

K₂ ground-state relaxation studies from transient process kinetics

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Abstract. Relaxation parameters of the optically depopulated (v'' , J'') $X^1\Sigma_g^+$ level of the K_2 molecule with $v''=1$ and $J''=72$ have been determined for thermal collisions with He, Ne, Ar, Kr and Xe atoms, using the method of laser-induced fluorescence kinetic monitoring. Rate constants of about $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ and effective cross sections between 0.5×10^{-14} and $1.6 \times 10^{-14} \text{ cm}^2$ have been obtained. Rectangular modulation of the He-Ne laser 628.8 nm intensity, exciting the transition $(1,72)X^1\Sigma_g^+ \rightarrow (8,72)B^1\Pi_u$, was employed making it change periodically from depopulating to probing. The time dependence of the probe-beam-induced fluorescence directly reflects the transient process restoring the thermally equilibrated populations of the lower level (v'' , J''). The kinetic equations were solved in the classical-limit $J'' \rightarrow \infty$ approximation, allowing for participation of two relaxation processes, namely collisions and collisionless exchange of molecules inside and outside the laser beam in their thermal motion. It is shown that the assumption of additive rates for both processes can lead to distortion of the concentration dependence of total relaxation rate. A description of the transient process is also given within the framework of irreducible tensor operators, permitting us to consider separately the contribution of population relaxation and of alignment. For the rovibronic state $(8,72)B^1\Pi_u$ from measurements of the degree of polarisation of the fluorescence it was found that cross sections for population and alignment relaxation coincide within 3% and would fit into the limits of the experimental error.

1. Introduction

The appearance of optically pumped Na_2 , K_2 , I_2 , Te_2 , Bi_2 and other dimer lasers has stimulated an increase in interest in processes which redistribute population over vibrational and rotational states. The experimental determination of the relaxation rate over the internal degrees of freedom encounters certain difficulties in such cases as homonuclear diatomic molecules in their electronic ground state. This is because radiative transitions within one electronic state are forbidden. Optical methods for relaxation studies require 'labelling' a certain level out of the great number of ground-state levels v'' , J'' and observing changes in its characteristics. According to Drullinger and Zare (1969, 1973, to be referred to as DZ) this can be achieved through 'optical pumping' of such a level by its depopulation in absorption. The basic process in its re-population is non-radiative mixing, i.e. thermalisation. The most sensitive method of detecting optical pumping consists in registering changes in laser-induced fluorescence (LIF). These may be changes in intensity, in degree of polarisation or circularity as measured by DZ (1973) on Na_2 , Grushevsky *et al* (1977) on K_2 , Clark and McCaffery (1978) on I_2 , as well as appearance of the ground-state

Hanle effect in LIF studied by Ferber *et al* (1979) on Na₂ and K₂. The most direct information on repopulation of an optically depopulated level can, however, be obtained through transient process kinetics in LIF, as recently performed by König and Weber (1980) and Auzin'sh *et al* (1980). It is this method that has been applied in the present work. A convenient subject has been found in K₂ in which the 632.8 nm He-Ne laser line excites the ($v'' = 1, J'' = 72$) X ¹Σ_g⁺ → ($v' = 8, J' = 72$) B ¹Π_u transition with high efficiency.

2. Experimental

The method is based on the following idea. If a laser beam of spectral power density ρ produces optical transitions $a \rightarrow b$, figure 1, at a rate $B\rho$, and if this rate is of the same order as the total relaxation rate γ_{Σ} of level a , then the latter has a stationary population which is smaller than at thermal equilibrium. We get an effect called 'optical pumping' by DZ (1969). Now let, as shown in figure 2(a), the excitation be subjected to amplitude modulation in the form of rectangular pulses with time intervals T and T_0 considerably exceeding γ_{Σ}^{-1} . The modulation depth $1 - \rho_{pr}/\rho$ is chosen in such a way that $B\rho_{pr} \ll \gamma_{\Sigma}$. This means that during the period T_0 the radiation of density ρ_{pr} is a probe. The signal $I(t)$ of LIF from the transition $b \rightarrow c$, figure 1, can be divided into the following regions, shown in figure 2(b): I, a transient process of duration about $\gamma_{\Sigma}^{-1} + (B\rho)^{-1}$; II, a stationary state with thermally unequilibrated population of level a ; III, a transient process of duration about γ_{Σ}^{-1} after attenuation of the light; IV, a thermally equilibrated state of level a . It is the transient process in the region of linear response of the system, III, which is directly determined by thermalisation of the optically depopulated lower level.

A block diagram of the experimental array is presented in figure 3. A He-Ne laser was used for excitation, with an output of about 1 W cm⁻² in the 632.8 nm line and with about 2 mm effective beam diameter. The beam was modulated by means

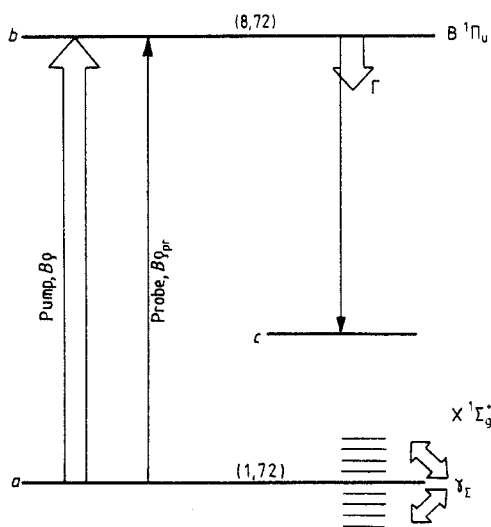


Figure 1. Transition scheme for optical pumping of K₂.

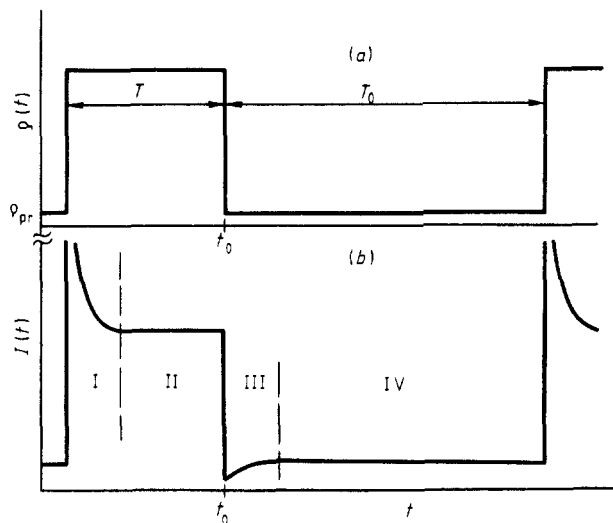


Figure 2. Time dependence of (a) excitation, (b) LIF.

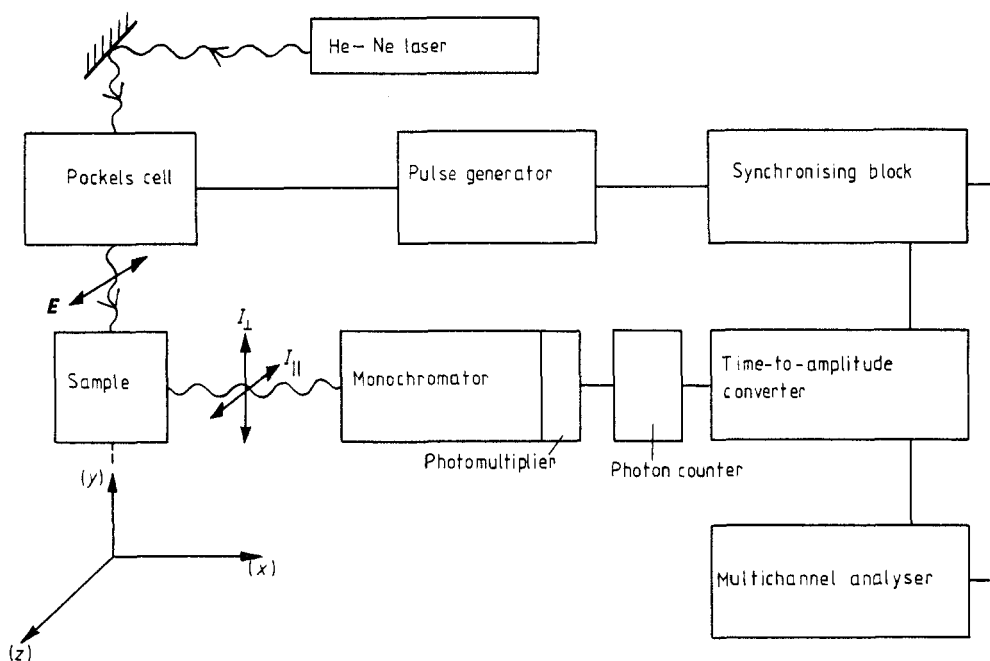


Figure 3. Block diagram of the experimental set-up.

of a Pockels electro-optical modulator. The characteristic modulation depth was 0.87–0.95, the pulse repetition frequency 9 kHz, the growth and decay duration of the edge of the pulses not exceeding 50 ns, $T = 30 \mu\text{s}$, $T_0 \approx 80 \mu\text{s}$. The beam is plane polarised with E vector directed along the z axis. The cell, containing metallic potassium, was heated to a temperature of 435 K, drift not exceeding 1 K; the

concentration of molecules $N_{K_2} = 0.82 \times 10^{10} \text{ cm}^{-3}$ and that of atoms $N_K = 0.21 \times 10^{14} \text{ cm}^{-3}$ after Nesmeyanov (1963). The cell was connected to the vacuum system through a dry stopper, thus making introduction of heated noble gases possible through a narrow aperture. The gas pressure was measured by a deformational discharge manometer with a volume division, the error not exceeding 5%. The Q_{16} line of the LIF progression was isolated by a monochromator with 0.5 nm mm^{-1} dispersion. An analyser was placed to separate a definite polarisation component. Registration was effected by a cooled PM tube. The time dependence of the signal was measured by the method of one-photon statistical analysis (OSA), cf Binkert *et al* (1972), Knight and Selinger (1973), using a time-to-amplitude converter (TAC). The amplitude distribution was analysed with the aid of a 256-channel analyser. The TAC sets a $10 \mu\text{s}$ time scale in the 256 channels (calibration accuracy about 1%).

3. Kinetic equations

Let absorption lead to depopulation pumping of $(v'', J'', M'', \nu_y)X^1\Sigma_g^+$ state a with fixed quantum numbers v'', J'', M'' and projection ν_y of the molecule velocity on the direction of the exciting beam. Collisions with atoms A cause the thermal equilibrium in population to be restored, proceeding through mixing with other states $(v''_i, J''_i, M''_i, \nu_{yi})$, characterised by the i th total of the above mentioned parameters



Under conditions when the region of laser beam action is much smaller than the volume of the cell, a non-collisional relaxation mechanism also appears. It consists of interchange of 'labelled' molecules inside the beam with thermally equilibrated ones outside the beam by the process of thermal motion through the laser beam.

Now we shall introduce kinetic equations including both collisional and 'fly-through' relaxation. For levels with high values of angular momentum the classical approach is feasible. Let us consider a group of molecules in an element of volume with dipole moment \mathbf{p} and orientation determined by spherical angles θ, ϕ . The group moves with velocity v_x along the x axis and impinges on the laser beam of output density $\rho(x, z)$ directed along the y axis. We shall investigate the distribution function $\sigma_a(x, z, \theta, \phi, t)$, for which the physical meaning of $\sigma_a d\Omega$ (where $d\Omega = \sin \theta d\theta d\phi$) is the concentration of molecules in ground state a , having \mathbf{p} directed within the $d\Omega$. The kinetic equation for σ_a is

$$\dot{\sigma}_a = -B\rho(x, z)C^{\text{abs}}(\theta, \phi)\sigma_a + \gamma(\sigma_a^{\text{IV}} - \sigma_a). \quad (2)$$

The first term of the right-hand side describes absorption, C^{abs} being the coefficient of angular dependence of the absorption probability. The next term describes collisional relaxation to the thermal equilibrium state σ_a^{IV} , where γ denotes the rate of collisional relaxation. We assume here that $\gamma \neq \gamma(\theta, \phi)$, neglecting reorienting collisions, see § 4. Spontaneous radiation is not accounted in (2) due to the large number of transitions allowed in LIF. Stimulated radiation also contributes little ($\sim 10^{-2}$ at the experimentally achieved values of $B\rho \sim 10^6 \text{ s}^{-1}$) and is ignored in (2). Since $\Gamma \gg \gamma_{\Sigma}$, neither process manifests itself in the transient process (III), figure 2(b). For the stationary region (II) $\sigma_a^{\text{II}}(x, z, \theta, \phi)$ can be easily written down as the solution of a linear differential equation, obtained from (2) by the substitution $dt = dx/v_x$. The initial condition is $\sigma_a^{\text{II}} = \sigma_a^{\text{IV}}$ at $x \rightarrow -\infty$. After the depopulating beam has been switched

off at time t_0 (attenuated to probe level), the concentration relaxes from σ_a^{II} to σ_a^{IV} in the transient process (III)

$$\sigma_a^{\text{III}}(x, z, \theta, \phi, t) = \sigma_a^{\text{IV}} - [\sigma_a^{\text{IV}} - \sigma_a^{\text{II}}(x - v_x(t - t_0), z, \theta, \phi)] \exp[-\gamma(t - t_0)] \quad (3)$$

where $\sigma_a^{\text{II}}(x - v_x(t - t_0), z, \theta, \phi)$ is an above mentioned solution of (2) with delay along the x axis, thus accounting for translational motion. Such notation assumes that the molecules in state a either fly freely through the beam, or pass onto some other state as a result of collisions at a rate γ . The intensity of LIF of definite polarisation $I^{\text{III}}(t)$ excited by probe beam $\rho_{\text{pr}}(x, z)$ and including the 'fly-through' relaxation is

$$I^{\text{III}}(t) = \int F(u) C^{\text{abs}}(\theta, \phi) C^{\text{fl}}(\theta, \phi) B \rho_{\text{pr}} \sigma_a^{\text{III}}(x, z, \theta, \phi, t) \sin \theta \, du \, dx \, dz \, d\theta \, d\phi \quad (4)$$

where $F(u) = 2 \exp(-u^2)u \, du$ is the Maxwell distribution function in the xz plane; $u = v/v_p$, v_p being the most probable velocity, $C^{\text{fl}}(\theta, \phi)$ is the angular coefficient of radiation probability. For sufficiently low particle concentrations, the relaxation is only caused by thermal molecular motion through the beam ($\gamma \approx 0$) and is only determined by the beam profiles. Let us consider the Gaussian profiles of the beams $\rho_0 \exp[-(x^2 + z^2)/r_0^2]$. Figure 4(a) presents numerically calculated curves of $I_{\parallel}^{\text{III}}(\tau)$, $\tau = v_p t/r_0$, when the distribution $\rho(x, z)$ is cut off, assuming $\rho(x, z) = \rho_{\text{pr}}(x, z) = 0$ for $x^2 + z^2 > 2r_0^2$. The figure shows that for a large optical pumping parameter $\chi = B\rho_0 r_0/v_p$ the dependence is essentially non-exponential with delay at low τ values (curves 2 and 3). At not too large values, $\chi \sim 1$, the dependence approaches an exponential shape

$$I^{\text{III}}(\tau) = c_1 - c_2 \exp(-A/\tau) \quad (5)$$

however, the exponential index A is χ dependent. Curves 1-3 in figure 4(b) were calculated by the Monte-Carlo method for unlimited and spatially coinciding Gaussian profiles of the pump and probe beams. The difference in shape of the curves in 4(a)

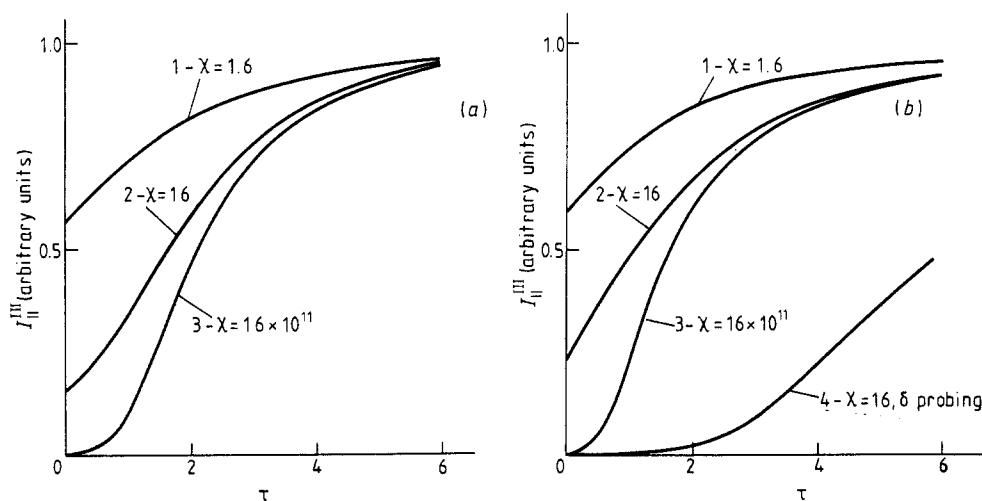


Figure 4. Numerically calculated LIF curves of the transient process in the absence of collisions: (a) cut-off Gaussian profile; (b) full Gaussian profile.

and 4(b) is due to the effect of the 'wings' of the Gaussian distribution. It is noteworthy that if we have a very narrow probe beam $\rho_{pr}(x, z)$, in the form of a δ function, then relaxation does not take place for a certain lapse of time, cf curves 2 and 4, figure 4(b) due to the fact that there exists a region around the probe beam which is practically free of molecules in the labelled state. This demonstrates a possibility, in principle, to study the transient process during the span of time when 'fly-through' relaxation has not yet set in. In the case where collisions are prevalent ($\gamma \gg \nu_p/r_0$) the signal of the transient process $I^{III}(\tau)$ will be of exponential shape (5) with $A = \gamma r_0/\nu_p$ for any profile of beam.

In most general case $\gamma \sim \nu_p/r_0$ the Monte-Carlo method was applied for integration, and the signals $I_{\parallel}^{III}(\tau)$ and $I_{\perp}^{III}(\tau)$ were calculated for an unscreened Gaussian profile of the beams. Expressions obtained also permit the calculation of the degree of polarisation in the stationary process (II), figure 2(b)

$$P = (I_{\parallel}^{II} - I_{\perp}^{II}) / (I_{\parallel}^{II} + I_{\perp}^{II}). \quad (6)$$

It was just the degree of polarisation or circularity of the fluorescence which was measured by DZ (1973), Grushevsky *et al* (1977), Ferber (1979) and Clark and McCaffery (1978). In order to determine γ_{Σ} the calibration curve $P_0(B\rho_0/\gamma_{\Sigma})$ was calculated by DZ (1969, 1973). They omitted spatial coordinates in the balance equation and introduced a certain 'fly-through' relaxation rate α_0 , assuming

$$\gamma_{\Sigma} = \alpha_0 + \gamma. \quad (7)$$

It is worth examining a connection between γ_{Σ} and the rate of collisional relaxation γ entering into (2). This was achieved by equalising P_0 and P determined according to (6). Such a dependence is presented in figure 5. P was calculated assuming approximately the same conditions as in the experiment performed by DZ (1973) with Na_2 : $r_0 \approx 1.5$ mm (for e^{-1}), temperature $T = 468$ K. The value of $B\rho_0$ was chosen to be equal to 10^7 s^{-1} . Under such conditions $P = 0.36$ for $\gamma = 0$. As shown in figure 5, curve 1, γ_{Σ} and γ are non-linearly connected, which indicates non-agreement with (7). The curve shows a break point which can be explained as follows. At high pressures, when $\gamma \gg \nu_p/r_0$ the dependence is linear. With diminishing pressure we approach the case $\gamma \sim \nu_p/r_0$, where collisions and fly-through become competitive. This leads to the disappearance of the linearity because of non-exponential kinetics of fly-through relaxation. If $B\rho_0$ is reduced by an order of magnitude (to 10^6 s^{-1}), the time dependence of the relaxation approaches an exponential one (figure 4), and the break in the $\gamma_{\Sigma}/B\rho_0$ dependence of γ becomes less pronounced (cf figure 5, curve 2). Measurements in Na_2 (DZ 1973) and I_2 (Clark and McCaffery 1978) revealed a similar break in the pressure dependence of $\gamma_{\Sigma}/B\rho_0$, treated by the authors as the effect of filling Bennett holes in elastic collisions. We suggest that the appearance of the break can be easily explained, simply on the basis of the results presented in figure 5. The region of the break γ' corresponds, incidentally, to a concentration $N'_{Ar} = \gamma'/k$ at which a break was observed by DZ (1973) if one assumes a rate constant $k = 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ for $\text{Na}_2\text{-Ar}$, as directly measured by König and Weber (1980). No break in the curve was, however, observed in similar studies by Ferber (1979) and Grushevsky *et al* (1977). This may be due to the sufficiently high pressures ($\geq 10^{-2}$ Torr).

We shall now analyse the information given by the method of transient process kinetics. For this purpose 'true' $I_{\parallel}^{III}(t)$ curves, calculated for several γ values after (2)–(4) were approximated by exponentials of the type (5), passing from τ and A to

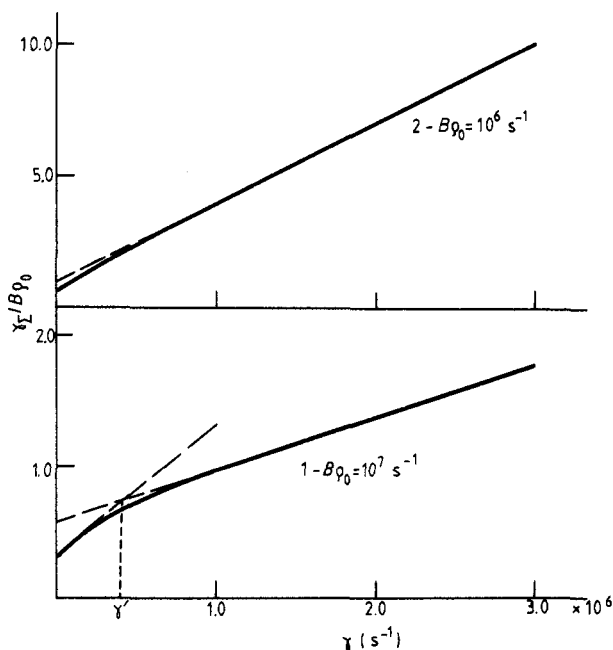


Figure 5. Calculation according to scheme $\gamma \Rightarrow P = P_0 \Rightarrow \gamma_Z/B\rho_0$ of connection between collisional relaxation rate $\gamma = kN$ and the ratio $\gamma_Z/B\rho_0$ (the latter determined after Drullinger and Zare 1969).

real time t and rate α . The $\alpha(\gamma)$ dependence thus obtained is presented in figure 6 as employed in experiment with $\chi \leq 2$. It is well described by the linear function $\alpha = \alpha'_0 + \gamma$ in which the changes $\Delta\alpha$ obtained equal the changes $\Delta\gamma$ within about 2%. This permits us to determine the rate constant $k = \Delta\gamma/\Delta N \approx \Delta\alpha/\Delta N$.

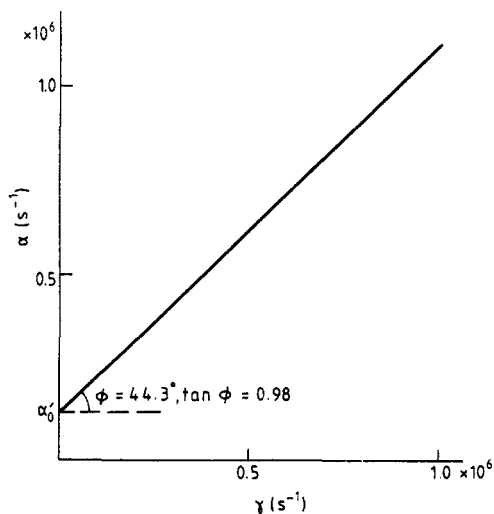


Figure 6. Calculated dependence of index α of exponent approximating $I_{\parallel}^{III}(t)$ on collisional relaxation rate γ .

4. Experimental results and discussion

The recorded characteristic pulses of the exciting beam and of LIF observed in the transition $(8,72) B^1\Pi_u \rightarrow (16,72) X^1\Sigma_g^+$ in the transient process region are presented in figure 7(a) and (b). As can be seen from figure 7(a), a parasitic periodic component is superimposed on the base of the exciting pulse. This is due to the electrically stimulated mechanical oscillations of the crystal of the Pockels cell. The fluorescence signal, after having these oscillations removed, background and 'pile-up' (according to Binkert *et al* 1972) corrected by computer processing, is presented in figure 7(c). The full curve in figure 7(c) is traced according to (5), varying c_1 , c_2 and α by the least-squares method.

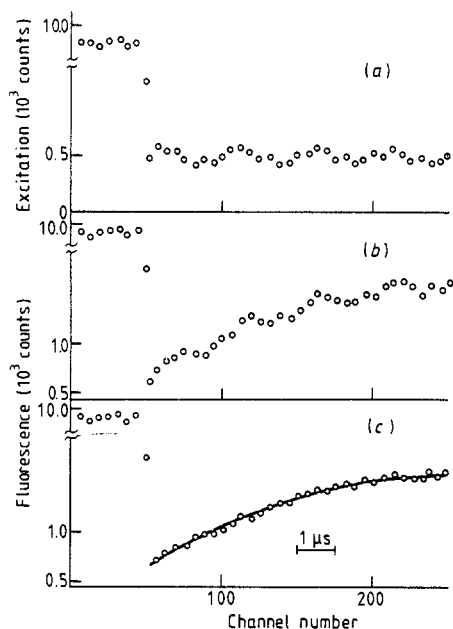


Figure 7. Signals registered by analyser (end of the rectangular impulse and base); (a) excitation signal; (b) corresponding LIF signal; (c) the same LIF signal after excitation and 'pile-up' correction.

The dependence of α on pressure of admixed Xe is presented in figure 8. The error in α (here and elsewhere one standard deviation is given) accounts only for the statistical noise of the signal. Similar dependences have also been obtained for the other noble gases He, Ne, Ar and Kr. They have all been found to be linear, which made it possible to determine rate constants k and averaged cross sections $Q(K_2 + A)$ of the collisional processes; these are presented in table 1. Errors given in the table account for the spread of points $\alpha(N)$ only (figure 8) and do not include the possible systematic experimental errors mentioned in § 2.

We wish to point out the coincidence (within the error limits) in the values of k for the whole series of gases in table 1. Similar rate constants have been obtained by König and Weber (1980) for Na_2 in collisions with He, Ne, Ar, with slightly higher values in collisions with Kr and Xe. Table 1 yields a cross section ratio $Q(K_2 +$

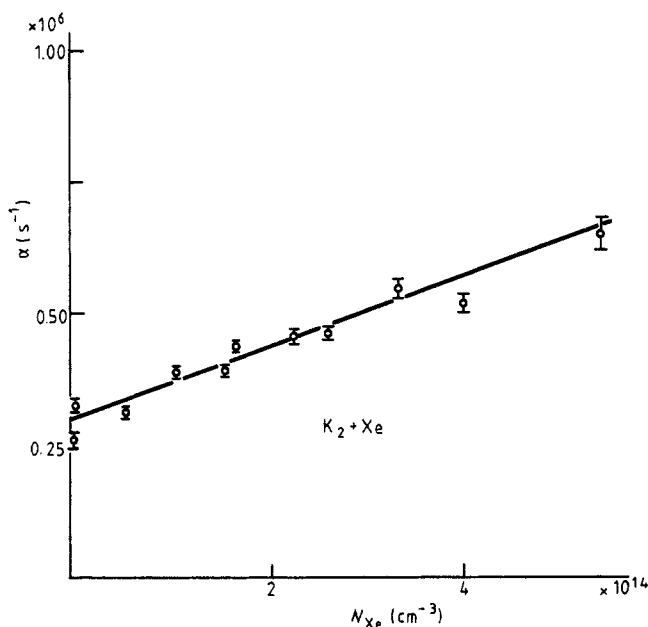


Figure 8. Experimentally obtained dependence of the index α of exponent approximating $I_{\parallel}^{\text{III}}(t)$ on concentration N_{Xe} of admixed Xe.

Table 1

A	k ($10^{-9} \text{ cm}^3 \text{ s}^{-1}$)	$Q(\text{K}_2 + \text{A})$ (10^{-16} cm^2)	Q_c (10^{-16} cm^2)
He	0.83 ± 0.08	52 ± 5	52
Ne	0.79 ± 0.15	106 ± 18	66
Ar	0.90 ± 0.08	154 ± 12	102
Kr	0.75 ± 0.04	159 ± 7	117
Xe	0.68 ± 0.08	155 ± 12	136

$\text{He})/Q(\text{K}_2 + \text{Xe}) = 0.33 \pm 0.06$. This agrees with the values obtained by Grushevsky *et al* (1977). Table 1 also contains rough theoretical estimates of the capture cross sections $Q_c = \pi b_c^2$, where b_c is the impact parameter of capture calculated according to Grushevsky *et al* (1977) under assumption of a Van der Waals interaction potential.

The experimentally recorded signal shape for the conditions when the main process is relaxation in the course of flying through the beam is presented in figure 9. The full curve is calculated according to the method expounded in § 3. The space distribution of the pump beam $\rho(x, z)$ and of the probe beam $\rho_{\text{pr}}(x, z)$ were determined experimentally by scanning over both coordinates of the diaphragm of 0.1 mm diameter. The distribution did not differ drastically from a Gaussian shape. Only one parameter—the Einstein coefficient B —was varied in the fitting process. Figure 9 shows that the time development of the transient process is not an exponential one.

All results presented above were obtained by registering $I_{\parallel}^{\text{III}}$ of LIF. Measurements of I_{\perp}^{III} performed in the presence of Kr, $N = 2.7 \times 10^{14} \text{ cm}^{-3}$, yielded a value $\alpha_{\perp} = (0.39 \pm 0.01) \times 10^6 \text{ s}^{-1}$. Under the same conditions a value of α_{\parallel} was equal to $(0.37 \pm$

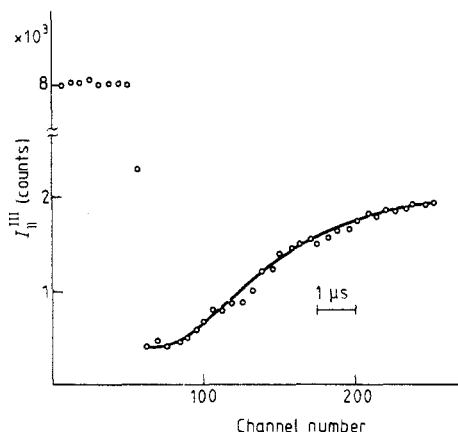


Figure 9. Experimentally recorded (dots) and theoretically calculated (full curve) kinetics of the transient process in case of prevalent fly-through relaxation.

$0.04) \times 10^6 \text{ s}^{-1}$. It follows, however, from an analysis in terms of polarisation moments, as performed in the appendix, that such data cannot be used as confirmation of the assumption (cf König and Weber 1980) of the absence of pure reorientation (changing only the projection M'') collisions.

Unlike the ground state, an excited electronic state lends itself to precise measurement of the ratios between the rates Γ_2/Γ_0 and the cross sections Q_2/Q_0 of relaxation of alignment and population, cf (A.12), (A.13) in the appendix. We considered it useful to perform such measurements in view of a possible analogy in the collision

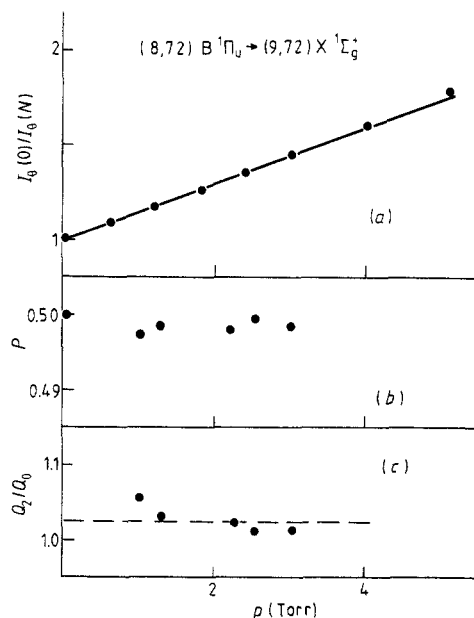


Figure 10. Experiment with excited K_2 molecules in $(8,72) \text{ B } ^1\Pi_u$ state, $T = 624 \text{ K}$; (a) quenching of LIF; (b) depolarisation of LIF; (c) ratio between cross sections for alignment relaxation Q_2 and those for population Q_0 .

processes in both states. The experimental results are presented in figure 10, yielding $Q_2/Q_0 = 1.03 \pm 0.01$. Hence, in the (8,7₂)B ¹Π_u state of K₂ the probability of purely reorienting collisions is negligible in comparison with inelastic (quenching) ones. The cross section $Q_0(K_2 + Ar) = (68 \pm 1) \times 10^{-16} \text{ cm}^2$ was found from the slope of the straight line in figure 10(a), assuming the radiation lifetime to be equal to 11.6 ns (Ferber *et al* 1979).

5. Conclusions

The paper contains an investigation of relaxation of the (*v''*, *J''*) level of the electronic ground state from a transient process being recorded by laser-induced fluorescence (LIF). Relaxation is caused both by collisions, as well as by spatial exchange of molecules inside and outside the laser beam due to their free thermal motion. This case requires the solution of kinetic equations including the dependence of absorption on coordinates. It is shown that the form of the signal may differ strongly from an exponential one. However, if depopulation is not excessively strong, the transient process is satisfactorily approximated by a mono-exponential dependence. The exponent index can depend on the absorption rate, but its change with concentration permits the determination of the rate constant of collisional relaxation.

The method does not permit the determination of the partial contributions of separate collisional processes. Nevertheless, absolute values of the total effective cross sections, as measured by the transient process method, can serve as useful additions to state-to-state differential relative cross sections obtained in beam experiments by Bergmann *et al* (1980) and Serri *et al* (1980).

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Appendix

Application of irreducible tensor operators makes it possible to obtain an expression for the intensity of *b* → *c* fluorescence through the polarisation moments f_Q^K of state *b* (cf Dyakonov 1964)

$$I(e') = (-1)^{J'_b + J''_c} (2J'_b + 1)^{1/2} \sum_K (2K + 1) \begin{Bmatrix} 1 & 1 & K \\ J'_b & J'_b & J''_c \end{Bmatrix} \sum_Q (-1)^Q \Phi_{-Q}^K(e') f_Q^K. \tag{A.1}$$

Here $\Phi_Q^K(e')$ is the tensor, introduced by Dyakonov (1964) for the given type of observed polarisation *e'*. Let us consider (cf also Ferber *et al* 1982) the kinetic equations for f_Q^K and ϕ_a^κ of ground state *a*

$$\frac{df_Q^K}{dt} = B\rho \sum_{X\kappa} \kappa \mathcal{F}^{X\kappa} \{ \Phi^{(X)} \otimes \phi^{(\kappa)} \}_Q^K - \Gamma_K f_Q^K \tag{A.2a}$$

$$\frac{d\phi_a^\kappa}{dt} = -B\rho \sum_{X\kappa'} {}^\kappa A^{X\kappa'} \{\Phi^{(X)} \otimes \phi^{(\kappa)}\}_a^\kappa - \gamma_\kappa \phi_a^\kappa + \lambda_a^\kappa \delta_{\kappa 0} \delta_{q 0}. \quad (\text{A.2b})$$

Here

$$\{\Phi^{(X)} \otimes \phi^{(\kappa)}\}_Q^K = \sum_{\xi q'} C_{X\xi\kappa q'}^{KQ} \Phi_\xi^X(\mathbf{e}) \phi_{q'}^\kappa$$

is a tensor product, \mathbf{e} is the polarisation vector of the exciting light, $C_{X\xi\kappa q'}^{KQ}$ the Clebsch–Gordan coefficients. The term $\lambda_a^\kappa \delta_{\kappa 0} \delta_{q 0}$ describes restoration of population ϕ_0^0 ; γ_κ and Γ_L are the rates of destruction of ϕ_a^κ and f_Q^K . In the asymptotic limit $J', J'' \rightarrow \infty$ the coefficients ${}^\kappa A^{X\kappa'}$ and ${}^K \mathcal{F}^{X\kappa}$ turn out to coincide for coinciding indices and can be found from

$${}^\kappa A^{X\kappa'} = (-1)^\Delta \left(\frac{(2X+1)(2\kappa'+1)}{2\kappa+1} \right)^{1/2} C_{1\Delta 1-\Delta}^{X0} C_{\kappa 0 X 0}^{\kappa'0} \quad (\text{A.3})$$

where $\Delta = J'_b - J''_a$. Since $\Gamma_\kappa \gg \gamma_\Sigma$, $df_Q^K/dt = 0$ and for moments differing from zero we have from (A.2a) in the case of Q -transitions $J''_a = J''_b = J''_c$

$$f_0^0(t) = \frac{1}{3} B\rho \Gamma_0^{-1} (\phi_0^0(t) + 2\phi_0^2(t)) \quad (\text{A.4})$$

$$f_0^2(t) = B\rho \Gamma_2^{-1} \left(\frac{2}{15} \phi_0^0(t) + \frac{11}{21} \phi_0^2(t) + \frac{12}{35} \phi_0^4(t) \right). \quad (\text{A.5})$$

Zero-range moments characterise population, those of range two alignment, those of range four the presence of a hexadecapole moment. Moments ${}^{\text{III}}\phi_0^\kappa(t)$ for transient process (III) (figure 2) are relaxing for $\kappa = 0$, as

$${}^{\text{III}}\phi_0^0(t) = -({}^{\text{IV}}\phi_0^0 - {}^{\text{II}}\phi_0^0) \exp[-\gamma_0(t-t_0)] + {}^{\text{IV}}\phi_0^0 \quad (\text{A.6})$$

and for $\kappa = 2$ or 4 as

$${}^{\text{III}}\phi_0^\kappa(t) = {}^{\text{II}}\phi_0^\kappa \exp[-\gamma_\kappa(t-t_0)]. \quad (\text{A.7})$$

Moments ${}^{\text{II}}\phi_0^\kappa$ were obtained from (A.2b) by expansion in a series including terms up to $(B\rho/\gamma_\kappa)^3$. Let us consider the case of equal rates of relaxation of ϕ_0^κ , moments $\gamma_\kappa = 1.1B\rho$ for $\kappa = 0, 2, 4$, assuming $\Gamma_0 = \Gamma_2$. Calculated intensities are equal (rounding off to 0.001)

$$I_{\parallel}^{\text{III}}(t) \approx 1 - 0.245 \exp(-\gamma_0 t) - 0.281 \exp(-\gamma_2 t) + 0.005 \exp(-\gamma_4 t) \quad (\text{A.8})$$

$$I_{\perp}^{\text{III}}(t) \approx 0.333 - 0.082 \exp(-\gamma_0 t) - 0.023 \exp(-\gamma_2 t) - 0.002 \exp(-\gamma_4 t) \quad (\text{A.9})$$

and for the case when $\gamma_0 = 1.1B\rho$, and $\gamma_2 = \gamma_4 = 2\gamma_0$

$$I_{\parallel}^{\text{III}}(t) \approx 1 - 0.233 \exp(-\gamma_0 t) - 0.126 \exp(-\gamma_2 t) + 0.001 \exp(-\gamma_4 t) \quad (\text{A.10})$$

$$I_{\perp}^{\text{III}}(t) \approx 0.333 - 0.077 \exp(-\gamma_0 t) - 0.010 \exp(-\gamma_2 t) - 0.001 \exp(-\gamma_4 t). \quad (\text{A.11})$$

It can be seen that in (A.8) the contributions of ${}^{\text{III}}\phi_0^0$ and ${}^{\text{III}}\phi_0^2$ to the signal are almost equal, but with an increase in γ_2/γ_0 the contribution of ${}^{\text{III}}\phi_0^2$ rapidly diminishes. It is also possible to show that, using the mono-exponential approximation separately for $I_{\parallel}^{\text{III}}(t)$ from (A.10) and $I_{\perp}^{\text{III}}(t)$ from (A.11), the difference in index value of the exponent does not exceed 15%. That indicates the low sensitivity of such measurements on the role of pure reorienting collisions. In the limit $B\rho/\gamma_\kappa \rightarrow 0$ only ϕ_0^0 differs

from zero in (A.4) and (A.5), and the expression for the degree of plane polarisation of fluorescence, using (A.1), will simply be

$$P = \frac{3}{5\Gamma_2/\Gamma_0 + 1}. \quad (\text{A.12})$$

Assuming $\Gamma_K = \Gamma + Q_K \bar{v}_r N$ we have for the excited state the cross section ratio

$$\frac{Q_2}{Q_0} = \frac{(\frac{3}{5}P^{-1} - \frac{1}{5})I_\theta(0)/I_\theta(N) - 1}{I_\theta(0)/I_\theta(N) - 1} \quad (\text{A.13})$$

where $I_\theta(N)$ is the intensity in the presence of a noble gas of concentration N , and $I_\theta(0)$ its value at $N = 0$, the analyser in registration being directed at such an angle with respect to Oz that $\cos \theta = 1/\sqrt{3}$. In this case $\phi_0^2(e) = 0$ in (A.1).

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