The vibrational population inversion and relaxation kinetics of C_2^*, $d^3\Pi_g$ state

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In order to determine the possiblility of stimulated emission between the C_2^*, $d^3\Pi_g$ and $a^3\Pi_u$ states, we undertook the study of the relative populations and quenching and vibrational relaxation rates of C_2^*, $d^3\Pi_g$ state in argon and nitrogen gas in reaction of $Na + CCl_4$ by using the heat-pipe-oven technique. The chemiluminescent spectrum was obtained by a scanning double-grating monochromator (GDM-100). The photoelectron signal was sent into a pre-amplifier (Keithley 103 A) and a lock-in amplifier (Keithley 840), then to a X-Y recorder. The relative populations of C_2^*, $d^3\Pi_g$ state were calculated by the relative emission intensities of $\Delta v = -1$ sequence of Swan band system obtained in the experiment. The calculated result is shown in the following table.

The relative population of C_2^*, $d^3\Pi_g$ state obtained by the reaction of $Na + CCl_4$ at different P_{Ar}, P_{N2} and 340 °C

	P_{Ar} (torr)						P_{N2} (torr)		
	5	10	15	19	29		3	5	14
N_1	1.00	1.00	1.00	1.00	1.00	N_1	1.00	1.00	1.00
N_2	1.76	1.65	1.45	1.44	1.08	N_2	2.60	1.55	1.10
N_3	2.55	2.59	2.51	2.38	2.02	N_3	4.46	2.20	1.52
N_4	5.71	5.16	4.98	4.85	4.01	N_4	7.63	5.20	2.77
N_5	12.04	10.14	9.32	8.93	6.59	N_5	18.10	9.00	4.73
N_6	57.60	48.56	43.93	34.21	26.49	N_6	109.10	48.10	18.00

From this table, it can be seen that the $d^3\Pi_g$ state exhibits population inversion with particularly high population in $v' = 6$ level. A reasonable mechanism could be proposed that the $b^3\Sigma_g^-$ state is firstly formed in the elementary step $C + CCl$ of the reaction of $Na + CCl_4$, and then undergoes a radiationless transition into the $d^3\Pi_g$ $v' = 6$ level. But the vibrational population $v' < 6$ level is formed by collisional relaxation. At steady-state condition, by using the method of least squares, the quenching and relaxation rates of C_2^*, $d^3\Pi_g$ state in argon gas were obtained as 1.9×10^6 $torr^{-1}$. sec^{-1} and 2.2×10^6 $torr^{-1}$. sec^{-1} respectively. These rate constants in nitrogen gas were a little higher than those in argon gas. The calculated result of multiquantum transition is an order of magnitude smaller than one quantum transition, and three quantum transition is two orders of magnitude smaller than one quantum transition. The quenching rate of C_2^*, $d^3\Pi_g$ state by sodium is of an order of 10^7 $torr^{-1}$. sec^{-1}.

It was proposed that the fast quenching of C_2^*, $d^3\Pi_g$ state may proceed by either way: (a) The C_2^*, $d^3\Pi_g$ state crosses with neighbouring electrionic states, thus a nonadiabatic

transition may take place during collisions. This phenomenon also reflected in our experiment in which some anomalous spectrum was observed and an unexpected negative value in $v' = 3$ level of C_2^*, $d^3\Pi_g$ state was obtained; (b) the C_2^*, $d^3\Pi_g$ state could form a long-lifetime complex with the sodium atom (^2s). The same conclusion may be drawn from Benson's result in which the emission spectra of sodium having obtained energy from C_2^*, $d^3\Pi_g$ show that the population distribution in each electronic state of sodium is statistical. We planned to investigate further the quenching and relaxation rates of C_2^*, $d^3\Pi_g$ state by laser-induced fluorescence technique.

$C_2^*d^3\Pi_g$ 态的振动布居反转和弛豫动力学

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为了要确定 C_2^*，$d^3\Pi_g$ 和 $a^3\Pi_u$ 态间受激发射的可能性，我们利用热管炉技术研究了 $Na+CCl_4$ 反应中 C_2^*，$d^3\Pi_g$ 态在氩气、氮气和钠原子中的振动弛豫和电子猝灭速率。化学发光光谱是用双光栅单色仪(GDM-1000)进行测量，光电信号则利用低噪声前置放大器 (Keithley 103A)和锁相放大器 (Keithley 840) 放大后在 X-Y 记录器上记录。C_2^*、$d^3\Pi_g$ 态的相对布居是采用 Swan 带中 $\Delta V=-1$ 带序的相对发射强度进行计算而得到。计算结果列于下表：

在 340°C 和不同氩气和氮气压力下利用 $Na+CCl_4$ 反应得到的 C_2^*，$d^3\Pi_g$ 态的相对布居

	P_{Ar} (托)						P_{N_2} (托)		
	5	10	15	19	29		3	5	14
N_1	1.00	1.00	1.00	1.00	1.00	N_1	1.00	1.00	1.00
N_2	1.76	1.65	1.45	1.44	1.08	N_2	2.60	1.55	1.10
N_3	2.55	2.59	2.51	2.38	2.02	N_3	4.46	2.20	1.52
N_4	5.71	5.16	4.98	4.85	4.01	N_4	7.63	5.20	2.77
N_5	12.04	10.14	9.32	8.93	6.59	N_5	18.10	9.00	4.73
N_6	57.60	48.56	43.93	34.21	26.49	N_6	109.10	48.10	18.00

从表中可以看到 $d^3\Pi_g$ 态呈现布居反转，其中第六振动能级具有特别高的布居。我们认为用下面的机理进行解释是比较合理的，在 $Na+CCl_4$ 反应中基元步骤 C+CCl 首先生成 $b^3\Sigma_g^-$态，然后通过无辐射跃迁进入 $d^3\Pi_g$ 第六振动能级。由于碰撞弛豫结果使低于第六振动能级的低能级得到布居。在稳态条件下利用最小二乘方拟合实验数据的方法，我们得到了 C_2^* $d^3\Pi_g$ 态在氩气中电子猝灭的速率为 1.9×10^6 托$^{-1}$ 秒$^{-1}$；振动弛豫速率为 2.1×10^6 托$^{-1}$ 秒$^{-1}$。在氮气中这两个速率都略高一些。

我们计算了碰撞中多量子跃迁速率，计算结果表明双量子跃迁比单量子跃迁低一个数量级；三量子跃迁比单量子跃迁低二个数量级。

我们还初步考察了钠原子对 C_2^*，$d^3\Pi_g$ 态的猝灭速率，其数量级为 10^7 托$^{-1}$ 秒$^{-1}$。

C_2^* $^2\Pi_g$ 态被氩气、氮气和钠原子的快猝灭可能归结为以下两种原因：

(1) C_2^* $d^3\Pi_g$ 态与相邻电子态存在着交叉，因此在碰撞中可能发生非绝热跃迁。这种现象亦反映在我们得到的 $d^3\Pi_g$ 态第三振动能级的弛豫速率具有不合理的负值；同时我们还在较高的气压下得到了第三振动能级具有不正常高的发射强度。

(2) C_2^* $d^3\Pi_g$ 态与 Na(^{2}S)可以形成中间络合物，这可以从 S·W·Benson 的实验中引出同样的结论，即从 C_2^* $d^3\Pi_g$ 态得到能量的钠原子所发射的光谱中看到不同电子态的钠原子的布居是统计分布的。

我们计划进一步用激光诱导荧光法测量 C_2^*，$d^3\Pi_u$ 态的脱活速率，以便确定，C_2^* $d^3\Pi_g$ 态和 $a^3\Pi_u$ 态在气相反应中布居反转的可能性。