

## Kinetic Spectroscopic Studies of Cl(3p<sup>5</sup> 2P<sub>3/2</sub>, 1/2) in the Vacuum Ultraviolet

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Citation: *J. Chem. Phys.* **50**, 4115 (1969); doi: 10.1063/1.1671678

View online: <http://dx.doi.org/10.1063/1.1671678>

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proach to equilibrium. Since the measured relaxation times for the slow component are much faster than the known  $T-V$  excitation rates for  $N_2$ , the slow component of the  $\nu_3$  emission is a measure of the  $V-V$  exchange.

The procedure developed by Taylor and Bitterman<sup>2</sup> to arrive at  $V-V$  exchange probabilities from the  $\nu_3$  emission in  $N_2-CO_2$  was applied to the present  $N_2-N_2O$  experiment. The resulting probabilities per collision as a function of the average temperature behind the shock are shown in Fig. 1. The room-temperature point at  $8.7 \times 10^{-4}$  is a fluorescence measurement of Yardley.<sup>9</sup> The solid curve is a calculation of the SB theory for the process  $N_2(1) + N_2O(00^0) \rightarrow N_2(0) + N_2O(00^1) + 107 \text{ cm}^{-1}$ , where the  $V-V$  exchange is due only to the long-range interaction between the  $N_2$  quadrupole moment and the  $N_2O$  dipole moment for mode  $\nu_3$ .<sup>10</sup> The inverse temperature behavior and the magnitude of the data are seen to be in reasonable agreement with the SB calculation. Thus, it would appear that the long-range dipole-quadrupole interaction is important in understanding the  $V-V$  exchange between  $N_2$  and mode  $\nu_3$  of  $N_2O$  in the temperature range  $300^\circ-1200^\circ\text{K}$ .

This study was the result of discussions with Dr. R. L. Taylor. The authors wish to thank Dr. R. D. Sharma for making available the theoretical calculation.

\* This work was supported by a grant from the National Science Foundation.

† This work was done in partial fulfillment of the requirement for the Ph.D. degree at Lehigh University.

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subject of a number of investigations by kinetic absorption spectroscopy in the vacuum ultraviolet.<sup>1,2</sup> Time-resolved studies on spontaneous<sup>3</sup> and stimulated emission<sup>4</sup> from  $I(5^2P_{1/2})$  in the infrared have also been described. These techniques have led to a quantitative understanding of diffusion, spin-orbit relaxation, and chemical reaction involving the excited atoms. We now wish to report the observation of both  $Cl(3^2P_{1/2})$  and  $Cl(3^2P_{3/2})$  in the photolysis of a number of chlorides together with data on the collisionally induced spin-orbit relaxation of the excited atom. The study of electronically excited chlorine atoms ( $\Delta E = 881 \text{ cm}^{-1}$ ) is highly pertinent to an understanding of the appropriate molecular emission and kinetics in flow discharges<sup>5-7</sup> and shock tubes,<sup>8-9</sup> as well as to a general interest in electronic energy transfer from atoms. Both  $Cl(3^2P_{3/2})$  and  $Cl(3^2P_{1/2})$  have been detected hitherto by EPR spectroscopy.<sup>10,11</sup> The experimental arrangement used here for vacuum-ultraviolet flash photolysis has been described previously.<sup>12</sup> Similar designs were used in conjunction with both the 1-m vacuum spectrograph at Cambridge and the 3-m instrument at Washington to monitor the kinetics of the atoms.

Figure 1 shows the transitions of  $Cl(3^2P_{1/2})$  and  $Cl(3^2P_{3/2})$  observed in absorption following the flash photolysis of  $CCl_4$ . Table I summarizes the results of the atomic spectral intensities for those chlorides whose photolyses were investigated. Low pressures of the parent molecule were employed to penetrate the molecular continua, typically  $p_{CCl_4} = 0.02\tau$ ; 50–200 $\tau$  of argon were used for all experiments to prevent a significant rise in temperature on flashing. While  $Cl(3^2P_{1/2})$  is expected as a primary product of the low-wavelength photolysis of  $Cl_2$ , in accord with the other halogens,<sup>1,13</sup> the transition at  $1351.7 \text{ \AA}$  was obscured by  $Cl_2$  itself. However, the  $Cl(3^2P_{3/2})$  atom could be observed at  $1335.8 \text{ \AA}$  through a "window" in the spectrum of  $Cl_2$ . The spectral intensities in Table I relate to different scales for the atoms in the two states. While the  $f$  values for the  $1347.3$ - and  $1351.7$ - $\text{\AA}$  transitions are close to equal,<sup>14</sup> the absorption intensity for the  $Cl(3^2P_{1/2})$  transition was always very much weaker in these experiments. Thus the photolysis of  $CF_2Cl$ , in particular, does not give rise to a population inversion between the

## Notes

### Kinetic Spectroscopic Studies of $Cl(3p^5 \ ^2P_{3/2, 1/2})$ in the Vacuum Ultraviolet

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(Received 27 November 1968)

Electronically excited iodine and bromine atoms in the optically metastable  $np^5(^2P_{1/2})$  state have been the

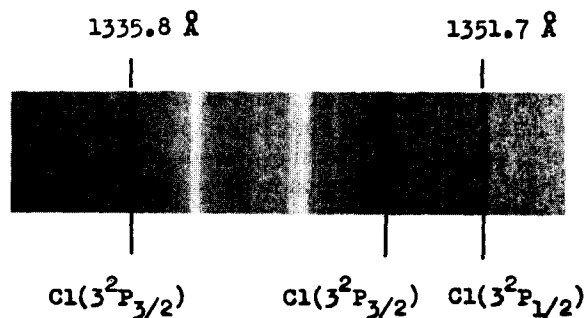


FIG. 1.  $Cl(3^2P_{3/2})$  and  $Cl(3^2P_{1/2})$  in the vacuum-ultraviolet flash photolysis of  $CCl_4$ .  $p_{CCl_4} = 0.02\tau$ ;  $p_{Ar} = 50\tau$ ; delay =  $10 \mu\text{sec}$ .

TABLE I. Summary of results on the production of  $\text{Cl}(3^2P_{1/2})$  and  $\text{Cl}(3^2P_{3/2})$  in primary photochemical processes.<sup>a</sup>

	HCl	Cl <sub>2</sub>	AsCl <sub>3</sub>	CCl <sub>4</sub>	CF <sub>3</sub> Cl
$\text{Cl}(3^2P_{3/2})$ (1347.3 Å)	s	s (1335.8 Å)	s	s	s
$\text{Cl}(3^2P_{1/2})$ (1351.7 Å)	w	...	...	s	m
Transitions <sup>b</sup>			1335.8 Å	$3p^44s(3^2P_{1/2}) \leftarrow 3p^5(3^2P_{3/2}^0)$	
			1347.3 Å	$3p^44s(2^2P_{3/2}) \leftarrow 3p^5(2^2P_{3/2}^0)$	
			1351.7 Å	$3p^44s(2^2P_{1/2}) \leftarrow 3p^5(2^2P_{1/2}^0)$	

<sup>a</sup> s is strong; m is medium; w is weak.<sup>b</sup> C. E. Moore, Natl. Bur. Std. (U. S.) Circ. No. 467, 1, 195 (1958).TABLE II. Probability (*P*) for the collisional deactivation of  $\text{Cl}(3^2P_{1/2})$  by various species M.

M	CCl <sub>4</sub>	CF <sub>3</sub> Cl	HCl	H	H <sub>2</sub>
<i>k</i> (cm <sup>3</sup> molecule <sup>-1</sup> ·sec <sup>-1</sup> )	$5 \times 10^{-11}$	$2.5 \times 10^{-13}$	$\sim 6 \times 10^{-13}$	$\sim 7 \times 10^{-10}$	$7 \times 10^{-13}$
<i>P</i>	0.15	$7.8 \times 10^{-4}$	$3 \times 10^{-2}$	1	$8 \times 10^{-3}$

$2P_{1/2}$  and  $2P_{3/2}$  states unlike the cases for Br and I in the photolyses of  $\text{CF}_3\text{Br}$  and  $\text{CF}_3\text{I}$ , respectively.<sup>1</sup> Hence the construction of an atomic-chlorine photodissociation laser, similar to that for the iodine atom,<sup>4</sup> appears remote.

The kinetics of  $\text{Cl}(3^2P_{1/2})$  produced in the photolyses of  $\text{CF}_3\text{Cl}$  and  $\text{CCl}_4$  are consistent with a mechanism involving quenching by the parent molecule rather than by any radical species present. Furthermore, quenching by argon was found to be negligible for pressures up to 1 atm. First-order rate coefficients were obtained following plate photometry taking into account a Beer-Lambert exponent for the 1347.3-Å transition of  $\frac{1}{2}$  [i.e.,  $\Delta(\text{O.D.}) \propto [\text{Cl}]^{1/2}$ ]. Second-order quenching constants derived from this data are given in Table II, and are correct to within a factor of 2. Quenching by  $\text{H}_2$  was determined by adding increasing partial pressures of this gas to a photolysis mixture containing  $\text{CCl}_4$ , until the concentration of  $\text{Cl}(3^2P_{1/2})$  had been reduced to one-half of its value in the absence of  $\text{H}_2$ . The quenching half-pressure determined in this way, taken with the data on  $\text{CCl}_4$  itself, yields a second-order quenching constant of  $7 \times 10^{-12}$  cm<sup>3</sup> molecules<sup>-1</sup>·sec<sup>-1</sup>.

The kinetics of  $\text{Cl}(3^2P_{1/2})$  produced in the photolysis of HCl are apparently more complex than the cases outlined above, and are consistent with a mechanism involving quenching by HCl and H atoms. The available data indicate that both these species make comparable contributions to the over-all decay, thus as  $[\text{H}] \sim 10^{-2}[\text{HCl}]$ , relaxation must occur at every collision with the hydrogen atom. In general the rates of spin-orbit relaxation for  $\text{Cl}(3^2P_{1/2})$  are considerably faster than those for  $\text{I}(5^2P_{1/2})$  or  $\text{Br}(4^2P_{1/2})$  as expected on the basis of the lower electronic energy. The near unit quenching efficiencies observed for several species suggest that strong chemical interaction is

involved, possibly leading to a crossing of potential surfaces. The case for  $\text{H} + \text{Cl}(3^2P_{1/2})$  is particularly interesting in this respect, as a crossing from the  $3\Pi_0+$  state to the  $1\Pi$  or  $2\Pi_1$  states may occur.<sup>15</sup>

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## Dielectric Properties of Liquid Ammonia and Sodium-Ammonia Solutions

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(Received 23 October 1968)

We report the first installment of microwave measurements of the dielectric properties of liquid ammonia and sodium-ammonia solutions.

A cylindrical  $E_{010}$  cavity with axial quartz capillary containing liquid<sup>1,2</sup> was used in transmission. Details