TIME-RESOLVED LMR STUDY ON THE REACTIONS OF CI ATOMS IN THE GROUND $({}^{2}P_{3/2})$ AND EXCITED $({}^{2}P_{1/2})$ SPIN–ORBITAL STATES WITH CINO

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CINO photolysis by the third (354 nm) and fourth (266 nm) harmonics of a Nd: YAG laser has been shown to result in population inversion of the Cl fine structure levels. The rate constant of $Cl(^{2}P_{3/2}) + CINO \rightarrow Cl_{2} + NO$ has been determined to equal $(7.7 \pm 1.7) \times 10^{-11}$ cm³/s, with the photolysis of Cl₂ (354 nm), S₂Cl₂ (266 nm) and ICl (530 nm) as a source of $Cl(^{2}P_{3/2})$. The reactivity of $Cl(^{2}P_{1/2})$ has been shown to be much lower than that of $Cl(^{2}P_{3/2})$. The deactivation (relaxation + reaction) rate constant of $Cl(^{2}P_{1/2})$ has been determined to equal $(1.8 \pm 0.4) \times 10^{-11}$ cm³/s, the photolysis of ICl (530 nm) and CINO (354; 266 nm) used as a source of $Cl(^{2}P_{1/2})$. All results were obtained at a temperature of 298 ± 5 K.

1. Introduction

The reaction of chlorine atoms with nitrosyl chloride is the titration reaction widely used to measure absolute concentrations of Cl atoms in flow experiments [1-3],

$$Cl + ClNO \rightarrow Cl_2 + NO.$$
 (1)

Also this reaction is important for Cl recombination in the presence of NO following via reactions

$$Cl + NO + M \rightarrow ClNO + M$$
 (2)

and (1) [4].

The rate constant of reaction (1), $(3.3 \pm 1.0) \times 10^{-12} \text{ cm}^3/\text{s}$ at room temperature, was determined indirectly [5] by analyzing the COCl₂ formation kinetics under photolysis of CO/Cl₂ mixtures in the presence of CINO. The discharge flow-resonance fluorescence studies of reaction (1) yielded $k_1 = (3.0 \pm 0.5) \times 10^{-11} \text{ cm}^3/\text{s}$ [6] and $k_1 = (7.2 \pm 2.4) \times 10^{-11} \text{ cm}^3/\text{s}$ [7] (T = 298 K). Vibrationally excited NO molecules were observed [8] in the pulsed photolysis of CINO used to generate chlorine atoms. Assuming these NO molecules to arise in reaction (1), the rate constant of this reaction was obtained $k_1 = (5.40 \pm 0.47) \times 10^{-12} \text{ cm}^3/\text{s}$ [8]. The value $k_1 = (1.65 \pm 0.32) \times 10^{-11} \text{ cm}^3/\text{s}$ was measured [9] by the resonance fluorescence

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method, with the CINO photolysis by an excimer laser (XeF, 350 nm) as a source of chlorine atoms (T = 298 K). At last, we employed CINO as an inhibitor to study the chain branching reaction of silane chlorination [10] and obtained preliminary value $k_1 = (6.0 \pm 2.0) \times 10^{-11} \text{ cm}^3/\text{s}$ at T = 298 K. Such essential variations in the reaction (1) rate constant obtained in refs. [7,10] and [5,6,8,9] have stimulated our interest to the reaction.

2. Experimental

The experimental arrangement and the principle of the time-resolved laser magnetic resonance (LMR) have already been described in detail [11]. The reagents were pumped through a reactor mounted inside the cavity of the LMR spectrometer.

The photolyzing pulse of the 2nd, 3rd, or 4th harmonics of a Nd: YAG laser (pulse duration 15 ns, repetition rate up to 100 Hz) was directed to the flow reactor at a small angle (about 2°) to the CO₂-laser monitoring beam axis (beam diameter about 4 mm). This geometry ensured a great overlap area of the beams. The observation zone (limited by the modulation field length) was 12 cm long. The resonant modulation of the magnetic

field at 150 kHz by a double amplitude of 6 mT was used [12,13].

The chlorine atoms were detected in the LMR spectrum at the 11P36 line of a ${}^{13}C^{16}O_2$ laser at $E \parallel H$ in a field of some 0.1 T [14,15]. The reagents were pumped through the observation zone with the rate ensuring complete changing of the reaction mixture between the pulses at a pulse repetition rate of 12.5 Hz. The output radiation of the CO₂ laser was detected by a Ge-Au photoresistor cooled with liquid nitrogen. The photoresistor signals were detected synchronously at the magnetic field modulation frequency, digitized by a ADC (256 time channels, 6 bits, up to 50 ns/channel), and collected in the memory of an Electronika-60 minicomputer. The time constant of the synchronous detector was 3 μ s. Usually 10³ kinetic curves were added, which provided a minimum detected (S/N = 1) Cl concentration of about 4×10^{10} cm⁻³ [11]. The reagent flow rates were measured with linear heat-transfer mass-flow meters. The flow of argon employed as a gas carrier, was measured with a calibrated rotameter. The pressure in the reactor was measured by a silicone oil manometer (accurate to ± 5 Pa).

Chlorine atoms were generated by the photolysis of Cl₂ (354 nm), ICl (530 nm), S_2Cl_2 (266 nm), ClNO (354 nm, 266 nm). The typical pulse energy of the Nd: YAG laser was 1–2 mJ for the second harmonic and 0.5 mJ for the third and the fourth harmonics.

The chlorine produced by KMnO₄ + HCl reaction was repeatedly distilled in vacuum from 178 to 77 K. Nitrosyl chloride was generated as described [16], and distilled repeatedly from 178 to 77 K prior to measurements. We used commercial CCl₄, S₂Cl₂, and freon-12 CF₂Cl₂ without further purification. The purity of ICl, generated as described [17], was not checked. Argon, 99.992% pure, and commercial oxygen, 99.0% pure, were not purified additionally. All the experiments ran at $T = 298 \pm 5$ K.

3. Results

3.1. Cl_2 photolysis; $Cl(^2P_{3/2})$ reaction with CINO

To generate $Cl({}^{2}P_{3/2})$, we photolyzed chlorine molecules [18,19] by the third harmonic of the

Nd: YAG laser (354 nm, 0.5 mJ),

$$Cl_2 + 354 \text{ nm} \rightarrow 2Cl(^2P_{3/2}),$$
 (3)

$$\operatorname{Cl}({}^{2}P_{3/2}) + \operatorname{ClNO} \to \operatorname{Cl}_{2} + \operatorname{NO}.$$
 (4)

Fig. 1 shows kinetic curves of Cl disappearance at various ClNO concentrations. Since in our experiments $[ClNO] \gg [Cl]$, i.e. the conditions of pseudo-first-order kinetics hold, the dependence of the inverse lifetime of Cl atoms on the ClNO concentration obeys the simple expression

$$\tau^{-1} = k_4 [\text{CINO}] + \tau_0^{-1}.$$
 (5)

The constant term τ_0^{-1} is associated with Cl diffusion from the observation zone, as well as with the reaction with possible impurities. Fig. 2 shows this dependence. The slope of the straight line yields the rate constant of reaction (4), $k_4 = (6.90 \pm 0.88) \times 10^{-11} \text{ cm}^3/\text{s} (\pm 2\sigma)$.

Note that the IR-radiation intensity in the CO_2 -laser cavity sufficed to saturate the Cl fine structure transition [11,20]. Therefore, to remove saturation and also to quickly mix the populations of the hyperfine structure sublevels (8 sublevels in the ${}^2P_{1/2}$ state and 16 sublevels in the ${}^2P_{3/2}$ state)



Fig. 1. Kinetic curves of Cl(${}^{2}P_{3/2}$) disappearance after Cl₂ photolysis (354 nm) with various ClNO concentrations. [ClNO] = 0, 0.3×10¹⁴, 2.7×10¹⁴ cm⁻³ for curves 1, 2, 3, respectively. [Cl₂] = 6.5×10¹⁵ cm⁻³, [O₂] = 2.2×10¹⁷ cm⁻³.



Fig. 2. The inverse lifetime of $Cl(^2P_{3/2})$ versus CINO concentration; Cl_2 photolysis as source of Cl.

[20], we took the measurements in oxygen, $[O_2] = 2.2 \times 10^{17} \text{ cm}^{-3}$. For comparison fig. 3 shows the kinetic curves of Cl lifetime without oxygen (curve 1) and in the presence of oxygen (curve 2). Curve 1 is strongly non-exponential due to the saturation process [20].

3.2. S_2Cl_2 photolysis; $Cl({}^2P_{3/2})$ reaction with ClNO

We used S_2Cl_2 instead of Cl_2 to produce Cl atoms [21] to verify whether S_2Cl_2 was a good Cl source when employed in kinetic measurements of processes involving Cl in cases when Cl_2 cannot be such a source. The S_2Cl_2 absorption cross section for the fourth radiation harmonic of the Nd: YAG laser ($\sigma = 1.7 \times 10^{-17}$ cm² [22]) exceeds substantially the Cl_2 absorption cross section for the third harmonic ($\sigma = 1.1 \times 10^{-19}$ cm²). Therefore, the same Cl concentration can be generated by a smaller amount of S_2Cl_2 than Cl_2 .

The S_2Cl_2 and CCl_4 pressures in the reactor were determined by argon flows. They passed through calibrated rotameters, were saturated with S_2Cl_2 and CCl_4 vapours, and went then to the reactor. We used CCl_4 to remove the transition saturation of the Cl fine structure [11] and also to quench any $Cl({}^2P_{1/2})$ [23] arising in S_2Cl_2 photolysis.



Fig. 3. Kinetic curves of Cl disappearance after Cl₂ photolysis (354 nm); (1) $[Ar] = 1.6 \times 10^{17} \text{ cm}^{-3}$, $[O_2] = 0$; (2) [Ar] = 0, $[O_2] = 2.2 \times 10^{17} \text{ cm}^{-3}$.

For comparison fig. 4 shows the kinetic curves of Cl lifetimes without CCl₄ (curve 1) and with 10^{16} cm⁻³ CCl₄ (curve 2). The rise in the LMR signal (curve 1) results from Cl(²P_{1/2}) deactivation on S₂Cl₂, whilst the fall of this signal is induced by the reaction of Cl(²P_{3/2}) with S₂Cl₂.



Fig. 4. Kinetic curves of Cl disappearance after S_2Cl_2 photolysis (266 nm): (1) [CCl₄] = 0; (2) [CCl₄] = 10^{16} cm⁻³.



Fig. 5. Kinetic curves of $Cl({}^{2}P_{3/2})$ disappearance after S_2Cl_2 photolysis (266 nm) for various CINO concentrations. [CINO] = 0, 0.9 × 10¹⁴, 5.0 × 10¹⁴ cm⁻³ for curves 1, 2, 3, respectively. $[S_2Cl_2] = 7.5 \times 10^{14} \text{ cm}^{-3}$, $[CCl_4] = 10^{16} \text{ cm}^{-3}$, $[Ar] = 2 \times 10^{17} \text{ cm}^{-3}$.

With amounts of CCl₄ (curve 2) the LMR signal rise time is determined by the time resolution of the apparatus ($\tau_e = 4 \ \mu s$) [11].

Fig. 5 shows the kinetic curves of Cl disappearance after S_2Cl_2 photolysis by the fourth harmonic of the Nd : YAG laser (266 nm, 0.5 mJ) for various ClNO concentrations in the presence of CCl₄. Since [ClNO] \gg [Cl] (about 1% of S_2Cl_2 dissociates under UV irradiation), the dependence of the inverse lifetime of Cl atoms on the ClNO concentration obeys eq. (5). Fig. 6 shows this dependence. The initial intercept contains an additional contribution from Cl reaction with S_2Cl_2 . The slope of the straight line yields the rate constant of reaction (4), $k_4 = (7.93 \pm 0.40) \times 10^{-11}$ cm³/s ($\pm 2\sigma$). This value is in good agreement with that obtained for Cl₂ photolysis.

3.3. ICl photolysis; reactions $Cl({}^{2}P_{3/2}) + ClNO$ and $Cl({}^{2}P_{1/2}) + ClNO$

The photolysis of ICl by the second harmonic of the Nd: YAG-laser is accompanied [24] by the population inversion of the Cl fine structure. Therefore, ICl photolysis can be employed to gen-



Fig. 6. The inverse lifetime of $Cl({}^{2}P_{3/2})$ versus ClNO concentration; $S_{2}Cl_{2}$ photolysis as a source of Cl.

erate $Cl({}^{2}P_{1/2})$ and investigate the processes involving chlorine atoms in this state.

Let us discuss the following processes involving



Fig. 7. The chlorine atom LMR signal kinetics as function of the relation between $\kappa - \kappa^*$ and κ_q ($\beta_0 > 1/3, \kappa > \kappa^*$). The values κ_q , separating regions A and B, B and C, C and D, D and E are $[(1-\beta_0)/3\beta_0](\kappa - \kappa^*) - [(3\beta_0 - 1)/3\beta_0]\kappa^*$, $(1-\beta_0)(\kappa - \kappa^*)$, $(2/3)(\kappa - \kappa^*)$ and $\kappa - \kappa^*$, respectively. The dashed horizontal lines show asymptotic limits for C_{κ} and C_{λ} at $\kappa_q \to \infty$ ($\beta_0 = 0.55$).

excited and unexcited Cl in the pseudo-first-order conditions for all the processes,

$$Cl^* \xrightarrow{\kappa_q} Cl,$$

$$Cl^* \xrightarrow{\kappa^*} \text{products},$$

$$Cl \xrightarrow{\kappa} \text{products}.$$
(6)

Here $Cl^* \equiv Cl({}^2P_{1/2})$, $Cl \equiv Cl({}^2P_{3/2})$, κ_q and κ^* are pseudo-first-order rate constants of the excited-state relaxation and reaction, respectively, κ is pseudo-first-order reaction rate constant of Cl in the ground state.

This scheme is described by a set of two linear differential equations,

$$\frac{\mathrm{d}}{\mathrm{d}t} \begin{pmatrix} [\mathrm{Cl}^*] \\ [\mathrm{Cl}] \end{pmatrix} = \begin{pmatrix} -\kappa_{\mathrm{q}} - \kappa^* & 0 \\ \kappa_{\mathrm{q}} & -\kappa \end{pmatrix} \begin{pmatrix} [\mathrm{Cl}^*] \\ [\mathrm{Cl}] \end{pmatrix}.$$
(7)

Under the initial conditions $[Cl^*](t=0) = [Cl^*]_0$, [Cl] $(t=0) = [Cl]_0$ the system is solved as

$$[Cl^*](t) = [Cl^*]_0 \exp\left[-(\kappa_q + \kappa^*)t\right],$$

$$[Cl](t) = \left\{ [Cl]_0 + \kappa_q [Cl^*]_0 / (\kappa_q + \kappa^* - \kappa) \right\}$$

$$\times \exp(-\kappa t)$$

$$- \left(\kappa_q [Cl^*]_0 / (\kappa_q + \kappa^* - \kappa))\right)$$

$$\times \exp\left[-(\kappa_q + \kappa^* - \kappa)t\right].$$
(8)

In our case, the experimentally observable quantity is the absorption of radiation from the CO₂ laser adjusted to the transition between individual hfs sublevels of the ${}^{2}P_{1/2}$ and ${}^{2}P_{3/2}$ states, which are completely splitted in a magnetic field (8 sublevels of the ${}^{2}P_{1/2}$ state, 16 sublevels of the ${}^{2}P_{3/2}$ state). Under the assumption of a fast hfs sublevel mixing we derive for the absorption coefficient

$$\alpha = \sigma_0([\operatorname{Cl}]f - [\operatorname{Cl}^*]f^*). \tag{9}$$

Here σ_0 is the cross section of the transition between the sublevels considered, f and f^* are equilibrium portions of atoms at these sublevels relative to the populations of the lower ${}^2P_{3/2}$ and the upper ${}^2P_{1/2}$ state, respectively (f = 1/16, $f^* = 1/8$). Substituting eq. (8) to eq. (9), we derive

$$\alpha(t) = f\sigma_0 [Cl^*]_0 (C_{\kappa} e^{-\kappa t} + C_{\lambda} e^{-\lambda t}).$$
(10)

Here

$$C_{\kappa} = 1/\beta_0 - 1 - \kappa_q/(\kappa - \lambda),$$

$$C_{\lambda} = \kappa_q/(\kappa - \lambda) - f^*/f,$$

$$\beta_0 = [Cl^*]_0/([Cl^*]_0 + [Cl]_0),$$

$$\lambda = \kappa_q + \kappa^*.$$

Analysis of eq. (10) shows that different situations may arise depending on the relationship between $(\kappa - \kappa^*)$ and κ_q (fig. 7, $\beta_0 > 1/3$, $\kappa > \kappa^*$).

As a result, by choosing corresponding experimental conditions, thus varying the relationship between $\kappa - \kappa^*$ and κ_q , one can employ ICl photolysis to investigate processes involving Cl(²P_{3/2}) and Cl(²P_{1/2}).

Fig. 8 shows the kinetic curves corresponding to the situation E in fig. 7 for various CINO concentrations. The excited Cl atoms were relaxed by adding $[O_2] = 9.6 \times 10^{16}$ cm⁻³ into the reactor. The CINO concentration dependence of the inverse lifetime of Cl(²P_{3/2}) obeys eq. (5) (fig. 9). The kinetic curves were processed by their final



Fig. 8. The chlorine atom LMR signal kinetics after ICl photolysis (530 nm) for various ClNO concentrations. [ClNO] = 0, 9.8×10^{13} , 20.3×10^{13} cm⁻³ for curves 1, 2, 3, respectively. [ICl] = 8.0×10^{14} cm⁻³, [O₂] = 9.6×10^{16} cm⁻³.



Fig. 9. The inverse lifetime of $Cl(^{2}P_{3/2})$ versus CINO concentration; ICl photolysis as a source of Cl.

lengths with a negligible contribution from $Cl({}^{2}P_{1/2})$ to the signal kinetics. The initial interception results from the $Cl({}^{2}P_{3/2})$ reaction with ICl. The slope of the straight line yields the rate constant of reaction (4), $k_{4} = (7.89 \pm 1.44) \times 10^{-11}$



Fig. 10. Kinetic curves of $Cl({}^{2}P_{1/2})$ disappearance after ICl photolysis (530 nm) for various ClNO concentrations. [ClNO] = 0, 1.2×10^{15} cm⁻³ for curves 1, 2, respectively. [ICl] = 3.2×10^{15} cm⁻³, [O₂] = 2×10^{16} cm⁻³.

 cm^3/s ($\pm 2\sigma$), which fairly well agrees with those obtained above.

To measure the overall rate of the processes

$$Cl({}^{2}P_{1/2}) + CINO \rightarrow Cl({}^{2}P_{3/2}) + CINO,$$

$$Cl({}^{2}P_{1/2}) + CINO \rightarrow Cl_{2} + NO,$$
 (11)

we chose conditions corresponding to the situation C in fig. 7. Fig. 10 shows the kinetic curves for this case obtained at various ClNO concentrations. The inverse lifetime of $Cl({}^{2}P_{1/2})$ against ClNO concentration obeys an expression similar to eq. (5),

$$\tau^{-1} = k_{11} [\text{CINO}] + \tau_0^{-1}.$$
(12)

Fig. 11 shows this dependence. The kinetic curves are approximated by the only exponent $(e^{-\lambda t})$; the contribution from the other exponent $(e^{-\kappa t})$ can be neglected. The slope of the straight line gives the sum of the rate constants (11), $k_{11} = (1.83 \pm 0.38) \times 10^{-11} \text{ cm}^3/\text{s}$. The initial interception cannot be completely accounted for by $\text{Cl}(^2\text{P}_{1/2})$ deactivation at those amounts of ICl and O₂ introduced into the reactor. Most likely, the deactivation results mainly from some impurity in ICl (possibly I₂). However, since the ICl flow rate is constant, the deactivation at the impurity shifts



Fig. 11. The inverse lifetime of $Cl(^2P_{1/2})$ versus CINO concentration; ICl photolysis as a source of Cl.

the straight line, without affecting its slope. This assumption has been corroborated by experiments with ClNO photolysis as a source of excited $Cl({}^{2}P_{1/2})$.

3.4. CINO photolysis; population inversion of the Cl fine structure levels; $Cl({}^{2}P_{1/2})$ reaction with CINO

Studies on CINO photochemistry started as far back as 1930, when the quantum yield of NO in CINO photodissociation within 635 to 365 nm was shown to be approximately two [25]. The data obtained at a later time resulted in the following CINO dissociation mechanism [25–29]

$$CINO + h\nu \rightarrow CI + NO,$$

$$CI + CINO \rightarrow CI_2 + NO.$$
(13)

Although the vibrationally and electronically excited NO originated in CINO photolysis have been frequently observed [26-33], there are no data on the state of the newly generated Cl atoms.

Our experiments with ClNO as a source of Cl atoms have shown that the ClNO photolysis by both the third (354 nm) and the fourth (266 nm) harmonics of the Nd: YAG laser results in the population inversion of the Cl fine structure levels.

t

ABSORPTION

ClNO + 354nm → Cl+NO

2-[CF₂Cl₂] = 5×10¹

Fig. 12 depicts the kinetic curves of Cl lifetime after a pulse of the third harmonic of the Nd : YAG laser. Curve 1 corresponds to increasing intensity of the CO_2 laser radiation and is similar to the curves obtained for ICl photolysis.

After the addition of the relaxator CF_2Cl_2 (the $Cl(^2P_{1/2})$ quenching rate constant is 2.0×10^{-10} cm³/s [34,20]) at a concentration ensuring $Cl(^2P_{1/2})$ relaxation within about 1 µs, the CO₂-laser radiation amplification changes to absorption (curve 2). These experiments allow one to estimate the yield of $Cl(^2P_{1/2})$ arising in the photolysis. The CINO photolysis by the third and the fourth harmonics of the Nd: YAG laser results approximately in 50% of excited $Cl(^2P_{1/2})$.

Fig. 13 shows the kinetic curves of $Cl({}^{2}P_{1/2})$ disappearance at various CINO concentrations. The dependence of the inverse lifetime of $Cl({}^{2}P_{1/2})$ on CINO concentration obeys eq. (12) (fig. 14). Only the exponent $(e^{-\lambda t})$ is plotted by the experimental points, the contribution from the other exponent $(e^{-\kappa t})$ is negligible. The slope of the straight line gives the sum of the rate constants (11), $k_{11} = (1.77 \pm 0.24) \times 10^{-11} \text{ cm}^3/\text{s} (\pm 2\sigma)$, which is a good fit to the value obtained for ICl photolysis.



 $= 9.2 \times 10^{16} \text{ cm}^{-3}$.



Fig. 13. Kinetic curves of Cl(${}^{2}P_{1/2}$) disappearance after ClNO photolysis (354; 266 nm) for various ClNO concentrations. [ClNO] = 1.3×10^{15} , 3.5×10^{15} cm⁻³ for curves 1, 2, respectively. [Ar] = 1.2×10^{17} cm⁻³, [O₂] = 10^{16} cm⁻³.



Fig. 14. The inverse lifetime of $Cl(^{2}P_{1/2})$ versus CINO concentration; CINO photolysis as a source of Cl.

4. Discussion

Table 1 lists rate constants for the reaction Cl + ClNO available in the literature. The factors that might affect k_1 [5,6] have been discussed [8,9]. We have some considerations explaining the discrepancy between our data and those published [8,9].

We think Nelson and Johnston's data [9] can be more readily explained. As shown in the present work, the CINO photolysis by the third and the fourth harmonics of the Nd: YAG laser (354; 266 nm) gives roughly 50% of $Cl(^{2}P_{1/2})$, whilst the rate of $Cl({}^{2}P_{3/2})$ reaction with ClNO is nearly 4 times as high as the deactivation (reaction + relaxation) rate of $Cl({}^{2}P_{1/2})$ on ClNO. Nelson and Johnston [9] employed the dye laser photolysis of CINO at 500 nm and the excimer laser photolysis of CINO at 350 nm (XeF) as Cl atom sources. They added CCl₄ to quench completely any possible $Cl(^{2}P_{1/2})$ only in the initial experiments (dye laser CINO photolysis), with the relative CINO concentrations measured. The reaction rate observed did not decrease, and therefore Nelson and Johnston concluded that $Cl(^{2}P_{1/2})$ either reacted with the same rate as that of the ground

Table 1 Rate constants for the reaction Cl+ClNO

Method	$k(298 \text{ K}) (\text{cm}^3/\text{s})$	Ref.
photolysis of $CO + Cl_2$		
in the presence of		
CINO	$(3.3 \pm 1.0) \times 10^{-12}$	[5]
discharge flow-		
resonance fluorescence		
of Cl in VUV	$(3.0 \pm 0.5) \times 10^{-11}$	[6]
pulsed photolysis of		
CINO, IR-		
luminescence of NO	$(5.40\pm0.47)\times10^{-12}$	[8]
pulsed photolysis of		
CINO, resonance		
fluoresence of Cl in VUV	$(1.65 \pm 0.32) \times 10^{-11}$	[9]
discharge flow		
resonance fluorescence		
of Cl in VUV	$(7.2 \pm 2.4) \times 10^{-11}$	[7]
time-resolved LMR	$(6.0 \pm 2.0) \times 10^{-11}$	[10]
time-resolved LMR	$(7.7 \pm 1.7) \times 10^{-11}$	present work

Cl(${}^{2}P_{3/2}$), or was not present in the system originally. Therefore they made experiments with the laser photolysis of ClNO at 350 nm, taking no steps to relax possible Cl(${}^{2}P_{1/2}$) atoms. Moreover, they did not analyze the initial part (about 400 µs) of the fluorescence decay kinetics because of the cell fluorescence excited by the laser pulse. Therefore, Nelson and Johnston seemed to observe the quenching of Cl(${}^{2}P_{1/2}$) rather than the reaction of Cl(${}^{2}P_{3/2}$) with ClNO. That is why their result coincides with our value for the sum of the rate constants (11).

The data of Grimley and Houston [8] cannot be so readily coordinated with ours. Grimley and Houston investigated CINO photolysis and believed vibrationally excited NO* to arise by the reaction of chlorine atoms with CINO. This interpretation seems to be questionable. Firstly, the assumption that the NO* fluorescence increases due to reaction (1) makes unclear the origin of the initial interception for the inverse rise time in the NO* fluorescence against CINO concentration (approximately equal to 35×10^3 s⁻¹, see fig. 3 from ref. [8]). Secondly, taking into account our rate constants for the reactions of Cl(²P_{1/2}), Cl(²P_{1/2}) with CINO and assuming the vibrationally excited NO* to arise by reaction (1), we obtain that the fluorescence times vary from ≈ 2 μ s to 0.5 μ s for the Cl(²P_{3/2}) reaction, and from 8 μ s to 2 μ s for the Cl(²P_{1/2}) deactivation by ClNO. At the same time, the experimental time range of the NO* fluorescence rise was 14-5 µs, whilst that of the NO* fluorescence decay was 100-25 μ s [8]. So reaction (1) does not seem to result in vibrationally excited NO* molecules. This was also the conclusion made by Basco and Norrish [26], who did not observe vibrationally excited NO* in reaction (1), with Cl₂ photolysis as a source of chlorine atoms. We believe the generation mechanism of vibrationally excited NO* in investigations by Grimley and Houston [8] might be associated with either the energy transfer from vibrationally excited products of the secondary reactions [35], or the relaxation of electron-excited NO arising in CINO photolysis [26].

References

- [1] E.A. Ogryzlo, Can. J. Chem. 39 (1961) 2556.
- [2] E. Hutton and M. Wright, Trans. Faraday Soc. 61 (1965) 78.
- [3] M.A.A. Clyne and D.H. Stedman, Trans. Faraday Soc. 64 (1968) 1816.
- [4] H. Hippler and J. Troe, Intern. J. Chem. Kinetics 8 (1976) 501.
- [5] W.G. Burns and F.S. Dainton, Trans. Faraday Soc. 48 (1952) 52.
- [6] M.A.A. Clyne and H.W. Cruse, J. Chem. Soc. Faraday Trans. II 68 (1972) 1281.
- [7] D. Kita and D.H. Stedman, J. Chem. Soc. Faraday Trans. II 78 (1982) 1249.
- [8] A.J. Grimley and P.L. Houston, J. Chem. Phys. 72 (1980) 1471.
- [9] H.H. Nelson and H.S. Johnston, J. Phys. Chem. 85 (1981) 3891.
- [10] S.A. Chasovnikov and L.N. Krasnoperov, Chem. Phys. Letters 124 (1986) 248.
- [11] L.N. Krasnoperov, E.N. Chesnokov and V.N. Panfilov, Chem. Phys. 89 (1984) 297.

- [12] Yu.M. Gershenzon and V.L. Lifshitz, Kvantovaya Elektronika 6 (1979) 933.
- [13] V.R. Braun, L.N. Krasnoperov and V.N. Panfilov, Kvantovaya Elektronika 7 (1980) 1895.
- [14] M. Dagenais, J.W.C. Johns and A.R.W. McKellar, Can. J. Phys. 54 (1976) 1438.
- [15] V.R. Braun, L.N. Krasnoperov and V.N. Panfilov, Optika i Spektroskopya 52 (1982) 719.
- [16] R.G. Kalbandkeri, D.K. Padma and A.R.V. Murthy, Z. Anorg, Allgem. Chem. 450 (1979) 103.
- [17] Yu.V. Karyakin and I.I. Angelov, Pure chemical compounds (Khimiya, Moscow, 1974).
- [18] J.A. Coxon, Molecular spectroscopy, Vol. 1 (Chemical Society, London, 1973).
- [19] G.E. Busch, R.T. Mahoney, R.J. Morse and K.R. Wilson, J. Chem. Phys. 51 (1969) 449.
- [20] A.I. Chichinin and L.N. Krasnoperov, Chem. Phys. Letters 124 (1986) 8.
- [21] M. Braithwaite and S.R. Leone, J. Chem. Phys. 69 (1978) 839.
- [22] E.N. Chesnokov and V.N. Panfilov, Khim. Fiz. 10 (1982) 1349.
- [23] I.S. Fletcher and D. Husain, Chem. Phys. Letters 49 (1977) 516.
- [24] L.N. Krasnoperov and V.N. Panfilov, Kinet. i Kataliz 20 (1979) 540.
- [25] G.B. Kistiakowsky, J. Am. Chem. Soc. 52 (1930) 102.
- [26] N. Basco and R.G.W. Norrish, Proc. Roy. Soc. A 268 (1962) 291.
- [27] G.E. Busch and K.R. Wilson, J. Chem. Phys. 56 (1972) 3655.
- [28] M.A. Pollack, Appl. Phys. Letters 9 (1966) 94.
- [29] C.R. Giuliano and L.D. Hess, J. Appl. Phys. 38 (1967) 4451.
- [30] K.H. Welge, J. Chem. Phys. 45 (1966) 1113.
- [31] M. Lenzi and H. Okabe, Ber. Bunsenges. Physik. Chem. 72 (1968) 168.
- [32] L. Werner, B. Wunderer and H. Walther, Chem. Phys. 60 (1981) 109.
- [33] M.D. Moser, E. Weitz and G.C. Schatz, J. Chem. Phys. 78 (1983) 757.
- [34] R.H. Clark and D. Husain, J. Chem. Soc. Faraday Trans. II 80 (1984) 97.
- [35] J. Bechara, T. Morrow and W.D. McGrath, Chem. Phys. Letters 122 (1985) 605.