations back toward the equilibrium value, lifetimes and ultimately quenching rates could be determined. Part II in 1972 reported<sup>3</sup> rates obtained in this way for the collisional relaxation in a flowing helium afterglow of rotational levels of  $\text{He}_2(3p^3\Pi_g)$ , a state readily pumped from the metastable ( $2s^3\Sigma_u^+$ ) helium molecule. A single rotational state of this level was pumped and the unexpected conclusion was reached that the forbidden  $\Delta J = \pm 1$  channel accounted for more than half of the rate of rotational relaxation of this state. The rate for this channel



was found to be  $2.4 \times 10^{-11}$   $\text{cm}^3/\text{sec}$ . However, not reported at that time was a collection of fluorescence data from other bands excited by collisional transfer from the electronic level initially pumped by the laser. The complexity of this data and the extreme difficulty in obtaining it discouraged the further examination of the problem of excitation quenching in  $\text{He}_2$ , but a preliminary analysis of that data appeared in conference proceedings.<sup>4</sup> However, recent successes with excimer<sup>5</sup> and charge transfer lasers<sup>6</sup> have served to re-emphasize the importance of excitation transfer and quenching reactions in inert gas afterglows. It is the purpose of this paper to present a more thorough analysis of this unpublished excitation transfer data obtained in helium. From it a better understanding may be obtained of the dominant channels for the relaxation of electronic and rotational energy in  $\text{He}_2$ . It is shown

that the importance of the "forbidden"  $\Delta J = \pm 1$  channel of rotational relaxation is a consequence of a more general excitation transfer mechanism in which all product states allowed by conservation of both electronic spin and total energy are populated at rates of the order of  $10^{-10}$   $\text{cm}^3/\text{sec}$ . It is most likely that the excitation of the  $\Delta J = \pm 1$  channels occurs as a consequence of reaction chains involving other electronic states as intermediaries.

## II. METHOD

As discussed in Part II of this series, an enhanced population of the  $3p^3\Pi_g$  state of molecular helium was produced in the  $J=8$  rotational level of the vibrationless ground state by optically pumping near  $4630 \text{ \AA}$  the  $\text{He}_2(2s^3\Sigma_u^+)$  metastable population present in the flowing afterglow of a microwave discharge in pure helium. This particular level was chosen because the wavelength of the laser could be suitably removed from the fluorescence observed from product levels resulting from collisional transfer reactions. The actual pumping step was accomplished with a flashlamp pumped dye laser capable of emitting  $23 \mu\text{J}$  per pulse into the Doppler bandwidth of the absorption line. The population enhancement produced by the pumping was monitored by observing the fluorescence of the  $P_9$  transition  $55 \text{ \AA}$  to the red of the pumping line and, hence, free from spurious scattering of the laser beam. A tandem  $0.75 \text{ m}$  spectrometer provided adequate rejection of the scattered laser radiation. A fast photon counting system having  $20 \text{ nsec}$  resolution and coupled to an on-line computer was used to record the transient fluorescent intensities.

As discussed in Part II of this series, not only was fluorescence observed from the  $P_9$  transition from the  $J=8$  rotational level directly pumped, but also from the lower  $J=7$  rotational level. Additionally, however, fluorescence was observed from all levels lying within  $KT$  of the level directly pumped, except those to which collisional transfer of the pumped energy was forbidden by spin conservation.

Figure 1 shows a diagram of the energy levels at the

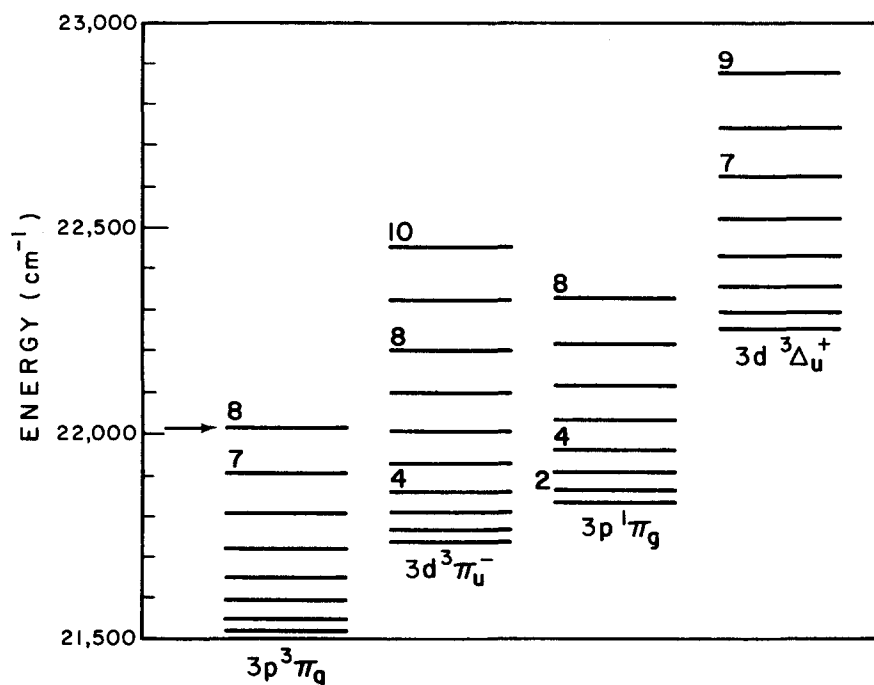


FIG. 1. Energy levels at the equilibrium internuclear separation of the various rotational and electronic states of  $\text{He}_2$  in near resonance with the particular state optically pumped. The pumped level is indicated by the arrow. Indicated  $J$  values identify those levels from which fluorescence was examined in these experiments. Energies are referenced to the  $2s^3\Sigma_u^+$  metastable  $\text{He}_2$  at the internuclear separation of the  $J=0$  level.

equilibrium internuclear separation of the various rotational and electronic states of  $\text{He}_2$  in near resonance with the particular level optically pumped. Indicated  $J$  values identify those levels from which fluorescence was examined in these experiments. Actual values of energy are referenced to the  $2s^3\Sigma_u^+$  metastable  $\text{He}_2$  at the internuclear separation of the  $J=0$  level.

In contrast to the analytical treatment used in Part II, it is evident that the excitation of such a large number of product states at such similar energies implies that that is the time dependence of the differences between populations and equilibrium values that contain information about relaxation rates rather than the populations themselves. Assuming a close coupling between initial and final states, the decay of populations can be described by the coupled equations

$$\frac{d}{dt} [N_i] = -K[N_i] + K \left( \frac{g_i}{g_f} \right) e^{-\Delta E/KT} [N_f], \quad (2)$$

$$\frac{d}{dt} [N_f] = +K[N_i] - K \left( \frac{g_i}{g_f} \right) e^{-\Delta E/KT} [N_f], \quad (3)$$

where  $[N_i]$  and  $[N_f]$  are the populations of the more energetic initial and less energetic final states, respectively, the  $g$ 's are statistical weights and  $K$  is the rate for the binary reaction transforming  $N_i$  into  $N_f$ . The combination of Boltzmann factors is required for detailed balancing. Combining equations gives the dependence of the adjusted population difference,

$$\phi = (N_i - g_i/g_f \exp(-\Delta E/KT) N_f), \quad (4a)$$

the form

$$\phi = \phi_0 \exp[-Kt(1 + g_i/g_f e^{-\Delta E/KT})], \quad (4b)$$

where  $\phi_0$  is the nonequilibrium population increment initially produced by the optical pumping. Consequently a logarithmic plot of the decay of the suitably weighted difference in fluorescence intensities from the initial

and product states should decrease at a rate given by Eq. (4b).

For fluorescent intensities from levels for which  $\phi \cong 0$  over the range of times which can be experimentally resolved,  $K$  can only be assumed greater than  $(\tau)^{-1}$ , the inverse of the resolution time of the measurement. In this case the comparison of the total yield of photons from the initial and product states gives a measure only of the relative coefficients for spontaneous radiation and not the rate coefficient assumed in Part II. It will be seen in the following section that all fluorescence detected from electronic states, other than the  $3\Pi_u$  state initially pumped, fell into the  $\phi=0$  category. Conversely, it was found  $\phi \neq 0$  for the fluorescence resulting from the "forbidden channel" of rotational relaxation for which  $\Delta J = \pm 1$ .

### III. RESULTS AND ANALYSIS

Figure 2 shows a plot of the equilibrium difference population  $\phi$  between the initial  $J=8$  and product  $J=7$  states of the  $3p^3\Pi_u$  state of  $\text{He}_2$ . The lifetime of the decay of the population difference is seen to be of the order of 71 nsec which, at 10 Torr of helium pressure, corresponds to an effective rate coefficient of  $4.4 \times 10^{-11} \text{ cm}^3/\text{sec}$ . However, according to Eq. (4) this effective coefficient must be reduced by the factor  $(1 + g_i/g_f e^{-\Delta E/KT})$  to obtain the rate coefficient for the rotational relaxation process [Reaction (1)]. Assuming for the moment the temperature is essentially the ambient temperature, this gives a value of

$$K_1 = 2.8 \times 10^{-11} \text{ cm}^3/\text{sec}, \quad (5)$$

where the subscript 1 has been appended to indicate the rate for Reaction (1). This value is to be compared with the value of  $2.4 \times 10^{-11}$  obtained from considerations of photon yield as reported in Part II.<sup>3</sup>

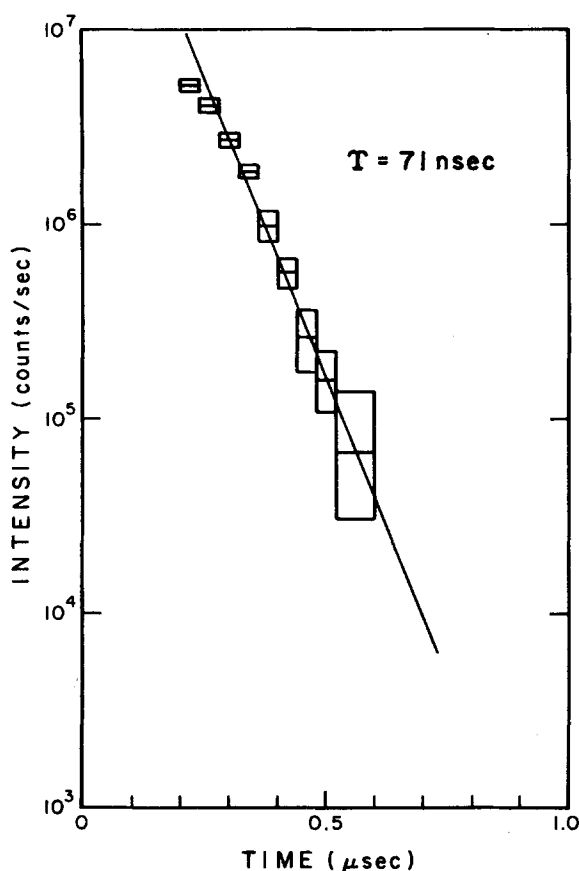


FIG. 2. Graph showing the decay toward equilibrium of the weighted population difference,  $\phi$ , between the initial  $J=8$  and product  $J=7$  rotational levels of the  $3p^3\Pi_g$  state of  $\text{He}_2$ . Differences are computed by Eq. (4a) and shown in terms of intensity differences radiated from the populations involved. The linear fit to the data corresponds to a lifetime of 71 nsec.

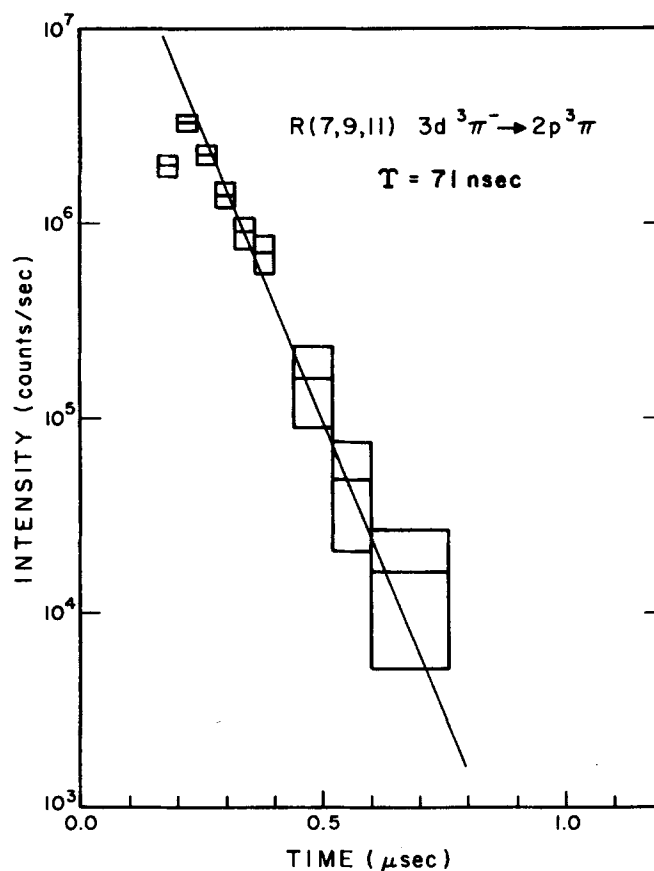
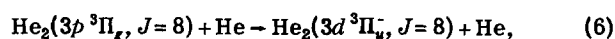


FIG. 3. Graph showing the decay of the fluorescent intensity of the unresolved band head comprising the  $R(7)$ ,  $R(9)$ , and  $R(11)$  lines from rotational levels  $J'=8, 10$ , and  $12$ , respectively, of the  $3d^3\Pi_u^-$  electronic state of  $\text{He}_2$ . Nominal wavelength of this fluorescence was  $5862 \text{ \AA}$ . For comparative purposes the 71 nsec lifetime has been shown.

Figure 3 shows the decay of the fluorescence of the band head in the  $R$  branch of the transition at  $5862 \text{ \AA}$  from the  $3d^3\Pi_u^-$  electronic state. This data corresponds to unresolved emission from the  $J=8, 10$ , and  $12$  rotational levels. The line corresponding to exponential decay at the 71 nsec lifetime has been drawn for comparison with Fig. 2. Since the relative transition probabilities are not generally known for different electronic states of  $\text{He}_2$ , the difference population  $\phi$  cannot be directly obtained from the fluorescence data. However, the ratio of intensities as plotted in Fig. 4 can give an indication of the time dependence of  $\phi$ .

As shown, the ratio of photon counting rates for transitions from the initial and final states is essentially constant to within experimental error, implying that  $\phi=0$  between  $3p^3\Pi_g$  and  $3d^3\Pi_u^-$ .

In this case the effective decay constant of Eq. (4b) must be greater than the inverse resolution time of the system, 20 nsec, and consequently the rate coefficient for the reaction



must be

$$K_6 \geq 10^{-10} \text{ cm}^3/\text{sec}. \quad (7)$$

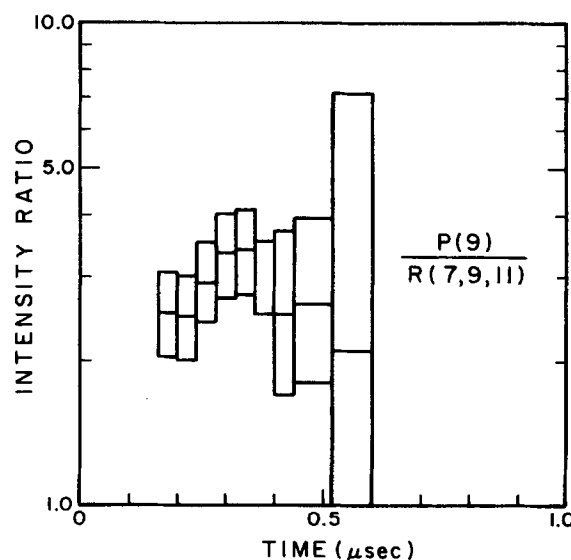
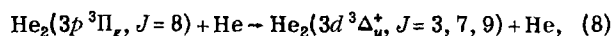


FIG. 4. Ratio of intensities as a function of time emitted from the  $J=8$  level of the initial  $3p^3\Pi_g$  state of the  $\text{He}_2$  to the  $J'=8, 10$ , and  $12$  levels of the product  $3d^3\Pi_u^-$  state. The absence of a trend of variation in the data implies  $\phi=0$  over this range of times.

TABLE I. Radiative lifetimes for transitions indicated normalized to that from the  $3p^3\Pi_g$  state obtained from the experimental data according to Eq. (11) and assuming  $T = 300^\circ\text{K}$ .

Electronic states	$J'$	$\gamma_t/\gamma_1$	$\tau_t/\tau_1$
$3d^3\Pi_u^- \rightarrow 2p^3\Pi_g$	4	1.38	$3.1 \pm 0.4$
$3d^3\Delta_u^+ \rightarrow 2p^3\Pi_g$	3	1.14	$1.0 \pm 0.2$
	7	1.43	$1.2 \pm 0.3$

Another consequence of the implication that  $\phi = 0$  is that the populations are, in fact, distributed in a thermal equilibrium and that an examination of the intensity of fluorescence from different rotational levels should show an equilibrium distribution. This was more readily examined in fluorescence from the  $3d^3\Delta_u^+$  electronic state because of the more open rotational structure. Integrated fluorescent yields were obtained separately for the  $R(2)$ ,  $R(6)$ , and  $R(8)$  lines of the electronic transition near  $5700 \text{ \AA}$  from the  $3d^3\Delta_u^+$  state. These yields were found to be consistent with a thermal distribution of population among the rotational levels of the  $3d^3\Delta_u^+$  state implying that the rate coefficient for the reaction



was similarly described by Eq. (7).

Finally, considering that the fluorescent yield in photons collected from a thermal distribution of population should be given by

$$Y_t = G_t \gamma_{tj}^* \tau_t^{-1} \ell^{-\Delta E_t/KT} N_i \left( \sum g_{it}^{-\Delta E_t/KT} \right)^{-1}, \quad (9)$$

where  $\gamma$  is a collection of Hönl-London line strengths,<sup>7</sup>  $S_j^*$ , for the  $X$  branch from the  $J$  rotational state. For  $X = P$  or  $R$ ,

$$\gamma_{tj}^* = S_j^* \left( \frac{S_j^*}{S_j^* + S_j^*} \right), \quad (10)$$

where  $\tau_t$  is the radiative lifetime for the emission of the detected transition from the final electronic state,  $G_t$  is the detector calibration factor including geometric effects,  $N_i$  is the total population increment of the initial state pumped by the laser, and the final summation over initial and final states divides this population by the effective partition function. More useful is the ratio of yields from final and initial states,  $R_t$ ,

$$R_t = Y_t/Y_1 = C_t (\gamma_{tj}^*/\gamma_{1j}^*) (\tau_1/\tau_t) \ell^{-\Delta E_t/KT}, \quad (11)$$

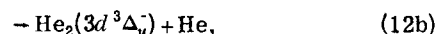
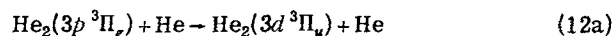
where  $C_t = G_t/G_1$ , a measure of the relative sensitivity of the detector at the two wavelengths. By solving Eq. (11) for the lifetime ratio in terms of values of measured  $R$ , calibrated  $C$ , and computed  $\gamma$  and  $e$  factors, experimental values of the lifetime ratios can be obtained. These are presented in Table I. Error

bounds resulting from photon statistics are shown.

The lifetime ratio for the singlet  $3p^1\Pi_g$  state could not be determined because no significant fluorescence was detected from this level indicating that either  $\tau_t$  was quite long for this level or that the excitation transfer reaction giving this state was forbidden, as would be expected from considerations of spin conservation.

#### IV. CONCLUSIONS

First, the agreement between radiative lifetimes for the  $J=3$  and  $7$  rotational levels of the  $3\Delta_u$  state tends to confirm the thermalization of the products of the excitation transfer from the  $3\Pi_g$  state initially pumped. This, together with the equilibrium inferred between the same initial  $3\Pi_g$  and final  $3\Pi_u$  state, gives rate coefficients for the reactions



in excess of  $10^{-10} \text{ cm}^3/\text{sec}$ . No selection rule on  $\Delta J$  for the reactions was evident, but the absence of fluorescence from the singlet states suggests that conservation of spin is required during excitation transfer.

These reactions most probably form intermediate steps in the "forbidden,"  $\Delta J = \pm 1$  channel of rotational relaxation given by Eq. (1) and found to have a rate coefficient of  $2.4 \times 10^{-11} \text{ cm}^3/\text{sec}$ .

Finally, the rapid thermal equilibration of the product states with the initial state allows for the determination of the relative radiative lifetimes of the product states. These are summarized in Table I. It can be seen that the  $3p^3\Pi_g \rightarrow 2s^3\Sigma_u^+$  and  $3d^3\Pi_u \rightarrow 2p^3\Pi_g$  transitions have approximately the same radiative transition probabilities while the transition  $3d^3\Delta_u^+ \rightarrow 2p^3\Pi_g$  has about one-third the transition probability.

\*Research supported by the National Science Foundation, NSF Grant ENG74-06262.

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