Quenching rate constants for metastable molecule \( \text{PCI} \left( b^1 \Sigma^+, v' = 0 \right) \)

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In this decade, great attention has been paid to PCI \( b^1 \Sigma^+ \) because of its potential importance in chemical laser. Coxon et al.\(^1\) studied the reaction of \( \text{Ar}(^3P_0, 2) \) with PCI and observed two band systems of PCI \( A^3Pi \rightarrow X^3Sigma^- \) and \( b^1 \Sigma^+ \rightarrow X^3 \Sigma^- \). Beielefeld et al.\(^2\) and Setser et al.\(^3\) measured the radiative lifetime of PCI \( b^1 \Sigma^+ \) and its quenching rate constants for some small molecule quenchers. Recently, we have prepared a clean source of PCI \( b, v' = 0 \) in the flow reactor through the \( \text{Ar}(^3P_0, 2) + \text{PCI}_3 \) reaction and observed the emission of PCI \( b \rightarrow X \) \( \Delta v = 1 \) for the first time. Furthermore, using 23 polyatomic molecules as quenchers, we have further investigated the decay kinetics of PCI \( b, v' = 0 \) at 300 K and discussed the factors that influence the quenching rate constants.

1 Experimental apparatus and techniques

The experimental apparatus employed in this work has been described previously\(^4\). The metastable atoms \( \text{Ar}(^3P_0, 2) \) were generated by a hollow cathode electrode discharge. The typical applied voltage for the discharge was approximately 400 V with current \( \sim 1 \) mA. In the experiments, PCI\(_3\) was added at the first reagent inlet downstream from the discharge and the quencher is added at the second inlet. The reactor was equipped with two observation windows for spectral measurement. The operating pressure was about \( 3.5 \times 10^2 \) Pa and the flowing
speed in the reactor was about 40 m/s. The quenching rate constants of PCl (b, $v' = 0$) for quenchers could be obtained from the slope of $\ln(I_0/I)$ vs. [Q] as indicated by

$$\ln(I_0/I) = (1/1.6)k_Q[Q]\Delta t,$$

where $I_0$ is the relative intensity of PCl(b, $v' = 0$) emission before the quenchers are added; I is the relative intensity of PCl(b, $v' = 0$) at the quencher concentration [Q]; $k_Q$ is the quenching rate constant; $\Delta t$ is the reaction time, i.e. the reagent flow time from the second inlet to the second window. $1.6^{[5]}$ is a correction coefficient for the parabolic flow of the gases in the reactor.

2 Results and discussion

2.1 The emission spectra of products from the Ar($^{3}P_{0,2}$) + PCl$_3$ reaction

Three bands were observed at 400—600, 820 and 780 nm in the Ar($^{3}P_{0,2}$) + PCl$_3$ reaction and were assigned to the $A^3\Pi \rightarrow X^3\Sigma^-$, $b^1\Sigma^+ \rightarrow X^3\Sigma^-$ $\Delta v = 0$ and $\Delta v = 1$ emissions of the electronically excited fragment PCl$, which, on the basis of the data from ref. [1] (see fig. 1). The $b^1\Sigma^+ \rightarrow X^3\Sigma^-$ $\Delta v = 1$ emission spectrum is reported for the first time. The weak signal at 750 nm in fig. 1 is probably $b^1\Sigma^+ \rightarrow X^3\Sigma^-$ $\Delta v = 2$ emission.

2.2 Quenching rate constants for PCl(b$^1\Sigma^+$, $v' = 0$)

In order to study PCl(b, $v' = 0$) electronic quenching reactions, it is necessary to prepare a clean source of PCl(b, $v' = 0$). For this purpose, we have taken two steps before performing the quenching measurement. The first one is to let the Ar pass merely through one liquid-N$_2$-cooled trap filled with molecular sieves to partially remove H$_2$O and C$_2$O in the Ar flow. The second one is to add excess PCl$_3$ at the first reagent inlet. The impurity remains in the Ar and the excess PCl$_3$ accelerate the vibrational relaxation of PCl(b). As a result, the only observable PCl(b$^1\Sigma^+ \rightarrow X^3\Sigma^-$) emission at the first window was the 0-0 band at 826.1 nm. The addition of excess PCl$_3$ also favored the increase in PCl(b, $v'$) concentration.

The quenching rate constants of PCl(b, $v' = 0$) for 23 quenchers were measured. Some semi-logarithm plots of the PCl(b, $v' = 0$) relative emission intensity vs. [Q] are presented in fig. 2. As an appraisal of the method, the rate constants of CH$_4$ and CO$_2$ were tested in the present work; the obtained results agree with those in refs. [2, 3]. The uncertainty of the rate constants was estimated to be $\pm 20\%$. Table 1 summarizes the PCl(b, $v' = 0$) quenching...