

COLLISIONAL DEACTIVATION OF $K(7s^2S)$ AND $K(5d^2D)$ BY NO

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Radiative lifetimes and total deactivation cross sections of $K(7^2S)$ and $K(5^2D)$ by collision with NO are studied. The K atomic vapor in either the 7^2S or the 5^2D state was prepared by two-photon absorption using a dye laser. The decay signal of the time-resolved fluorescence from the $7^2S - 4^2P_{1/2}$ or $5^2D - 4^2P_{3/2}$ transition was then monitored. Based on a Stern-Volmer analysis, the radiative lifetimes are 155 ± 8 ns and 561 ± 18 ns for the $K(7^2S)$ and $K(5^2D)$ states, respectively. The total deactivation cross sections are $88 \pm 1 \text{ \AA}^2$ and $70 \pm 2 \text{ \AA}^2$ for the $K(7^2S)$ -NO and $K(5^2D)$ -NO collisions, respectively. In the absence of NO collisions the radiative lifetimes obtained in this work show excellent agreement with those previously reported. The quenching cross sections for NO have been measured for the first time, and have values in a reasonable range, when compared with Na-N₂ collisions.

INTRODUCTION

Compared with the ground state, the alkali atom in its excited states appears more reactive, for it has an unpaired outer-shell electron loosely bound and a small energy defect from the ionization continuum. For example, the reaction cross section for $K(4^2S)$ with I₂ is 127 \AA^2 ,¹ in contrast to a much larger value of 210 \AA^2 given by $K(4^2P)$.² The quenching cross sections of Na by small molecules such as N₂ and CO are found to increase with an increase in the principal quantum number.^{3,4} Thus the excited alkali is also named "superalkali" due to its reactivity.

Thus far, most research into deactivation of the excited alkali atom has been confined to the lowest few states. The collision partners commonly employed are molecules such as the rare gases, H₂, N₂, CO, CO₂, O₂, I₂ and some other organic compounds.⁵ However, little information on the interaction of the excited alkali atom with NO gas has been reported, except for the case of $Na(3^2P)$ -NO, which was proved to proceed through a channel of electronic-to-vibrational energy transfer via a long-lived complex.^{6,7} Other metals which in their lower excited states, have been found to undergo depopulation processes by collisions with

NO, are Hg, Zn and Cd.⁸⁻¹⁰

Although the study of deactivation of the low-lying states of metal atoms has drawn the most attention, in fact, the high-lying states have quite different properties such as effective size, polarizability and reactivity.¹¹ The atoms in the high-lying states having an outer loosely bound electron behave in a reaction more like an ion. Therefore, a understanding of the reactivity of these states toward a collision partner should be conducive to providing insight into the correlation with the ion-molecule reaction. The Na atoms in various high-lying states quenched by the rare gases, N₂, CO and CH₄ have been investigated, with the cross sections appearing larger as the energy of the state becomes greater.^{3,4,12,13}

In this work we look into the processes of deactivation by NO of K in the 7^2S and 5^2D states. The objective is to determine the radiative lifetimes and the deactivation cross sections of these two states. They are metastable with respect to emission to the ground state, and can be prepared by means of two-photon excitation. The energy difference between them is only 88 cm^{-1} , possibly leading to a thermal equilibrium under the condition of high gas pressure, and thereby interfering with the measurement of the depopula-

*Dedicated to Professor Wei-Chuan Lin on the occasion of his retirement from National Taiwan University.

tion rate for an individual state. In our previous work, H_2 was used instead of NO and this led to the formation of KH , via a state-specific reaction with $K(7^2S)$. No product was observed from collisions with $K(5^2D)$.¹⁴ The collisions of excited K with H_2 , which is regarded as an inefficient quencher because its lowest unfilled orbital belongs to σ^* symmetry, show quenching cross sections of 50 \AA^2 for $K(5^2D)$ and 150 \AA^2 for $K(7^2S)$.¹⁴ In the later the surprisingly large value may be due to a chemical reaction channel and resonance enhancement. Compared with this nonpolar quencher, NO , which has a permanent dipole moment, may be expected to give a larger cross section.

In section II we describe the experimental apparatus. In section III of this work we deal with the data analysis as a basis for the depopulation measurement. Section IV contains our results and a discussion.

EXPERIMENTAL

The experimental set-up contains a dye laser beam to prepare the K atomic vapor in the 7^2S or 5^2D state. The decay signal of time-resolved fluorescence from the 7^2S -

$4^2P_{1/2}$ or $5^2D - 4^2P_{3/2}$ transition is then monitored. A schematic of the apparatus is depicted in Fig.1

The tunable dye laser employed was pumped by an 8 ns, 10 Hz Nd:YAG laser with DCM dye, emitting at about 660 nm to excite the $K(7^2S)$ or $K(5^2D)$ state by two-photon process. The laser power was monitored constantly by an energy meter and adjusted in the range of 1-3 mJ. A careful test was made by the measurement of power dependence of the atomic fluorescence across either the $7^2S - 4^2P_{1/2}$ or the $5^2D - 4^2P_{3/2}$ transition. A resulting slope of 2 was obtained for the plot of fluorescence intensity against the laser energy to ensure that the $K(7^2S)$ or $K(5^2D)$ state was populated simply following a two-photon process. In addition, no emission from the 8S or any states higher than the 4P state was detected in the absence of NO gas. This indicates that energy pooling by collisions between the excited potassium atoms was negligible.

The reagent K metal was deposited in the bottom reservoir of a six-armed quartz cell. The whole cell housed in a home-made fire-brick oven was heated with a pair of heating plates. The cell temperature was measured by a pair of thermocouples; one was attached to the cell body and the other to the reservoir. The temperature of the cell body was

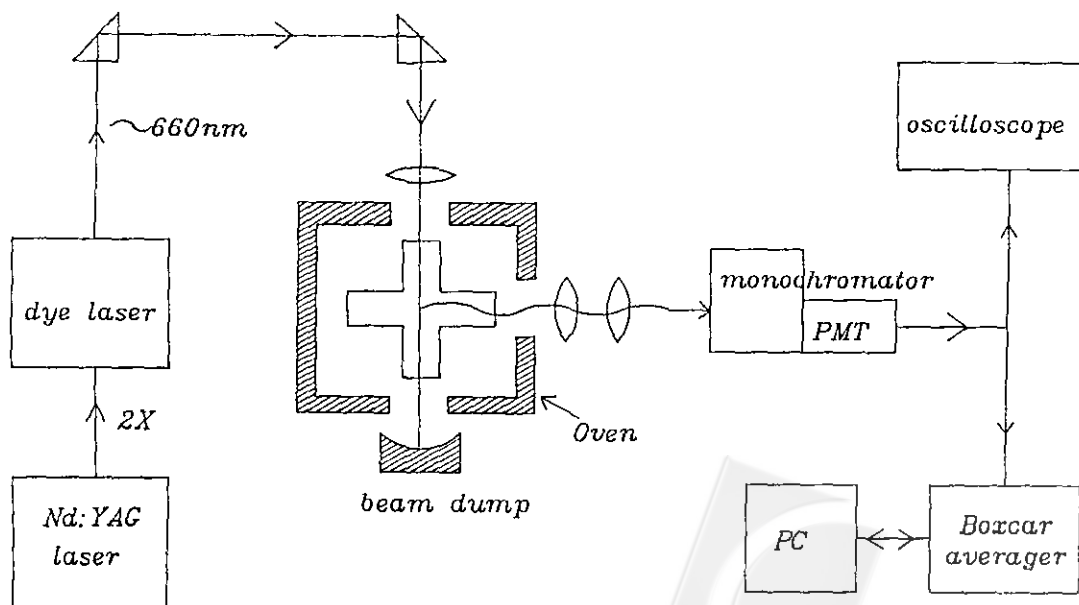


Fig. 1. Schematic diagram of the experimental apparatus.

controlled at 220°C, about 40°C above the temperature of the sample reservoir. This prevented potassium vapor from condensing onto the windows. The top arm of the cell was fed through the oven and connected to a vacuum line. The pressure inside the cell was pumped below 10^{-2} torr before the addition of the quencher. The system was purged several times with the gaseous NO to avoid interference with the quenching rate by the residual air. A MKS Baratron gauge was used to monitor the pressure.

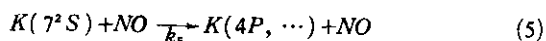
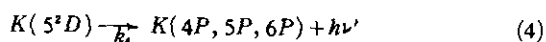
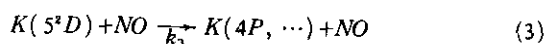
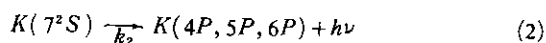
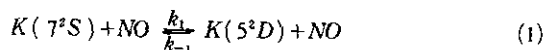
The resulting time-resolved fluorescence was collected with a pair of lens assemblies and focused onto the entrance slit of a monochromator. The slit opening was as narrow as 500 μm to allow for transmittance of the emission from either the $7^2S - 4^2P_{1/2}$ or the $5^2D - 4^2P_{3/2}$ relaxation. A photomultiplier tube, enclosed in a cooler at -20°C and attached to the monochromator, was used to detect the impinging fluorescence. The resulting signal was fed into a boxcar integrator to obtain an improved signal-to-noise ratio. A microcomputer interfaced to the integrator acquired the data for further treatment.

The use of a boxcar integrator to process a time-resolved signal demands particular care. To improve the quality of the signal, the sampling rate of the gate over the entire profile must be made slow. In this manner, averaging the whole fluorescence signal requires a period of time, during which a disturbance may possibly happen due to baseline drift or the instability of either the laser source or other equipment. In our experiment, the quartz cell may slightly react with the K vapor under the high temperature conditions as seen from the fact that it gradually turned brown during the prolonged working period. While the gate was swept slowly to recover the entire profile, we found the decay time of the excited potassium atom appeared 20-40 ns shorter. Thus error might be introduced, as the cell windows failed to resist reaction with the K vapor and the transmittance efficiency gradually decreased during collection of the data. To eliminate this error the following method was adopted. Instead of driving the gate in a slow successive movements, we scanned the gate rapidly by grasping only a few sample points across the entire profile,

but averaged 100 sweeps to enhance the signal-to-noise ratio. Because each spectral run was completed in a brief period, one may assume that the period taken for the signal was under the same conditions. We also repeated the time-resolved experiment using a transient digitizer to process the fluorescence obtained from the excited K vapor in a stainless-steel heat-pipe oven. The results were consistent with the method employed throughout this work.

DATA ANALYSIS

We treat the deactivation of the $K(^7s^2S)$ or $K(^5d^2D)$ atoms by gaseous NO using a model of rate equations. The depopulation processes for the case of $K(^7s^2S)$ may be expressed as follows:



Here, the 5^2D state is 88 cm^{-1} in energy below the 7^2S state, and thus the rate for collisional activation to the 7^2S state cannot be neglected. The coupled rate equations may be written as:

$$\frac{d[K(^7s^2S)]}{dt} = -\{(k_1 + k_5)[NO] + k_2\}[K(^7s^2S)] + k_{-1}[K(^5d^2D)][NO] \quad (6)$$

$$\frac{d[K(^5d^2D)]}{dt} = -\{(k_{-1} + k_3)[NO] + k_4\}[K(^5d^2D)] + k_1[NO][K(^7s^2S)] \quad (7)$$

where the usual notation is used. The solution is

$$[K(^7s^2S)](t) = [K(^7s^2S)]_0 \left\{ \frac{\lambda_2 - G_1}{\lambda_2 - \lambda_1} e^{-\lambda_1 t} + \frac{G_1 - \lambda_1}{\lambda_2 - \lambda_1} e^{-\lambda_2 t} \right\} \quad (8)$$

$$G_1 = (k_1 + k_5)[NO] + k_2 \quad (9)$$

$$G_2 = k_{-1}[NO] \quad (10)$$

$$G_3 = k_1[NO] \quad (11)$$

$$C_{22} = (k_{-1} + k_3)[NO] + k_4 \quad (12)$$

$$\lambda_{1,2} = \frac{1}{2} \left\{ (C_{11} + C_{22}) \pm [(C_{11} + C_{22})^2 - 4(C_{11}C_{22} - C_{12}C_{21})]^{1/2} \right\} \quad (13)$$

Early in the deactivation process, when t is very small, eq.8 simplifies to

$$\begin{aligned} [K(7^2S)](t) & \sim [K(7^2S)]_0 \left\{ \frac{\lambda_2 - C_{11}}{\lambda_2 - \lambda_1} (1 - \lambda_1 t) + \frac{C_{11} - \lambda_1}{\lambda_2 - \lambda_1} (1 - \lambda_2 t) \right\} \\ & = [K(7^2S)]_0 (1 - C_{11} t) \\ & \sim [K(7^2S)]_0 e^{-C_{11} t} \end{aligned} \quad (14)$$

At the beginning, the population in the $K(5^2D)$ state has accumulated so little that the collisional activation rate to the $K(7^2S)$ state is negligible. Accordingly, the decay curve of the $K(7^2S)$ can be treated as a single exponential function, from which the effective lifetime associated with $K-NO$ collisions may be derived without significant disturbance by the $K(5^2D)$ state.

On the other hand, when the population density of the NO gas is set very small, the values of λ_1 and λ_2 turn out to be k_2 and k_4 , respectively. Substitution into the eq.8 leads to

$$[K(7^2S)](t) \approx [K(7^2S)]_0 e^{-k_2 t} \quad (15)$$

It then is straightforward to determine the radiative lifetime of the $K(7^2S)$ state in the absence of NO gas. According to the Stern-Volmer equation, a plot of the reciprocal of the effective lifetime for the $K(7^2S)$ atom quenched by NO against its pressure yields a slope indicative of the total deactivation cross section, and an intercept, at which the NO pressure is zero, providing information on the radiative lifetime of the state. The equation is written,

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \sigma v_{K-NO} [NO] \quad (16)$$

where τ is the effective lifetime; τ_0 , the radiative lifetime in the absence of collisions with NO ; v_{K-NO} , the Maxwellian averaged relative velocity for $K-NO$ collisions; σ , the total deactivation cross section; $[NO]$, the population

Table 1. Radiative Lifetime and Total Deactivation Cross Section

levels	this work	others
$K(7^2S)(ns)$	155 ± 8	$158^a, 165 \pm 12^b, 155 \pm 6^c$
$K(5^2D)(ns)$	561 ± 18	$749^a, 610 \pm 90^b, 572 \pm 14^c, 553 \pm 16^d$
$K(7^2S)-NO(\text{\AA}^2)$	88 ± 1	-
$K(5^2D)-NO(\text{\AA}^2)$	70 ± 2	-

a. see Ref.16

b. see Ref.17

c. see Ref.18

density of NO .

Analogous to the treatment described above, the radiative lifetime and the deactivation cross section for the $K(5^2D)$ state, populated by two-photon absorption, may also be determined.

RESULTS AND DISCUSSION

Fig.2 shows the measurement of the $K(7^2S)$ depopulation. It shows a semi-log plot of the time-resolved fluorescence across the $7^2S - 4^2P_{1/2}$ transition at a residual gaseous NO pressure of 0.05 torr. The slope yields an effective lifetime 120 ns. When the NO is increased successively, the spectrum becomes significantly a combination of bi-exponential functions as expected in eq.8. For instance, with increase of the NO pressure to 0.7 torr, as shown in Fig.3, the time-resolved spectrum has obvious contributions from two components. In the early part of the decay, the population of the $K(7^2S)$ is simply dominated by the two-photon excitation; the decay curve provides information on the effective lifetime for the $K(7^2S)$ state by NO collisions. After a prolonged period of time, the additional part of the $K(7^2S)$ population contributed from the $K(5^2D)$ state and possibly other states becomes important, but the rise time may be slow because to the delay caused by the migration between two states.

Upon excitation of the $K(7^2S)$ state, the population in the $K(5^2D)$ state increases with an increase of the NO pressure, thereby leading to more intense emission of the $5^2D - 4^2P$ transition. This can be compared with the case in

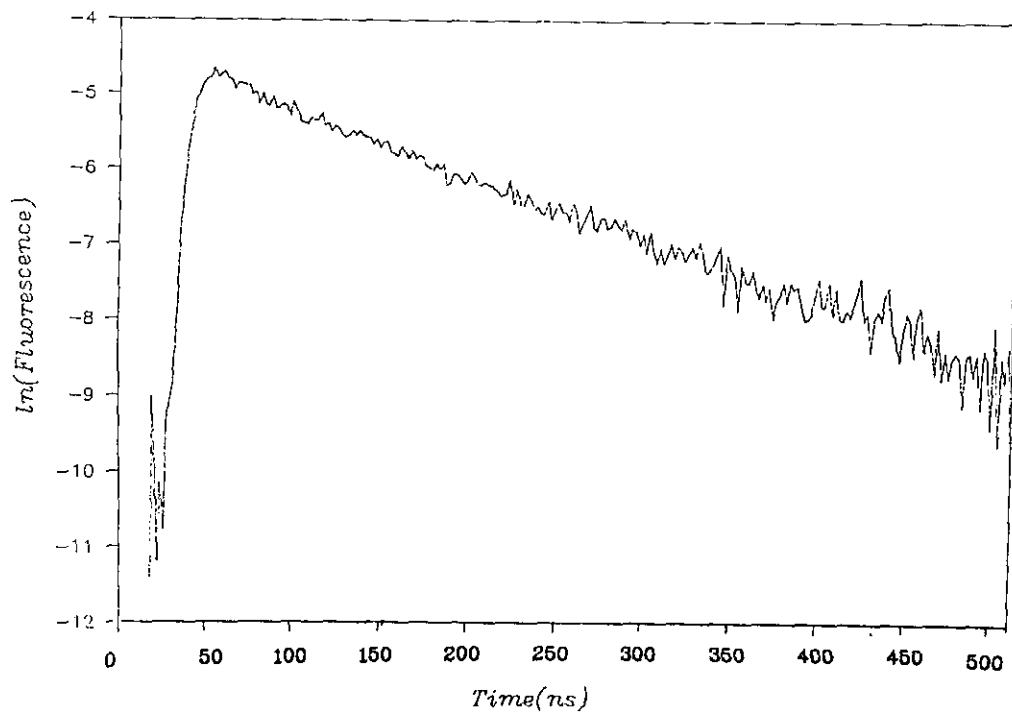


Fig. 2. Time-resolved fluorescence for the $K(7^2S)$ atom across $7^2S-4^2P_{1/2}$ transition. The pressure of NO is 0.05 torr. The effective lifetime gives 120 ns.

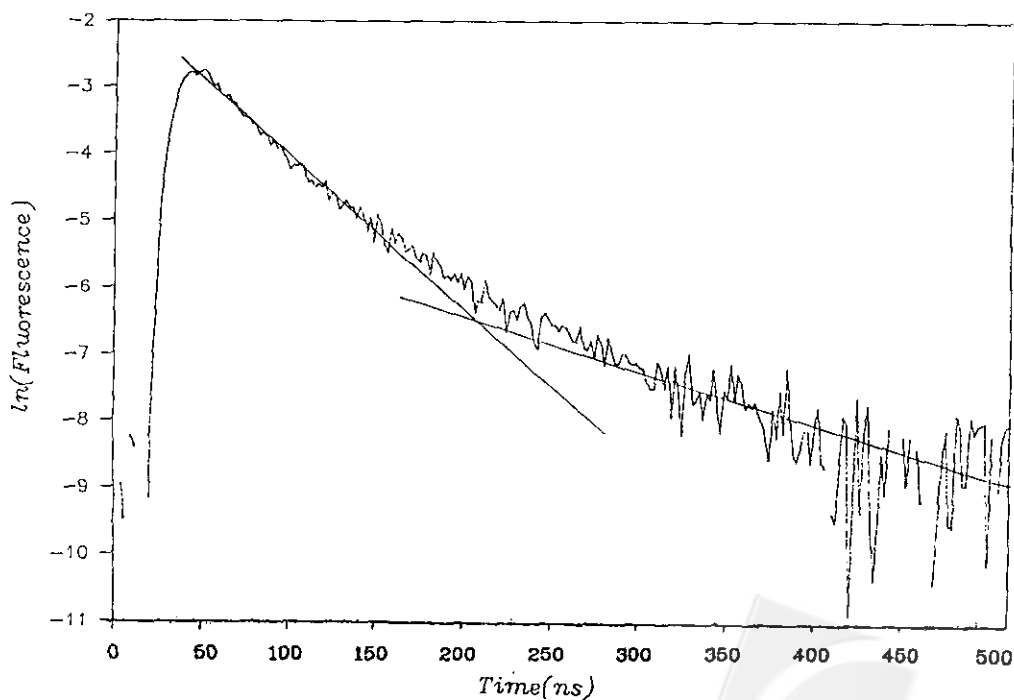


Fig. 3. Time-resolved fluorescence for the $K(7^2S)$ state across $7^2S-4^2P_{1/2}$ transition. The pressure of NO is 0.7 torr. The effective lifetime gives 45 ns.

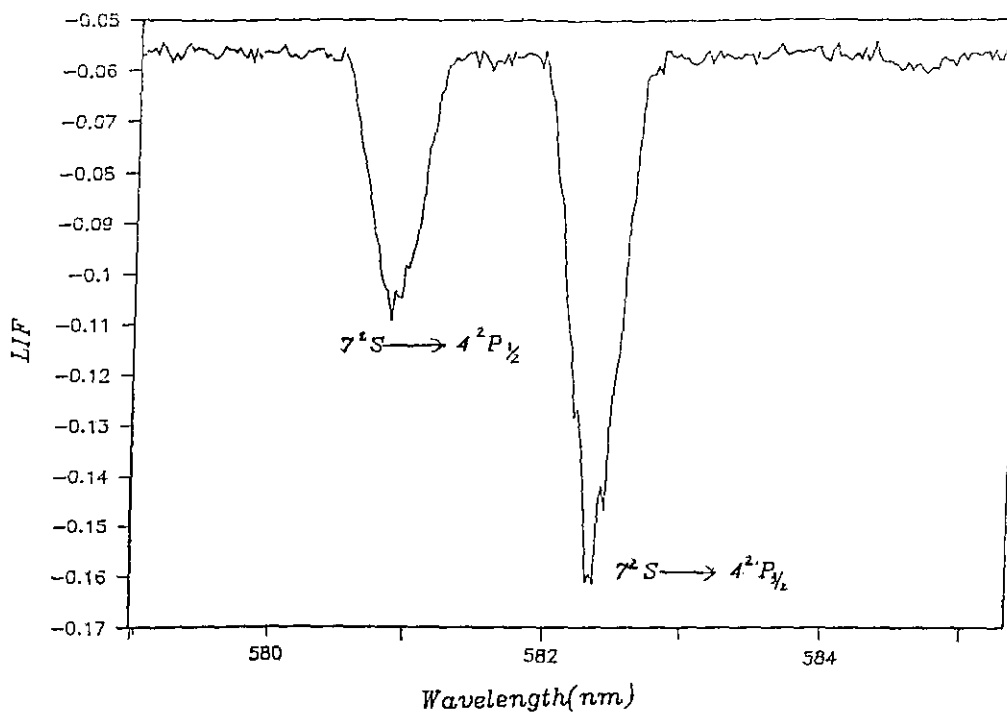


Fig. 4. Dispersed fluorescence, obtained by scanning the wavelength of the monochromator, as the dye laser is fixed at 660 nm for the $K(7^2S)$ excitation. The NO gas is present in trace amount.

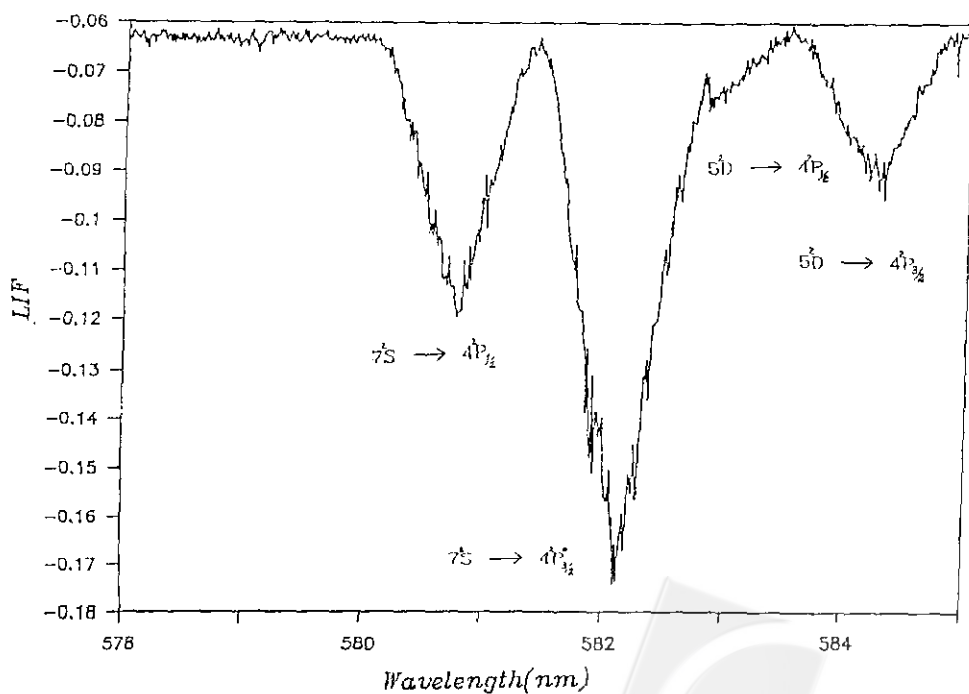


Fig. 5. Dispersed fluorescence, obtained by scanning the wavelength of the monochromator, as the dye laser is fixed at 660 nm for the $K(7^2S)$ excitation. The pressure of NO is about 0.1 torr.

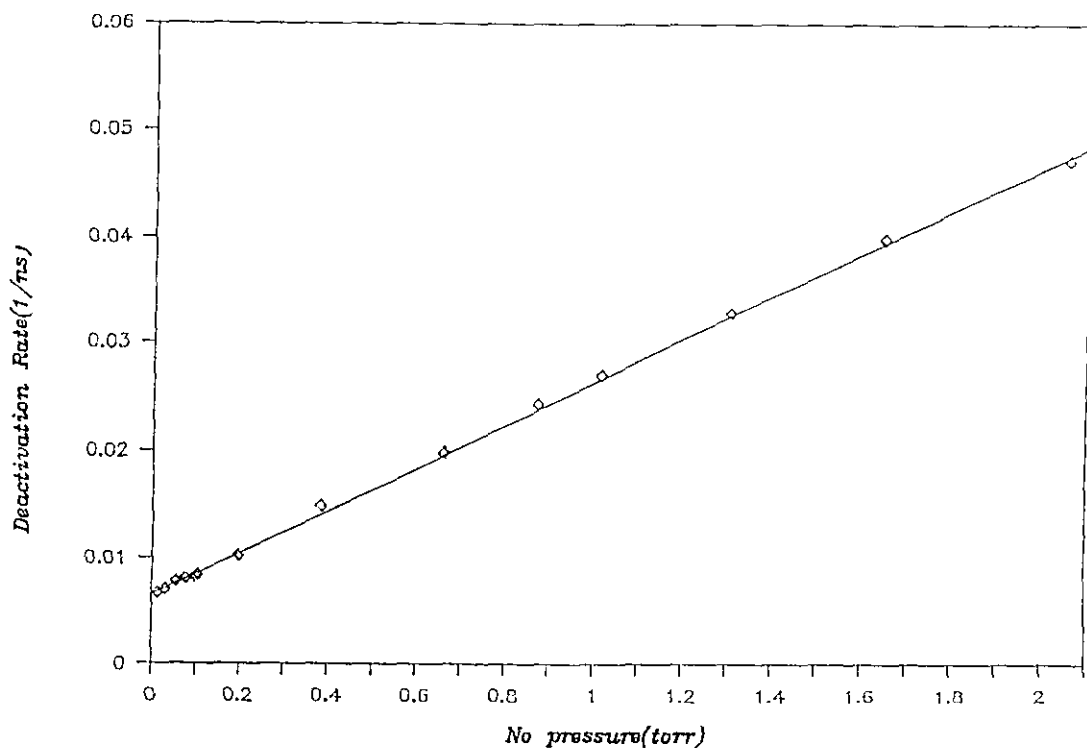


Fig. 6. Stern-Volmer plot of the reciprocal of effective lifetime for the $K(7^2S)$ -NO collisions against the NO pressure.

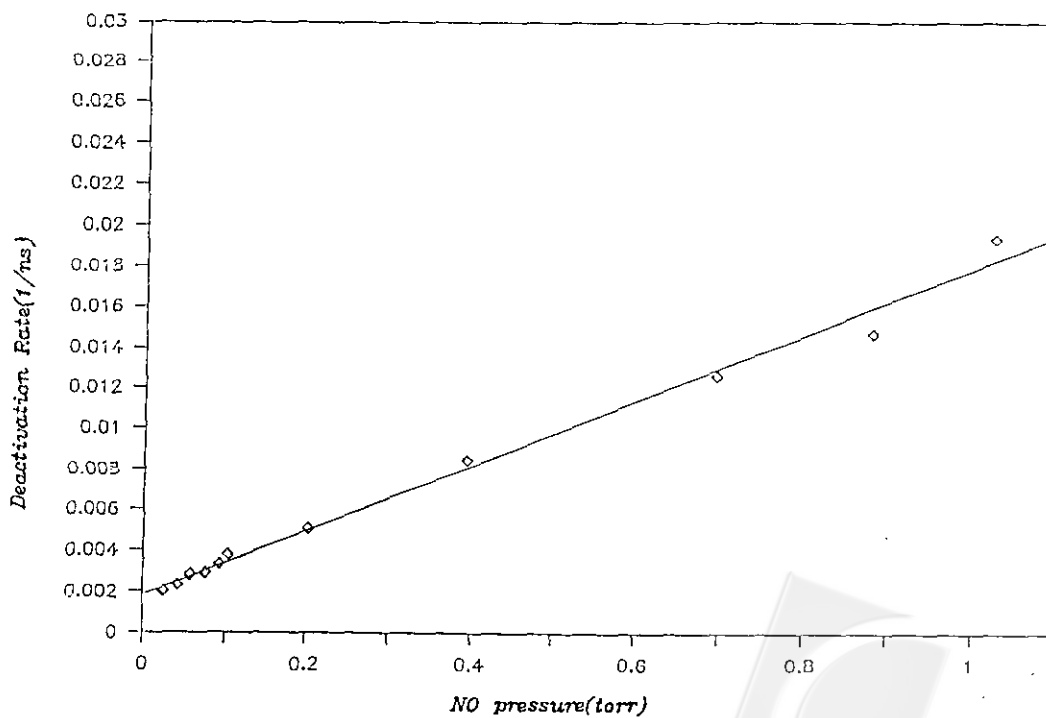


Fig. 7. Stern-Volmer plot of the reciprocal of effective lifetime for the $K(5^2D)$ -NO collisions against the NO pressure.

which the NO gas is almost absent. This fact is revealed in Fig. 4 and 5 in which the atomic LIF for the $7^2S-4^2P_{1/2}$ and the $5^2D-4^2P_{1/2}$ transition was obtained by scanning the wavelength of monochromator. Note that for measurement of the time-resolved fluorescence described above, the monochromator was adjusted to transmit only the $7^2S-4^2P_{1/2}$ emission. Accordingly, any disturbance from the emission other than this line may be safely avoided. The more NO gas is added, the more rapid the collisional activation rate from the 5^2D state becomes. It follows that the rise time of the delayed fluorescence becomes smaller and the intensity becomes larger. According to eq. 14, in this case, we may determine the effective lifetime by taking the portion within the early period with a slight correction from the

long-time decay curve.¹⁵ As exemplified in Fig. 3, the slope obtained in the early time yields a lifetime of 45 ns. Analogously, the depopulation lifetime of the $K(5^2D)$ state by collisions with NO can be treated in the same manner.

Based on the Stern-Volmer equation given in eq. 16, Fig. 6 and 7 show the resulting plot for the cases of $K(7^2S)$ and $K(5^2D)$. By comparison with the data available elsewhere, the total deactivation cross sections and the radiative lifetimes for both states in the absence of NO collisions are listed in Table I. The radiative lifetime of $K(7^2S)$ and $K(5^2D)$, 155 ± 8 ns and 561 ± 18 ns, respectively, are found to be in excellent agreement with the theoretical counterparts.¹⁶ In addition, our results are also in excellent agreement with those reported experimentally.^{17,18}

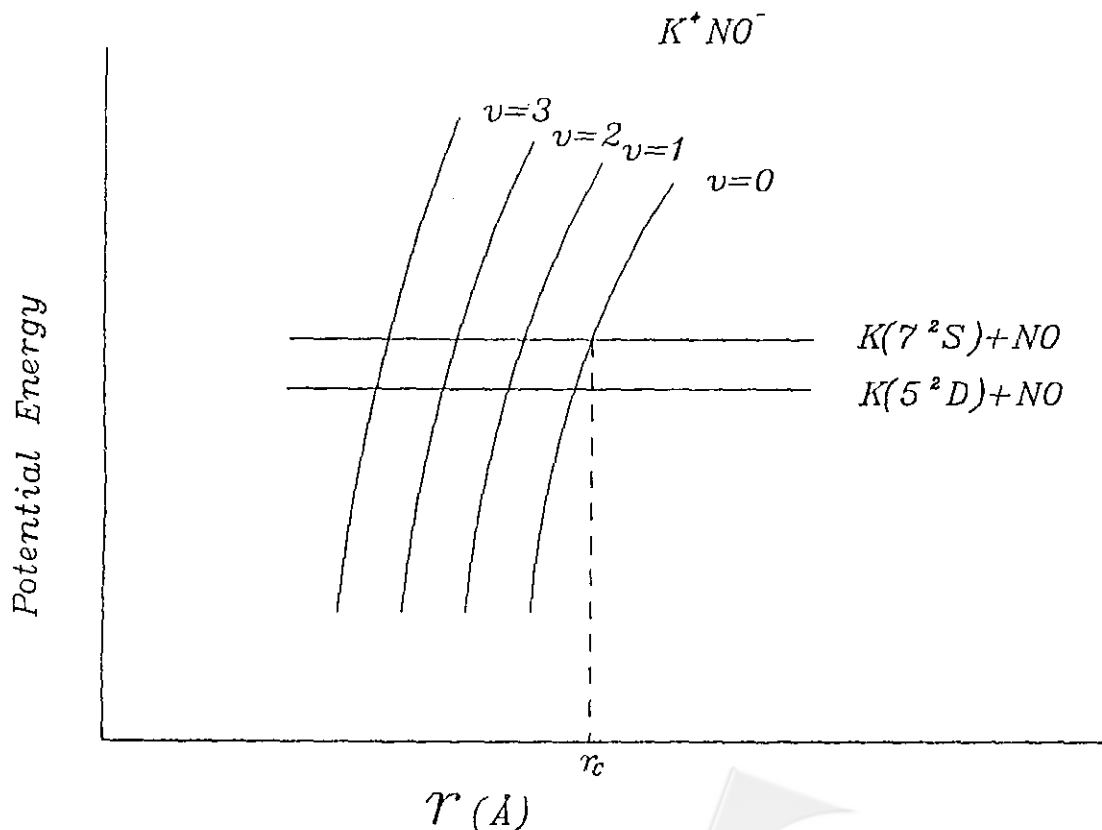
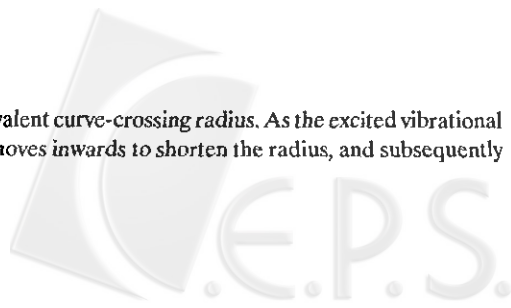


Fig. 8. Model of electron harpoon mechanism. r_c indicates the ionic-covalent curve-crossing radius. As the excited vibrational levels of the ionic complex are populated, the crossing region moves inwards to shorten the radius, and subsequently gives a smaller deactivation cross section.



It is not surprising to find such large total deactivation cross sections for the $K(7^2S)$ and $K(5^2D)$ states. First, the NO gas, possessing pairs of unshared electrons and the π bond, is regarded as an efficient deactivator¹⁹. NO is expected to be more effective than H_2 in the quenching process. The quencher H_2 can yield a value as large as 50 \AA^2 for the $K(5^2D) - H_2$ collisions.¹⁴ Second, the $K(7^2S)$ and $K(5^2D)$ atoms are in high-lying states, having a very weak binding energy for the outer-shell electron, and thus resulting in a very large size. For this reason, the deactivation cross sections for these states have proved to be much larger than those of the low-lying states.^{4,20,21} Because the deactivation cross section in this work was measured for the first time, literature data are lacking for comparison. It is found, however, that the cross sections for quenching by N_2 of $Na(7^2S)$ and $Na(5^2D)$ are $82 \pm 9 \text{ \AA}^2$ and $43 \pm 7 \text{ \AA}^2$, respectively.⁴ We would expect the cross section for $Na-N_2$ collisions to be similar to our results since the excited K atom is about the same size as the excited Na atom. We see the deactivation cross sections of Na are in reasonable agreement with our results.

An electron harpoon model has been employed successfully to interpret the large molecular quenching cross sections system such as $Na-N_2$, $Na-O_2$ and $K-H_2$.^{4,5,7,14} It is also employed in the collision of $Na(3^2P) - NO$ to explain the existence of a long-lived complex, Na^+NO^- , which has been observed by means of the infrared matrix-isolation technique.²² Based on this model, the ionic-covalent crossing radius r_c can be expressed as²³

$$\frac{e^2}{r_c} = I.P. (K7^2S) - E.A. (NO) \quad (17)$$

where $I.P.(K7^2S) = 0.59 \text{ eV}$ denotes the ionization potential of $K(7^2S)$ and $E.A.(NO) = 0.024 \text{ eV}$ the electron affinity of NO.²⁴ These values give $r_c = 25.6 \text{ \AA}$, which subsequently gives a total deactivation cross section of 772 \AA^2 by substituting into the following equation:

$$\sigma_{cal} = f\pi r_c^2 \quad (18)$$

where $f = 3/8$ (for the case of $K(7^2S)$) is the fraction of excited state potential surfaces that correlate with the

ionic surface in C_s symmetry. For the exceptionally large cross section, σ_{cal} , it is assumed that the ionic intermediate is formed in the ground vibrational level. If the excited vibrational levels are considered, then the crossing region moves inwards to shorten the radius r_c , as shown in Fig.8, and subsequently gives a smaller cross section. For example, as the excited vibrational level 3 is considered and the vibrational constant 1900 cm^{-1} is assumed to be the same as that of NO, this gives $r_c = 11.3 \text{ \AA}$, and thereby leads to $\sigma_{cal} = 150 \text{ \AA}^2$. In this sense, the comparison can be improved. However, problems still remain to challenge theoreticians to do a further model calculation.

In summary, we have measured the total deactivation cross sections and the radiative lifetimes in the absence of NO collisions for the $K(7^2S)$ and $K(5^2D)$ states. The results of radiative lifetimes agree satisfactorily with those previously reported. The quenching cross sections by NO have been measured for the first time, with values in a reasonable range in comparison with $Na-N_2$ collisions.

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Key Word Index-

deactivation cross section; radiative lifetime.

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