

## THE COLLISIONAL CROSS SECTIONS FOR QUENCHING OF OH( $A^2\Sigma^+$ ) BY HCl AND DCl DETERMINED BY TIME-RESOLVED RESONANCE FLUORESCENCE OH( $A^2\Sigma^+-X^2\Pi$ )

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### Summary

We present a study of the time-resolved resonance fluorescence OH( $A^2\Sigma^+-X^2\Pi$ , (0,0),  $\lambda = 307$  nm) following the pulsed irradiation of water vapour in the presence of excess helium. Stern-Volmer plots were constructed from the intercepts at  $t = 0$  of the A-X fluorescence in the presence of the gases HCl and DCl. Using previously published data for the fluorescence quenching of OH( $A^2\Sigma^+$ ) by  $H_2O$  and  $A_{nm}$  for the (0,0) transition as internal standards, quenching by helium being negligible, these plots were then employed to determine collisional cross sections for quenching for OH( $A^2\Sigma^+$ ). The following results were obtained:

$$\sigma_{HCl} = 68 \pm 18 \text{ \AA}^2$$

$$\sigma_{DCl} = 61 \pm 16 \text{ \AA}^2$$

which represent the first determination of these properties to the best of our knowledge. There is clearly no significant isotope effect. The cross sections are found to be in quantitative accord with correlations which indicate that the quenching processes are governed by the formation of an intermediate OH( $A^2\Sigma^+$ )-HCl (DCl) bound by the Lennard-Jones interaction energy.

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### 1. Introduction

The collisional quenching of OH( $A^2\Sigma^+$ ), 4.05 eV above the  $X^2\Pi$  ground state [1], is a topic of long-established fundamental interest within the general framework of electronic energy transfer from small molecules [2] and has been studied by a variety of techniques [3]. The recent measurements of Fairchild *et al.* [4], using laser-induced fluorescence of OH( $A^2\Sigma^+-X^2\Pi$ ) following laser pyrolysis, and of Clyne and Holt [5], who monitored resonance fluorescence of OH(A-X) in a flow discharge system in the pres-

ence of a large number of chlorocarbons, constitute useful summaries of modern measurements of fluorescence quenching of  $\text{OH}(\text{A}^2\Sigma^+)$ . From an experimental viewpoint, collisional quenching of  $\text{OH}(\text{A}^2\Sigma^+)$  is clearly of direct relevance in kinetic studies of ground state  $\text{OH}(\text{X}^2\Pi)$  where  $\text{OH}(\text{A}-\text{X})$  resonance fluorescence is used to monitor ground state OH radicals either in the steady mode in a flow discharge system or in the time-resolved mode in a pulsed system. The recent compilations of Baulch and coworkers [6, 7] and of Watson [8] essentially include reviews of the large number of kinetic studies of OH using A-X resonance fluorescence.

We have recently described detailed kinetic measurements of the reaction of  $\text{OH}(\text{X}^2\Pi)$  with HCl and DCl [9] following earlier investigations of the removal of OH by the hydrogen halides using time-resolved resonance fluorescence of  $\text{OH}(\text{A}-\text{X})$  following pulsed irradiation [10]. To the best of our knowledge, and to our surprise, the collisional cross sections  $\sigma$  for quenching of  $\text{OH}(\text{A}^2\Sigma^+)$  by neither HCl nor DCl have been reported. In this paper we describe the determination of these quantities using time-resolved resonance fluorescence. These are necessarily limited in accuracy in view of the effect of the sum of competing removal processes for  $\text{OH}(\text{A}^2\Sigma^+)$  from which that for collisional quenching by HCl or DCl must be extracted. Thus, in time-resolved resonance fluorescence measurements to study the reactions of OH with HCl, for example, where  $\text{H}_2\text{O}$  is the photochemical precursor and helium is the buffer gas in the flow system, removal of  $\text{OH}(\text{A}^2\Sigma^+)$  following optical excitation of the photochemically generated  $\text{OH}(\text{X}^2\Pi)$  will be governed by four competing processes. These are spontaneous emission for the A-X system and collisional quenching by  $\text{H}_2\text{O}$ , helium and HCl. Nevertheless, despite the fact that the contributions by HCl and DCl to the overall quenching of  $\text{OH}(\text{A}^2\Sigma^+)$  are relatively small in this type of system, values of  $\sigma$  for HCl and DCl have been determined. The results are compared with empirical correlations, between cross sections and Lennard-Jones interactions, that have been developed.

## 2. Experimental details

The details of the experimental arrangement for the kinetic study of  $\text{OH}(\text{X}^2\Pi)$  by time-resolved resonance fluorescence have been given in our previous paper [9]. Briefly,  $\text{OH}(\text{X}^2\Pi)$  was generated by the repetitive pulsed irradiation ( $E = 40 \text{ J}$ ;  $1 \text{ Hz}$ ) of  $\text{H}_2\text{O}$  through  $\text{CaF}_2$  optics ( $\lambda \geq 120 \text{ nm}$ ) in the presence of excess helium in a flow system kinetically equivalent to a static system [9, 10]. The photolysis source was a conventional spark discharge between molybdenum electrodes operating in a nitrogen atmosphere ( $1 \mu\text{F}$ ; about  $9 \text{ kV}$ ) with optical coupling to a stainless steel reactor further aided by means of an aluminized Cassegrain mirror. We have discussed the main photochemical processes for the photolysis of  $\text{H}_2\text{O}$  following Okabe [11] in the wavelength regions  $\lambda < 240 \text{ nm}$ ,  $\lambda < 177 \text{ nm}$  and  $\lambda < 140 \text{ nm}$  [9, 10]. It has been demonstrated that any  $\text{O}(2^1\text{D}_2)$  photochemically generated will

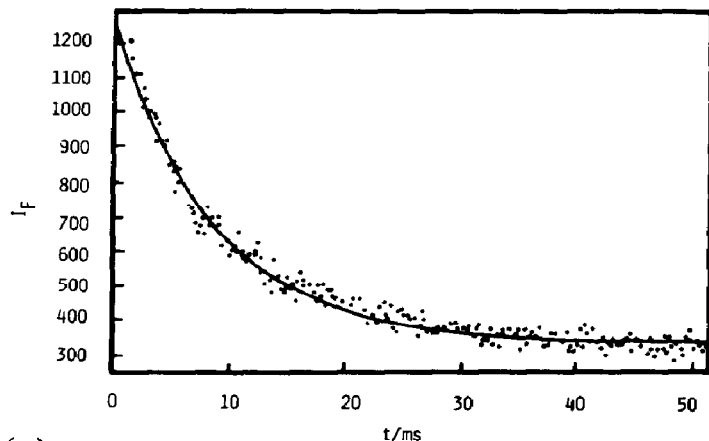
react rapidly to yield  $\text{OH}(\text{X}^2\Pi)$  [12 - 14] on the time scales of the kinetic measurements and that within these time scales any photochemically generated  $\text{OH}(\text{A}^2\Sigma^+)$  will be optically [15] and collisionally [2, 3] relaxed to  $\text{OH}(\text{X}^2\Pi)$ . Further, any  $\text{OH}(\text{X}^2\Pi, v'' = 1)$  resulting from pulsed irradiation will be deactivated to  $\text{OH}(\text{X}^2\Pi, v'' = 0)$  on a short time scale [16]. Thus,  $\text{OH}(\text{A}^2\Sigma^+)$  detected by the A-X resonance fluorescence arises only from  $\text{OH}(\text{X}^2\Pi)$  in the reactor, optically excited by means of the microwave-powered flow-lamp ( $2\% \text{H}_2\text{O}-\text{He}$ ;  $p_{\text{total}} \approx 0.8$  Torr (1 Torr =  $133 \text{ N m}^{-2}$ )) employing a Fehsenfeld cavity [17] and constituting the spectroscopic source. As before a "pinched plasma" was employed in the spectroscopic source [9] to reduce the effect of scattered light in the detection system. Optical isolation of the time-resolved resonance fluorescence at  $\lambda = 307 \text{ nm}$  ( $\text{OH}(\text{A}^2\Sigma^+-\text{X}^2\Pi, (0,0))$ ) was achieved by the combination of a broad band interference filter (Barr and Stroud type U1) with a long wavelength blocking filter (Oriel Scientific type UG11; thickness, 3 mm; transmission, about 74% at  $\lambda = 307 \text{ nm}$ , less than 0.1% at  $\lambda = 614 \text{ nm}$ ). The signals were detected by means of a high gain photomultiplier tube (EMI 9816 QB) (1.8 kV; Fluke power supply 408B) used with "pretrigger photomultiplier gating", initiated with the "thyatron double pulser" ( $\Delta T = 75 \mu\text{s}$ ) as described previously [10, 18]. Photon counting of the resonance fluorescence signals at  $\lambda = 307 \text{ nm}$  was carried out using an emitter follower for amplification and a discriminator (Panax Nucleonics AAU-11). The pulses were stored in the histogram module of a multiscalar (Data Laboratories DL 406), triggered externally by means of an aerial detecting electrical noise from the spark discharge. A decay trace was typically constructed from 128 individual sets of photon counts. In cases where a greater number of shots was necessary, full allowance was made in calculating the "counts per channel". The output was subsequently fed onto paper tape in ASCII code (Datadynamics 1133) for direct input into the University of Cambridge IBM 3081 computer. All materials were prepared as described previously [9].

### 3. Results and discussion

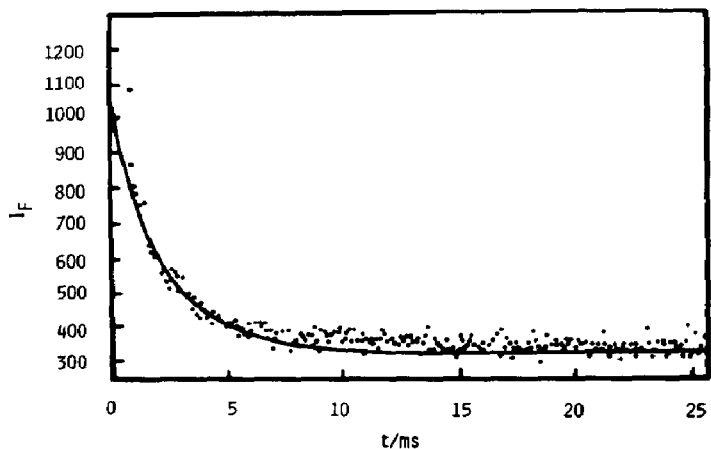
Figure 1(a) gives an example of the computerized output of the digitized time variation in the light intensity at  $\lambda = 307 \text{ nm}$ , indicating the decay of the A-X resonance fluorescence  $I_F$  at  $T = 300 \text{ K}$  due to ground state OH radicals following the pulsed irradiation of  $\text{H}_2\text{O}$  in the presence of excess helium buffer gas. Figure 1(b) shows the effect of the addition of HCl on the decay trace. We have shown [9, 10] that the resonance fluorescence decay signal is given by

$$I_F(\text{A-X}) = \frac{\phi[\text{OH}(\text{X}^2\Pi)_{t=0}] \exp(-k't)}{1 + \sum k_Q[\text{Q}]/A_{nm}} \quad (1)$$

where  $k'$  represents the overall first-order coefficient for the removal of  $\text{OH}(\text{X}^2\Pi)$  and is normally the object of kinetic interest as described [9, 10].



(a)



(b)

Fig. 1. Digitized time variation in the light intensity at  $\lambda = 307$  nm indicating the decay of resonance fluorescence  $I_F$  (counts per channel) ( $A^2\Sigma^+ - X^2\Pi$ , (0,0)) due to ground state OH radicals following the pulsed irradiation of  $H_2O$  in the presence of HCl at  $T = 300$  K for (a)  $[HCl] = 0.0$  molecules  $cm^{-3}$  and (b)  $[HCl] = 9.0 \times 10^{14}$  molecules  $cm^{-3}$  ( $E = 40$  J; repetition rate, 1 Hz; number of channels, 256;  $p_{He} = 5.8$  kN  $m^{-2}$ ;  $[H_2O] = 3.1 \times 10^{15}$  molecules  $cm^{-3}$ ): ..... , digitized data points; —,  $I_F = \theta_1 + \theta_2 \exp(-k't)$ .

$\phi$  represents the combination of terms due to excitation from the resonance source, light collection of the resonance fluorescence signal and electronic amplification. In the present experiments, it is the term  $\Sigma k_Q[Q]$ , representing fluorescence quenching of  $OH(A^2\Sigma^+)$  in the various rotational states that is of interest and, for the conditions of Fig. 1(b), would be given by  $k_{He}[He] + k_{H_2O}[H_2O] + k_{HCl}[HCl]$ . Thus,  $k_{HCl}$  would be the absolute second-order rate constant for the quenching of  $OH(A^2\Sigma^+)$  by HCl, for example.  $A_{nm}$  is the Einstein coefficient for  $OH(A^2\Sigma^+ - X^2\Pi, (0,0))$  and is taken as  $1.32 \times 10^6$   $s^{-1}$ , being the "preferred value" from the compilation of Schofield [3]. Radiation trapping is clearly negligible in this system involving photon counting (typically 40 counts per pulse) for an emitter of such relatively

low  $f$  value ( $f = 1.8 \times 10^{-4}$  [15]). The signals as presented in Fig. 1 are analysed according to the form [9, 10]

$$I_F(t) = \theta_1 + \theta_2 \exp(-k't) \quad (2)$$

where  $\theta_1$  represents steady scattered light due to the spectroscopic resonance source. Hence, the term  $\theta_2 \exp(-k't)$  is identified with the right-hand side of eqn. (1). The data are analysed according to eqn. (2) using the Lamfit procedure of Powell [19], yielding the full curves as given in Fig. 1. Thus, the term  $\theta_2$  is the object of determination in the present measurements.

We can see immediately from Fig. 1 that, apart from the decay of  $\text{OH}(\text{X}^2\Pi)$  being made more rapid with the addition of HCl, the intercept, *i.e.*  $\theta_2$ , is reduced. This represents the effect of fluorescence quenching of  $\text{OH}(\text{A}^2\Sigma^+)$  by HCl. For a series of measurements in which [HCl] is varied and  $[\text{H}_2\text{O}]$  and [He] are held constant, we may readily show from eqns. (1) and (2) that the ratio of the slope to the intercept for the plot of  $1/\theta_2$  against [HCl] is given by  $k_{\text{HCl}}/(A_{\text{nm}} + k_{\text{H}_2\text{O}}[\text{H}_2\text{O}] + k_{\text{He}}[\text{He}])$ . Firstly, the accuracy in the measurement of  $\theta_2$  is influenced by the value of  $\phi[\text{OH}(\text{X}^2\Pi)_{t=0}]$  which is in turn influenced by the reproducibility in OH photochemical generation and by the constancy in the light output from the spectroscopic resonance source. Secondly, the loss of  $\text{OH}(\text{A}^2\Sigma^+)$  resulting from quenching by HCl is a small fraction of the total loss. Hence, relatively small differences in the values of  $\theta_2$  with [HCl] are obtained. Thus, despite the ability to control [HCl],  $[\text{H}_2\text{O}]$  and [He], the present data do not support determination of all three collisional quenching rate constants. Hence, we employ the preferred value of  $A_{\text{nm}}$  following Schofield [3] ( $A_{\text{nm}} = 1.32 \times 10^6 \text{ s}^{-1}$ ) together with  $k_{\text{H}_2\text{O}} = 5.0 \pm 2.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [3]. Fairchild *et al.* [4] have shown this collisional quenching rate constant to be sensibly independent of temperature in contrast with previous workers [20]. The above value for  $k_{\text{H}_2\text{O}}$  corresponds to a cross section  $\sigma$  ( $k_{\text{Q}} = \sigma(8kT/\pi\mu)^{1/2}$ ) for quenching of  $59 \text{ \AA}^2$  ( $1 \text{ \AA} = 0.1 \text{ nm}$ ). Quenching of  $\text{OH}(\text{A}^2\Sigma^+)$  by helium can be neglected in the present system as the high pressure measurements of Black [3, 21] indicate that  $k_{\text{He}} < 10^{-14} \text{ cm}^3 \text{ atom}^{-1} \text{ s}^{-1}$  (300 K) ( $\sigma < 7 \times 10^{-4} \text{ \AA}^2$ ). Thus,  $k_{\text{He}}[\text{He}] < 1.3 \times 10^4 \text{ s}^{-1}$  for a typical experiment with  $p_{\text{He}} = 40 \text{ Torr}$  and is negligible compared with  $A_{\text{nm}}$ , for example. Thus, from the values of the ratios of the slopes to the intercepts of plots of  $1/\theta_2$  against [HCl] or [DCl] (Stern–Volmer plots), we can determine the collisional rate constants and cross sections for quenching for these two molecules.

Figure 2 gives examples of sets of Stern–Volmer plots for HCl in which [He] and  $[\text{H}_2\text{O}]$  are varied in each series of measurements. It can be seen that variations in  $\theta_2$  for concentrations of HCl that permit the determination of  $k'$  for  $\text{OH}(\text{X}^2\Pi)$  are only in the range from about 10% to 25%. Whilst  $k'$  is not the prime object of kinetic interest in the present investigations the decay of  $\text{OH}(\text{X}^2\Pi)$  must be carried out within a regime of [HCl] and [DCl] which allows the OH concentration profile to be fitted to eqn. (2). Considerably greater requirements are placed on reproducibility for the purpose

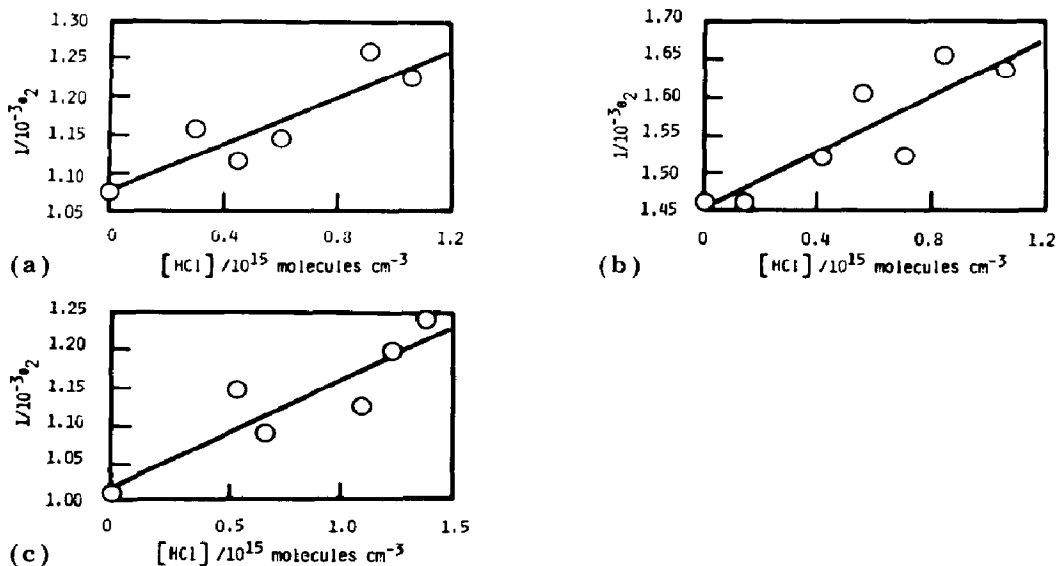


Fig. 2. Stern-Volmer plots ( $1/\theta_2$  vs.  $[\text{HCl}]$ ) for the collisional quenching of  $\text{OH}(\text{A}^2\Sigma^+)$  by  $\text{HCl}$  obtained by time-resolved resonance fluorescence measurements of  $\text{OH}(\text{A}^2\Sigma^+ - \text{X}^2\Pi, (0,0), \lambda = 307 \text{ nm})$  following the pulsed irradiation of  $\text{H}_2\text{O}$  in the presence of helium and  $\text{HCl}$  at  $T = 300 \text{ K}$ : (a)  $p_{\text{He}} = 5.8 \text{ kN m}^{-2}$ ,  $[\text{H}_2\text{O}] = 3.1 \times 10^{15} \text{ molecules cm}^{-3}$ ; (b)  $p_{\text{He}} = 5.9 \text{ kN m}^{-2}$ ,  $[\text{H}_2\text{O}] = 5.7 \times 10^{15} \text{ molecules cm}^{-3}$ ; (c)  $p_{\text{He}} = 1.34 \text{ kN m}^{-2}$ ,  $[\text{H}_2\text{O}] = 4.7 \times 10^{15} \text{ molecules cm}^{-3}$ .

of determining  $\theta_2$  than for  $k'$  which, when expressed in the standard form

$$k' = K + k_{\text{R}}[\text{R}] \quad (3)$$

where  $\text{R} \equiv \text{HCl}$  or  $\text{DCl}$  yielded

$$k_{\text{R}}^{\text{HCl}}(300 \text{ K}) = (6.70 \pm 0.46) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (error, } 2\sigma)$$

$$k_{\text{R}}^{\text{DCl}}(300 \text{ K}) = (3.75 \pm 0.22) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (error, } 2\sigma)$$

These are entirely in accord with the preferred values from extensive data compilations:

$$k_{\text{R}}^{\text{HCl}}(300 \text{ K}) = 6.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

from ref. 6 and

$$k_{\text{R}}^{\text{DCl}}(300 \text{ K}) = 3.43 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

from refs. 6 and 22. Hence, the ratios of the slopes to the intercepts in plots of the type given in Fig. 2, with similar plots for  $\text{DCl}$ , an example of which is given in Fig. 3, yield the following rate constants and quenching cross sections for  $\text{OH}(\text{A}^2\Sigma^+)$  ( $T = 300 \text{ K}$ ):

$$k_{\text{HCl}} = (5.0 \pm 1.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{DCl}} = (4.5 \pm 1.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

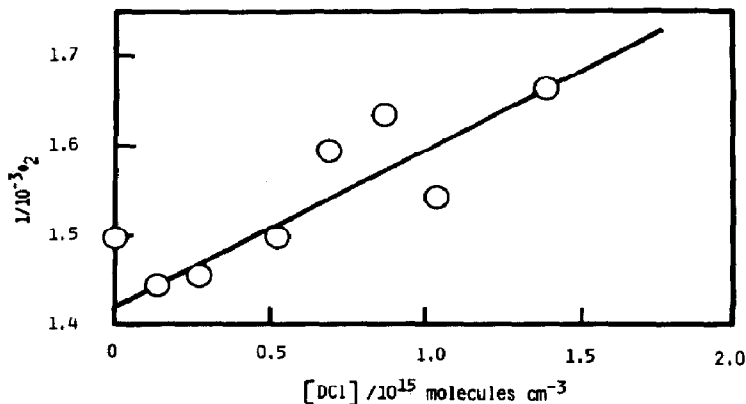


Fig. 3. Stern-Volmer plot ( $1/\theta_2$  vs.  $[\text{DCl}]$ ) for the collisional quenching of  $\text{OH}(\text{A}^2\Sigma^+)$  by  $\text{DCl}$  obtained by time-resolved resonance fluorescence measurements of  $\text{OH}(\text{A}^2\Sigma^+ - \text{X}^2\Pi, (0,0))$ ,  $\lambda = 307 \text{ nm}$  following the pulsed irradiation of  $\text{H}_2\text{O}$  in the presence of  $\text{DCl}$  at  $T = 300 \text{ K}$  ( $p_{\text{He}} = 1.40 \text{ kN m}^{-2}$ ;  $[\text{H}_2\text{O}] = 4.5 \times 10^{15} \text{ molecules cm}^{-3}$ ).

$$\sigma_{\text{HCl}} = 68 \pm 18 \text{ \AA}^2$$

$$\sigma_{\text{DCl}} = 61 \pm 16 \text{ \AA}^2$$

The confidence limits in these data represent one standard deviation from plots of the type shown in Figs. 2 and 3, averaged from the sets of data available. These results, to the best of our knowledge, represent the first measurements of these quantities.

Apart from their use in designing experimental measurements on  $\text{OH}(\text{A}-\text{X})$  resonance fluorescence in the presence of these gases, the immediate fundamental result is the absence of a significant isotope effect. The magnitudes of the results are similar to that for  $\text{H}_2\text{O}$  where the preferred value for  $k_{\text{H}_2\text{O}}$  [3] (see above) yields  $\sigma_{\text{H}_2\text{O}}$  in the range 35 - 83  $\text{\AA}^2$ . Finally, Fairchild *et al.* [4] have correlated cross sections for quenching for  $\text{OH}(\text{A}^2\Sigma^+)$  with the standard Lennard-Jones interaction energy  $\epsilon_{\text{MM}}$  for a range of gases (M). This correlation has been cast in a linear form consistent with the calculations of Lin *et al.* [23] who have calculated cross sections in general based on an intermediate complex  $\text{OH}(\text{A}^2\Sigma^+) - \text{M}$  bound by the Lennard-Jones interaction energy. The resulting correlation is of the form [4, 23]

$$\ln \sigma_{\text{M}} = \ln C + \beta \left( \frac{\epsilon_{\text{MM}}}{k} \right)^{1/2} \quad (4)$$

where  $\ln C = 0.6$  and  $\beta = 0.19 \text{ K}^{-1/2}$ . For a Lennard-Jones interaction energy for both  $\text{HCl}$  and  $\text{DCl}$  expressed in the form  $(\epsilon_{\text{MM}}/k)^{1/2} = 18.9 \text{ K}^{1/2}$  [23], this yields  $\sigma_{\text{HCl, DCl}} = 66 \text{ \AA}^2$ . The close agreement with the present result is fortuitous as there is a large spread in the data on which the correlation using eqn. (4) is based [4, 23]. However, the general nature of the agreement between the present results and the extrapolation to  $\text{HCl}$  and  $\text{DCl}$  using the correlation of Fairchild *et al.* [4, 23] does indicate that the Lennard-Jones interaction between  $\text{OH}(\text{A}^2\Sigma^+)$  and  $\text{HCl}$  and  $\text{DCl}$  dominates the rate of the collisional quenching process.

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