Kinetic study of the collisional quenching of spin–orbitally excited atomic chlorine, Cl(^{2}P$_{1/2}$), by H$_2$O, D$_2$O, and H$_2$O$_2$

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Abstract

Rate constants for the collisional quenching of spin–orbitally excited Cl(^{2}P$_{1/2}$) atoms by H$_2$O, D$_2$O, and H$_2$O$_2$ were determined at ∼295 K using laser-flash photolysis and laser-induced fluorescence techniques in the vacuum ultraviolet energy region. The rate constants reported for the quenchers of H$_2$O, D$_2$O, and H$_2$O$_2$, are $(3.9 \pm 0.3) \times 10^{-11}$, $(4.7 \pm 0.3) \times 10^{-11}$, and $(3.1 \pm 0.3) \times 10^{-10}$ cm^3 molecules^{-1} s^{-1}, where the uncertainties correspond to 1σ, respectively.
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1. Introduction

Since the elementary reactions of spin–orbitally excited halogen atoms give us a significant knowledge of fundamental electronic structures and reactive interactions, there have been a number of studies on the kinetics of physical and chemical relaxation processes of spin–orbitally excited atomic chlorine Cl(^{2}P$_{1/2}$) [1]. The two spin–orbit states, Cl(^{2}P$_{3/2}$) and Cl(^{2}P$_{1/2}$), are separated in energy by 882 cm^{-1}, with Cl(^{2}P$_{1/2}$) being higher in energy. The rate constants of the collisional quenching processes of Cl(^{2}P$_{1/2}$) with numerous quenchers have been obtained by several detection methods, e.g., atomic resonance absorption spectroscopy in the vacuum ultraviolet [2] or infrared regions [3] and the laser magnetic resonance technique [4]. However, several values for the same quenchers are quite scattered. For example, the quenching rate constants for water (H$_2$O) vapour, an important collisional quencher in the atmosphere, have been reported differently as $(0.26 \pm 0.05) \times 10^{-11}$ and $(7.8 \pm 2.3) \times 10^{-11}$ cm^3 molecules^{-1} s^{-1} by Clark and Husain [2] and by Chichinin

and Krasnoperov [5], respectively. The large discrepancy is probably due to the difficulty of accurate determination of the water concentration because it may stick to the cell walls or desorb from the walls. Moreover, there is lack of data for the quenching processes by isotopic water (D$_2$O). It would be interesting to examine how the difference of the vibrational frequencies between H$_2$O and D$_2$O affects the quenching rate constant of Cl(^{2}P$_{1/2}$).

Hydrogen peroxide (H$_2$O$_2$) formed in the self-disproportional process of HO$_2$ [6] is also important in studies on the atmospheric reactions of Cl atoms [7–10]. No experimental study referring to the quenching process of Cl(^{2}P$_{1/2}$) by H$_2$O$_2$ vapour has been reported, as far as we knew. The rate constant for the quenching from ^{2}P$_{1/2}$–^{2}P$_{3/2}$ by H$_2$O$_2$ is expected to be considerably faster because the available energy, i.e., 882 cm^{-1}, in the quenching process is very close to the vibrational energy, ∼870 cm^{-1}[11], of the v_3 mode, which corresponds to the local mode of O–O stretch in H$_2$O$_2$.

In the present study, laser-flash photolysis and laser-induced fluorescence spectroscopy in the vacuum ultraviolet (FP-LIF) have been applied to determine the rate constants of the collisional quenching of the ^{2}P$_{1/2}$ state by H$_2$O, D$_2$O, and H$_2$O$_2$ molecules at room temperature (∼295 K).

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2. Experimental method

Because the experimental setup used in this work is essentially the same as in our previous studies [12–14], the following FP-LIF technique is described in brief. Ar-dilute-gas mixtures of a small amount of HCl and an excess of quencher were slowly introduced into a photochemical reaction cell evacuated continuously by a rotary pump through a liquid nitrogen trap. For the quencher gas mixture, Ar gas was bubbled through H_2O or D_2O liquid. The concentrations of H_2O and D_2O in the gas mixture were monitored at the gas stream before the cell by a dew-point meter (General Eastern Optica+D-2). The total pressure in the cell was measured by a capacitance manometer (MKS, Baratron 622A). The HCl molecules in the cell were photodissociated by a 193-nm pulsed laser. The quantum yields in the photolysis of HCl at 193 nm are 0.41 and 0.59 for Cl production in the $^2P_{1/2}$ and $^2P_{3/2}$ states, respectively [15]. The $Cl(^2P_{1/2})$ atoms were detected using VUV-LIF excitation at 135.17 nm, corresponding to the $3p^44s(^2P_{1/2}) \leftarrow 3p^5(^2P_{1/2})$ transition. The tunable VUV radiation was generated by two-photon resonant four-wave difference frequency mixing in krypton gas [16]. The delay time between the pump and probe laser pulses was controlled by a pulse generator (Stanford Research, DG535). The VUV-LIF signal was detected using a solar blind photo-multiplier tube (EMR, 541J-08-17). The output of the photo-multiplier was pre-amplified and averaged over 10 laser pulses using a gated integrator (Stanford Research, SR-250).

A 30% w/v aqueous H_2O_2 solution was gently distilled under vacuum and stored in a glass bulb. The partial pressure of H_2O_2 in the reaction cell was calibrated by measuring photoabsorption at 193 nm. The photoabsorption cross section at 193 nm is reported as 5.89×10^{-19} cm^2 [17]. The same cell (optical path length 325 mm) and 193-nm pulsed laser were used as an absorption cell and a light source, respectively. The laser beam was introduced into the cell through an iris (4.5 mm in diameter) and a neutral-density filter (10% transmittance). The light intensity was measured at the exit window of the cell by a photodiode detector (Hamamatsu S1722-02). The signal output was acquired through the same gated integrator and the data were averaged for ∼60 s. From the slope of the photoabsorbances measured under 12 pressure conditions, the purity of the sample vapour was determined. The other reagents, D_2O (Wako, 99.96%), Ar (Nihon Sanso, 99.999%) and HCl (Sumitomo Seika, 99.8%) were obtained commercially and were used in the experiments without further purification.

3. Results and discussion

The loss of $Cl(^2P_{1/2})$ by all quenchers is regarded as following pseudo-first-order kinetics under the present experimental conditions. To obtain temporal profiles of $Cl(^2P_{1/2})$ concentration, the LIF intensity was measured by changing the delay time between photolysis laser and LIF-detection laser pulses. A typical temporal profile is shown in Fig. 1,
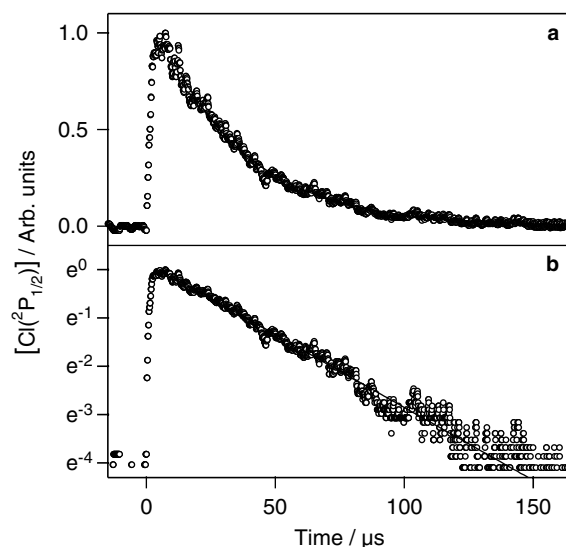

Fig. 1. Temporal profile, shown in: (a) linear and (b) logarithmic scales, of the $Cl(^2P_{1/2})$ concentration after the photodissociation of HCl at 193 nm. The solid lines are exponential decay fits to the temporal profiles.

in which 7.8 mTorr of HCl was photolyzed at 193 nm in the presence of 18.7 mTorr of H_2O and 1.23 Torr of Ar. Single exponential decay curves were observed as the temporal profiles under all experimental conditions. Since the total removal rate constants in collisions with HCl and Ar are $(7.8 \pm 0.8) \times 10^{-12}$ [13] and $\leqslant 5 \times 10^{-16}$ cm^3 molecules^{-1} s^{-1} [14], respectively, the contributions of HCl and Ar to removal rates are insignificant. Both the contributions of the photodissociation of H_2O, D_2O, or H_2O_2 and the reaction of $Cl(^2P_{1/2}) + H_2O_2$ can be ignored. The recommended reaction rate constant of the later process is only 4.1×10^{-13} cm^3 molecules^{-1} s^{-1} [17].

Fig. 2 shows the plots of the decay rates versus the concentrations of H_2O and D_2O. The ordinate values have been corrected for the contributions of HCl. The straight lines are the results of weighted least-squares fits analysis. The rate constants, $(3.9 \pm 0.2) \times 10^{-11}$ and $(4.7 \pm 0.2) \times 10^{-11}$ cm^3 molecules^{-1} s^{-1}, are given by the slopes of the fit lines in Figs. 2a,b, respectively, where the analytical uncertainties are taken as 1σ. The upper limit of the estimation uncertainty of the HCl contribution (5%), the systematic uncertainties (2%), the precision of the mass flow controllers and the capacitance manometer (2%), and the precision of the dew-point meter (1%) must be taken into account. Having taken all into account, we determine the values of $(3.9 \pm 0.3) \times 10^{-11}$ and $(4.7 \pm 0.3) \times 10^{-11}$ cm^3 molecules^{-1} s^{-1} as the rate constants of the collisional quenching processes by H_2O, D_2O, respectively.

Fig. 3 shows the plots of the decay rates versus the concentration of H_2O_2. The ordinate values have been corrected for the contributions of HCl and H_2O. Although the partial pressure of H_2O was about 37% of that for H_2O_2 in the photolysis cell, the contribution of H_2O to the decay rate was very small, since the reaction rate constant of $Cl(^2P_{1/2})$ with H_2O_2 was ∼10 times larger than that
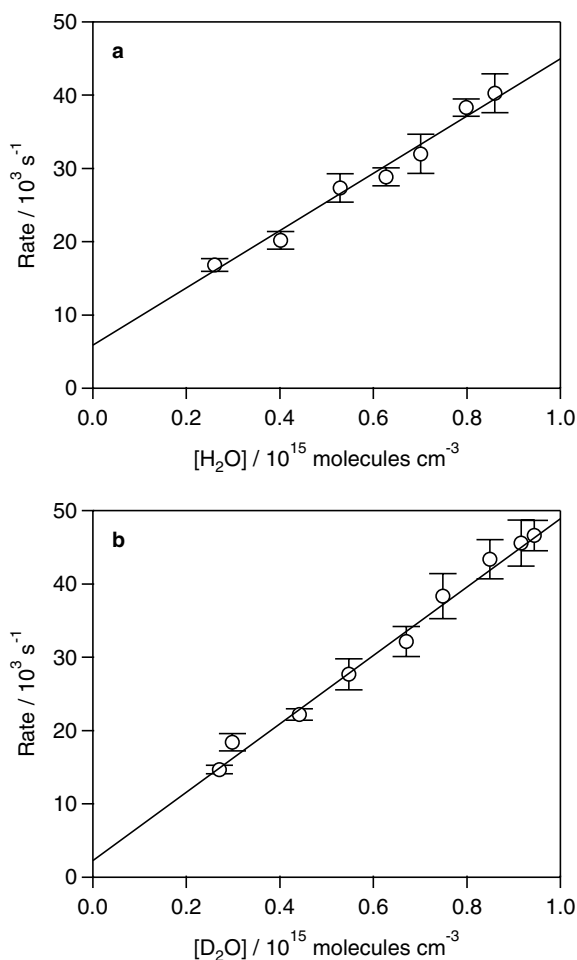
Fig. 2. Plot of decay rates against the concentrations of: (a) H_2O and (b) D_2O. The decay rates (open circles) are taken as averaged values over several measurements and error bars indicate those standard deviations. The contributions of the collisional quenching by HCl have been subtracted from the rate values.
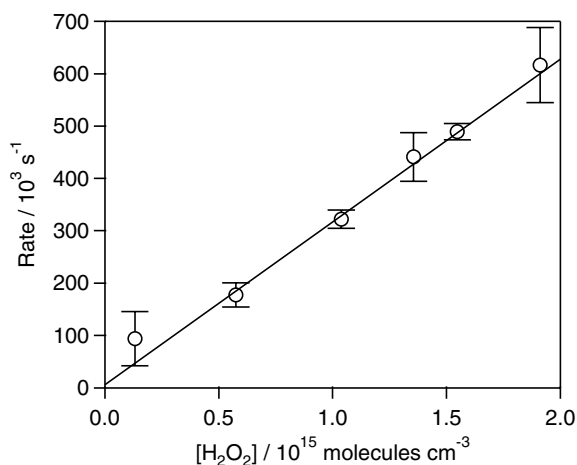

Fig. 3. Plot of decay rate values against the actual concentrations of H_2O_2. The decay rates (open circles) are taken as averaged values over several measurements and error bars indicate those standard deviations. The contributions of the collisional quenching by HCl and H_2O have been subtracted from the rate values.

of H_2O. The straight line is the results of weighted least-squares fits analysis. The rate constant of $(3.1 \pm 0.2) \times 10^{-10}$ cm^3 molecules^{-1} s^{-1} is given by the slope of the fit, where the analytical error is taken as 1σ. The upper limit of the estimation uncertainty of the H_2O contribution is 4%. After the uncertainty estimation for all the contributions, we determine the value of $(3.1 \pm 0.3) \times 10^{-10}$ cm^3 molecules^{-1} s^{-1} as the rate constant of the collisional quenching processes by H_2O_2.

A considerably fast process has been observed in the collisional quenching with H_2O_2. Energy exchange between the spin–orbit splitting energy of Cl atoms and the vibrational energy of H_2O_2 molecules seem to be driving this nonreactive relaxation process. A mathematical relationship between the quenching rate constant, k, and quencher's vibrations has been proposed by Chichinin [4]:

$$k = A \sum_i \frac{I_i}{\tilde{v}_i} \exp\left(-\frac{|\tilde{v}_i - \Delta\tilde{v}|}{B}\right), \quad (1)$$

where I_i and $\tilde{v}_i$ are the intensity and the wave number of the absorption band for the ith vibration mode in a quencher, respectively, $\Delta\tilde{v}$ is the spin–orbit splitting energy ($\Delta\tilde{v} = 882$ cm^{-1} in our case), $A = 145$ and $B = 77$ cm^{-1} are constants. Table 1 lists the rate constants k determined in the present experiment with the vibrational modes which seem to be dominant energy-exchange pathways. Since there is no available data for the band intensities, only the term for the vibrational resonance,

$$X_i = \exp\left(-\frac{|\tilde{v}_i - \Delta\tilde{v}|}{B}\right), \quad (2)$$

is listed in Table 1. The v_3 vibration in H_2O_2 is expected to be the mode most concerned with the collisional quenching. The vibration energies of v_3 in NF$_3$ (906 cm^{-1}), v_4 in COCl$_2$ (850 cm^{-1}), v_4 in CCl$_3$F (847 cm^{-1}), v_7 in CH$_2$Cl$_2$ (898 cm^{-1}), v_9 in CF$_2$Cl$_2$ (902 cm^{-1}), and v_6 in SF$_6$ (947 cm^{-1}) are close to the spin–orbit splitting energy; the quenching rate constants in collisions with these molecules are also large [4] and similar to the value for H_2O_2.

The rate constant for D_2O is 1.2 times larger than that for H_2O. This may be attributed to the fact that the vibrational frequency of D_2O is closer to the Cl spin–orbit energy difference than that of H_2O, although it is not quantitatively explained by the X_i values in Table 1. As both the

Table 1
Rate constants measured in the present study with the normal modes of the quenchers' vibrations which are expected to concern the energy-exchange from Cl($^2P_{1/2}$)

Quencher	Mode	$\tilde{v}_i$[a] (cm^{-1})	X_i	k (10^{-10} cm^3 molecules^{-1} s^{-1})
H_2O	v_2	1595	0.000095	0.39 ± 0.03
D_2O	v_2	1178	0.0098	0.47 ± 0.03
H_2O_2	v_2	1390	0.0021	3.1 ± 0.3
	v_3	870	0.86	
	v_4	370	0.0013	
	v_6	1270	0.0065	

[a] Refs. [10,18–22].

X_i values for H_2O and D_2O are quite small, it seems to be hard that the spin–orbit energy of Cl transfers to high-frequency vibrational modes. The energy-exchange between the spin–orbit energy and the rotational or translational energy in the collisional processes is suggested to be dominant [4,5]. The X_i factors are insufficient to interpret the present results quantitatively. Anyway, the mechanism of collisional relaxation processes of $Cl(^2P_{1/2})$ are not well understood so far. It may be useful for revealing the mechanisms to investigate isotope effects on the collisional quenching processes as performed in this study.

Acknowledgements

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