

THE EFFECT OF COLLISIONS ON THE INTENSITY AND POLARIZATION OF LASER-INDUCED $D^1\Pi \rightarrow X^1\Sigma^+$ FLUORESCENCE FROM NaK

M.P. AUZIN'SH, R.S. FERBER, Ya.A. HARYA and I.Ya. PIRAGS

P. Stuchka Latvian State University, Riga 226098, USSR

Received 8 August 1985; in final form 30 December 1985

Laser-induced fluorescence was applied for determining total deactivation cross sections of the level (17,94) $D^1\Pi$ of NaK molecules in collisions with He, Ne, Ar, Kr, Xe, as well as with K atoms. Relaxation cross sections of population and alignment were found to coincide within experimental error. The kinetics of the transient process was used for determining the cross section of thermalization of the optically depopulated level of the electronic ground state (5,67) $X^1\Sigma^+$ in NaK + Ar collisions.

1. Introduction

The NaK molecule has recently been the object of intense investigation by means of laser-induced fluorescence (LIF) [1-9]. This work was aimed at elucidation of the term structure and at studying relaxation processes in the deactivation of optical excitation energy where interesting peculiarities have been found. Energy transfer has been observed and studied from the $D^1\Pi$ term to the triplet $d^3\Pi$ term, with subsequent radiation into the $a^3\Sigma$ state [1,2,5]. Excitation mechanisms of Na and K resonance levels through molecular states were also investigated. Rather unexpected results have been reported by McCormack et al. [6] showing anomalous behaviour of the intensity and degree of circular polarization in the $D^1\Pi \rightarrow X^1\Sigma^+$ and $C^1\Pi \rightarrow X^1\Sigma^+$ fluorescence of NaK on addition of He. Within the pressure range up to 3 Torr of He, LIF intensity does not diminish, but increases, with a simultaneous increase in the circular polarization of the P, R transitions. In addition, noticeable circularity of several percent has been found in this work for $Q\uparrow$, $Q\downarrow$ transitions at low He pressures, which seems rather surprising for states of high rotational quantum number J' (a value of $J' = 93$ is mentioned, for instance). This implies an effective transition from alignment to orientation.

The present work presents an experimental study of collision effects with rare gases and with K atoms

on the intensity and linear polarization of $D^1\Pi \rightarrow X^1\Sigma^+$ NaK fluorescence with plane-polarized excitation. Lifetime values obtained for a number of levels (v', J') $D^1\Pi$ have made it possible to determine quenching collision cross sections [3]. By means of transient process kinetics of the repopulation of the optically depopulated ground-state level (5,67) $X^1\Sigma^+$ [10,11], the thermalization cross section in collisions with Ar atoms has been determined.

2. Experimental

A 1:4 mixture of sodium and potassium in an alkali-vapour-resistant glass cell was connected to a vacuum system through a dry stopper, thus making introduction of heated rare gases through a narrow aperture possible. The metal-containing ampul was kept at stabilized temperatures between 461 and 645 K. The optical part of the cell was cylindrically shaped, with 15 mm diameter and 30 mm height and positioned parallel to the entrance slit of the monochromator. Its temperature was slightly higher than that of the metal-containing ampul. LIF was excited by the 476.5 and 514.5 nm lines of an Ar laser operating in the multi-mode TEM_{00q} regime. The laser beam was introduced from the top end of the cell through an optical window perpendicular to the angle of observation of the fluorescence. The laser beam was plane-polarized at right

angles to the direction of observation. The lines of the LIF progression were separated by means of a grating double monochromator with a reciprocal dispersion of 0.5 nm mm^{-1} . The photomultiplier signal was operated in the photon-counting mode. LIF intensities I_{\parallel} and I_{\perp} were measured through two channels corresponding to alternate positions of the analyzer parallel to or at right angles to the electric vector E of the exciting beam. The channels were calibrated for equal intensity at E set parallel to the direction of observation of LIF.

This arrangement permits only creation of population and alignment in the excited state, which corresponds to polarization moments f_0^K in the range $K=0$ and $K=2$, respectively [12,13]. Assuming $J' > \infty$ we have, for $Q\uparrow$, $Q\downarrow$ transitions

$$I_{\parallel} = \frac{1}{3}A(f_0^0 + 2f_0^2), \quad (1)$$

$$I_{\perp} = \frac{1}{3}A(f_0^0 - f_0^2), \quad (2)$$

where A is a proportionality factor. It can be seen that definite linear combinations of I_{\parallel} and I_{\perp} contain either population f_0^0 or alignment f_0^2 only

$$I_0 = I_{\parallel} + 2I_{\perp} = Af_0^0 = \frac{1}{3}A\Gamma_p\Gamma_0^{-1}\varphi_0^0, \quad (3)$$

$$I_2 = I_{\parallel} - I_{\perp} = Af_0^2 = \frac{2}{15}A\Gamma_p\Gamma_2^{-1}\varphi_0^0, \quad (4)$$

where Γ_p is the pumping rate, Γ_0 and Γ_2 are the relaxation rates of population and alignment, and φ_0^0 is the ground-state population. Using eqs. (3) and (4) and knowing the rate of spontaneous decay, it is possible to go from the concentration dependences of I_{\parallel} and I_{\perp} to the rates Γ_0 and Γ_2 and to the effective relaxation cross sections Q_0 and Q_2 of the corresponding moments. The most accurate value of the ratio Q_2/Q_0 can be obtained by measuring the LIF linear polarization. For this purpose it is convenient to use the polarization rate, defined in a special way, and the so-called "alignment rate" P_{al} [13],

$$P_{al} = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp}) = I_2/I_0 = \frac{2}{5}\Gamma_0/\Gamma_2. \quad (5)$$

The limiting value of P_{al} is 0.4 in $Q\uparrow$, $Q\downarrow$ transitions, as distinct from the value of 0.5, as would be obtained for the degree of plane polarization P in the usually defined way, namely, $P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$.

3. Results and discussion

3.1. $D^1\Pi$ state

Considering that the characteristic lifetime of the $D^1\Pi$ state is 16–20 ns [3] at the experimental temperatures ($T \geq 540 \text{ K}$ in our case), an important part of the deactivation processes of optical excitation energy may be due to collisions with alkali atoms in the vapour, chiefly K atoms. Incidentally, K atoms were held responsible by McCormack et al. [6] for the anomalous behaviour of circularity. It is of interest to measure the temperature dependence of the alignment rate in LIF, which implies a potassium atom concentration dependence. Measurements were carried out for several (v', J') $D^1\Pi$ (NaK) levels at 476.5 and 514.5 nm line excitation[‡]. No change in P_{al} value was observed in any of these cases, within the experimental error range. The (17,94) $D^1\Pi$ level at 476.5 nm laser line excitation was studied most thoroughly. According to Pfaff et al. [3], this level is not perturbed and has a lifetime of $16.1 \pm 0.3 \text{ ns}$. After a detailed analysis of the experimental spectrum and its comparison with numerically reconstructed progressions excited by the 476.5 nm line in both NaK and Na_2 molecules, the line (17,94) $D^1\Pi \rightarrow (38,94) X^1\Sigma^+$ was finally chosen as the most "spectrally pure" while possessing high transition strength. Identification was confirmed by coincidence of relative intensities of transitions (17,94) $D^1\Pi \rightarrow (v'',94) X^1\Sigma^+$ with those given in ref. [3]. P_{al} values, measured at various temperatures, are presented in fig. 1. The potassium atom concentrations N_K used in the plot have been calculated for the case of the binary mixture Na : K = 1 : 4, assuming validity of Raoult's law, and are, accordingly,

[‡] Data kindly put at our disposal by Professor W. Demtröder were used for identification of transitions.

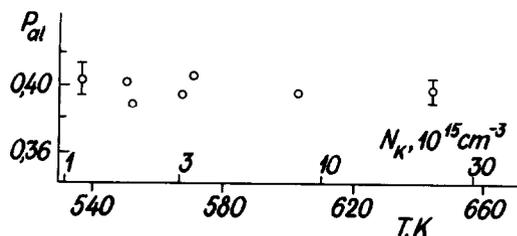


Fig. 1. Temperature dependence of the alignment rate P_{al} .

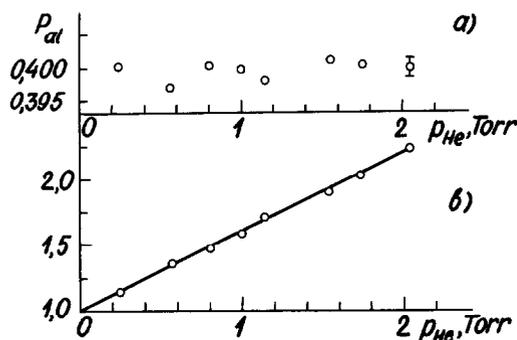


Fig. 2. He pressure dependence of (a) the alignment rate P_{al} ; (b) the intensity ratio $I_0(0)/I_0(p)$. Temperature $T = 584$ K.

no more than estimates. Thermodynamic constants have been taken from ref. [14]. The absence of concentrational depolarization of LIF suggests that the discrepancy between Γ_2 and Γ_0 does not exceed 5%. It ought to be mentioned that the continuous radiation background, changing with concentration [5], has been accounted for in the measurements. For this purpose, $I_{||}$ and I_{\perp} values were measured on both sides of the line and were taken into account in the calculations. In order to eliminate non-linear effects of optical alignment of the $(0,94) X^1\Sigma^+$ level (see further), the laser beam was attenuated.

No depolarization of LIF was observed on addition of rare gases He, Ne, Ar, Kr, Xe within the pressure range up to 2 Torr. Data obtained for $\text{NaK}^* + \text{He}$ mixture are presented in fig. 2a.

For the determination of quenching cross sections of the (v', J') $D^1\Pi$ state, Stern–Volmer plots were obtained for dependences of the ratio $I_0(0)/I_0(p)$ on the pressure of the rare gas admixture. Within the pressure range up to $p = 2$ Torr these dependences were linear with satisfactory accuracy (see fig. 2b). However, passing over from the slope coefficient to the cross section for the destruction of population Q_0 , it is necessary to take into account the effect of $\text{NaK}^* + \text{K}$ collisions, which is substantial under the given experimental conditions. For this purpose Stern–Volmer plots were obtained for various temperatures between 540 and 645 K. For further treatment it is convenient to present the results obtained in form of the following dependences:

$$\frac{1}{b} = \frac{a\Gamma_{sp}}{\bar{v}(R)Q_0(R)} + \frac{aQ_0(K)\bar{v}(K)N_K}{Q_0(R)\bar{v}(R)}, \quad (6)$$

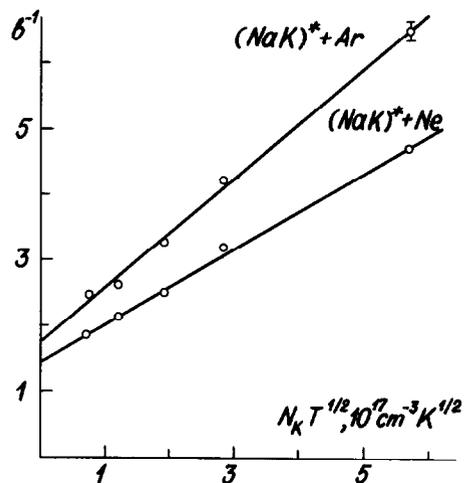


Fig. 3. Coefficient b^{-1} , where b is the slope of the Stern–Volmer plot, as a function of $N_K T^{1/2}$, where N_K is the potassium atom concentration and T is the temperature of the cell.

where b is the slope coefficient of the Stern–Volmer plot in coordinates as in fig. 2b, Γ_{sp} is the rate of spontaneous decay, $Q_0(R)$ and $Q_0(K)$ are relaxation cross sections of state population in collisions with atoms of the rare gas and potassium, respectively, $\bar{v}(X) = (8kT/\pi\mu_{\text{NaK-X}})^{1/2}$ is the average relative velocity, $X = R$ or K , and $a = k(TT_0)^{1/2}/133.3$, where T_0 is the temperature of the reservoir with rare gas. It may be easily seen from eq. (6) that it is convenient to use the b^{-1} versus $N_K T^{1/2}$ plot, as in fig. 3 for the case of collisions with Ne and Ar atoms. Then the slope coefficient of the plot yields the ratio $Q_0(K)/Q_0(R)$, and from the ordinate value at $N_K T^{1/2} = 0$ the magnitude $Q_0(R)$ may be obtained. This makes separate determination of $Q_0(R)$ and $Q_0(K)$ possible. Table 1 presents relaxation cross sections of the $(17,94) D^1\Pi$ (NaK) level obtained by means of the above method. The errors correspond to one standard deviation. Dependences of the type presented in fig. 3 for all rare gases have been used for obtaining cross section values $Q_0(K)$ for collisions between $(17,94) D^1\Pi$ (NaK) and potassium atoms. The value of $Q_0(K)$, as obtained using eq. (6) and averaged over all five gases, equals $900 \pm 50 \text{ \AA}^2$.

3.2. Thermalization in the $X^1\Sigma^+$ state

In the case of sufficiently effective absorption,

Table 1
Effective cross sections $Q_0(R)$ of the destruction of the $(17,94) D^1\Pi$ (NaK) state population in collisions with rare gas atoms R

	R = He	R = Ne	R = Ar	R = Kr	R = Xe
$Q_0(R)$ (\AA^2)	138 ± 4	213 ± 5	219 ± 6	257 ± 6	312 ± 8

when its rate Γ_p is comparable with the total relaxation rate γ of the initial level $(v'', J'') X^1\Sigma^+$ to the thermal equilibrium, the latter is depopulated. Such an effect is known as "optical pumping" by depopulation [15] and it enables the determination of the value of γ . In the present work, a method of direct measurement of γ has been applied, based on the growth kinetics of LIF after rapid attenuation of the pumping beam down to the probe value (see fig. 4a). A detailed description of the method is given in refs. [10,11]. The main experimental parameters were as follows: the duration of the depopulating beam was $30 \mu\text{s}$, the repetition frequency was 9 kHz, detection through one-photon statistical analysis in the photon count regime [16], time-amplitude transformation and storage by means of a 256-channel analyser. The 514.5 nm laser-line-induced transition $(5,67) X^1\Sigma^+ \rightarrow (1,67) D^1\Pi$ was applied for excitation. Detection was performed at the Q_{13} line of the LIF fluorescence spectrum. A typical example of the signal obtained is presented in fig. 4a. After pile-up correction [16], elimination of the background, and allowance for excitation pulse shape, the following approximated expression was obtained for the time dependence of the

LIF at $t > t_0$, t_0 being the moment of attenuation of the excitation:

$$I(t - t_0) = I(\infty) - [I(\infty) - I(0)] \exp[-\gamma(t - t_0)]. \quad (7)$$

The viability of such an approximation is discussed in ref. [11]. Values of γ obtained through minimization as a function of the pressure of the admixed rare gas Ar, are presented in fig. 4b. This yields the effective relaxation cross section of the optically depopulated level $(5,67) X^1\Sigma^+$, $\sigma(\text{Ar}) = 100 \pm 30 \text{\AA}^2$. We wish to note that at a temperature of 461 K, collisions with K atoms cause difficulties due to lowering of the signal amplitude and by causing additional systematic errors, such as those due to temperature drift.

3.3. Discussion

It follows from figs. 1 and 2 and the corresponding text that collisions with K or rare gas atoms do not lead to any noticeable changes in the degree of linear polarization within the tested pressure range. At the same time collisions with He atoms, for instance, produce quenching of the LIF by a factor of two at 2 Torr. Combining P_{al} data with those obtained from Stern-Volmer plots, one can easily go from eq. (5) to the relaxation cross section ratio of alignment and population:

$$\frac{Q_2}{Q_0} = \frac{0.4 P_{\text{al}}^{-1} I_0(0)/I_0(p) - 1}{I_0(0)/I_0(p) - 1}. \quad (8)$$

Results presented in fig. 2 lead to $Q_2/Q_0 = 0.99 \pm 0.01$. For all other kinds of collisions investigated, Q_2 also coincides with Q_0 within experimental error. Such results are typical for diatomic molecules of alkali metals [11]. The total deactivation cross section values (as presented in table 1) are also typical for alkali molecules [17]. Incidentally, one can find in ref. [17] a plot of the K concentration dependence of Γ_{sp} for $(17,94) D^1\Pi$ of NaK, yielding $Q(\text{K}) \approx 1000 \text{\AA}^2$, which agrees well with our result. There may be, however, a systematic error in the calculation of the K

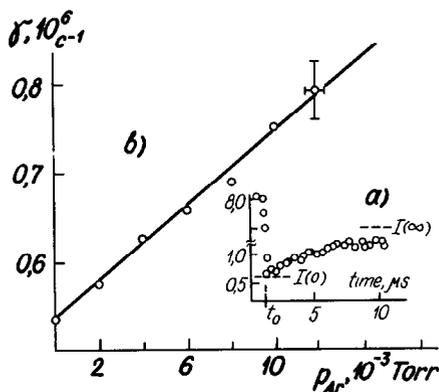


Fig. 4. (a) Back front of the LIF pulse; (b) relaxation rate γ for $(5,67) X^1\Sigma^+$ NaK as a function of Ar pressure at $T = 461 \text{ K}$.

atom concentration. The appearance of more accurate data will easily permit correction of the cross section values.

We see that collisions of $D^1\Pi$ NaK with K atoms and with admixed rare gases do not produce any anomalies. In particular, collisions with He atoms produce linear quenching of the LIF, in contradiction to the results presented by McCormack et al. [6] showing a rise in the LIF intensity with increases in He pressure up to 3 Torr. Nothing definite can be said at this stage about the cause of this discrepancy. It may be worthwhile to give careful consideration to the degree of circularity, which, according to McCormack et al. [6], is supposed to have a value of ≈ 0.09 in $Q\uparrow$, $Q\downarrow$ transitions in D-X and C-X progressions of NaK.

If a Q transition is excited by circularly polarized light, the circularity is negligibly small at high J' values, being on the order of $1/J'^2$. In terms of polarization moments f_Q^K this means that at $J \rightarrow \infty$ the polarization moment $f_0^1 \rightarrow 0$, and at the same time moments f_0^2 and f_0^0 differ from zero [12,13]. It therefore remains to assume that f_0^1 is produced in certain relaxation processes from moments f_0^2 and f_0^0 , in which case one has to admit mixing of polarization moments of differing ranges K . For a spherically symmetric relaxation process, each one of the polarization moments relaxes separately, without mixing [12,13]. Among anisotropic processes, let us first consider the case of axially symmetric relaxation. Under conditions described in ref. [6], such a case might be due to, for instance, longitudinal gas flow along the beam in a cell of the "heat-pipe" type or to single-mode laser excitation. However, for mixing of f_0^0 , f_0^2 , and f_0^1 the symmetry with respect to reflection in the plane containing the quantization axis Z must be disturbed [13]. Such a kind of symmetry is present only in the case of an axial vector, but such gas flow is characterized by a polar vector. Let us now consider a case where there is no axial symmetry, i.e. there exists some kind of a transverse perturbing process, for instance, a transverse flow. This makes a transition from f_0^2 to $f_{\pm 1}^2$ possible, which in turn is capable of creating a moment $f_{\pm 1}^1$ [18,19]. Yet even this cannot produce the degree of circularity in the experimental scheme of ref. [6], since no longitudinal orientation is produced. In conclusion, it is therefore difficult to make the effect compatible with the experimental conditions described in ref. [6], and the explanation given there does not seem satisfactory. It may be noted that the

process of transition from alignment to orientation has been studied theoretically [13,18-21] as well as experimentally for atomic systems, in particular for Ne atoms [22,23]. In all cases there existed relaxation processes (magnetic fields, anisotropic collisions) which perturbed the spherical symmetry in the problem, in agreement with the abovementioned requirements.

References

- [1] E.J. Bredford and F. Engelke, *Chem. Phys. Letters* 53 (1978) 282.
- [2] D. Eisel, D. Zevgolis and W. Demtröder, *J. Chem. Phys.* 71 (1979) 2005.
- [3] J. Pfaff, M. Stock and D. Zevgolis, *Chem. Phys. Letters* 65 (1979) 310.
- [4] J. McCormack and A.J. McCaffery, *Chem. Phys. Letters* 64 (1979) 98.
- [5] H. Kato and C. Noda, *J. Chem. Phys.* 73 (1980) 4940.
- [6] J. McCormack, A.J. McCaffery and M.D. Rowe, *Chem. Phys.* 48 (1980) 121.
- [7] J. McCormack and A.J. McCaffery, *Chem. Phys.* 51 (1980) 405.
- [8] C. Noda and H. Kato, *Chem. Phys. Letters* 86 (1982) 415.
- [9] M.S. Mehde, F.J.M. Al-Ijarah and A.J. McCaffery, *Chem. Phys. Letters* 96 (1983) 595.
- [10] M.P. Auzin'sh, I.Ya. Pirags, R.S. Ferber and O.A. Shmit, *Pis'ma Zh. Eksp. Teor. Fiz.* 31 (1980) 589 [English transl. *Soviet Phys. JETP Letters* 31 (1980) 554].
- [11] M.P. Auzin'sh, R.S. Ferber and I.Ya. Pirags, *J. Phys. B* 16 (1983) 2759.
- [12] M.I. Dyakonov, *Zh. Eksp. Teor. Fiz.* 47 (1964) 2213 [English transl. *Soviet Phys. JETP* 20 (1965) 1484].
- [13] A. Omont, *Progr. Quantum Electron.* 5 (1977) 69.
- [14] *Termodinamicheskiye svoistva individualnih veshchestv*, Vol. 2, Part 1 (Nauka, Moscow, 1982).
- [15] R.F. Drullinger and R.N. Zaro, *J. Chem. Phys.* 51 (1969) 5532.
- [16] Th. Binkert, H.P. Tchanz and P.E. Zinsli, *J. Luminescence* 5 (1972) 187.
- [17] W. Demtröder, *Laser spectroscopy* (Springer, Berlin, 1981).
- [18] V.N. Rebane, *Opt. i Spektroskopiya* 24 (1968) 309.
- [19] T. Manabe, T. Yabuzaki and T. Ogawa, *Phys. Rev. A* 20 (1979) 1946.
- [20] A.G. Petrashen', V.N. Rebane and T.K. Rebane, *Opt. i Spektroskopiya* 53 (1982) 985.
- [21] E.N. Kotlikov and M.P. Chaika, *Opt. i Spektroskopiya* 55 (1983) 242.
- [22] T. Manabe, T. Yabuzaki and T. Ogawa, *Phys. Rev. Letters* 46 (1981) 637.
- [23] N.G. Lukomsky, V.A. Polishchuk and M.P. Chaika, *Opt. i Spektroskopiya* 58 (1985) 474.