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## ADVERTISEMENT



## Time-resolved resonance Raman study of the spectroscopy and kinetics of the $Cl_2^-$ radical anion in aqueous solution

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The resonance Raman spectrum of the chlorine molecular anion  $Cl_2^-$  has been obtained using pulsed laser photolysis as a radical production method. The fundamental and nine overtone transitions are observed. Analysis of the vibrational progression gives the vibrational constants  $\omega_e = 277.0 \pm 0.3 \text{ cm}^{-1}$  and  $\omega_e \chi_e = 1.83 \pm 0.05 \text{ cm}^{-1}$ ; these constants give an upper limit dissociation energy of  $1.3 \pm 0.1 \text{ eV}$  (all errors are  $1\sigma$ ). Time-resolved resonance Raman spectroscopy has been employed to study the kinetics of  $Cl_2^-$  disproportionation. A disproportionation rate coefficient of  $(11 \pm 7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  is obtained where the reported error includes  $1\sigma$  precision and estimates of systematic errors. A resonance Raman detection limit for  $Cl_2^-$  of  $5 \times 10^{-6}$  M has been obtained.

#### INTRODUCTION

Environmental concern over the problem of acid deposition has led to a renewed interest in the kinetics and mechanisms of acid generation in cloud water.<sup>1-8</sup> We are attempting to develop experimental techniques based on pulsed laser photolysis (PLP) coupled with long path absorption (LPA) and time-resolved resonance Raman spectroscopy  $(TR^3)$  to study the aqueous phase kinetics of a number of small inorganic species [including OH, HO<sub>2</sub>, NO<sub>3</sub>,  $SO_x^-$ (x = 3-5), and  $Cl_2^{-1}$  which are thought to be reactive intermediates in cloud water chemistry. Pulsed laser photolysis offers several advantages over radical production techniques such as pulse radiolysis and broad band flash photolysis which have been commonly used in aqueous kinetic studies. These include (i) monochromatic photolysis which allows high selectivity in radical production, (ii) accurate calculation of initial radical concentrations requiring only the absorption coefficient of the precursor, the quantum yield for radical production, and the photon flux, and (iii) submicrosecond time resolution. Recent studies of NO<sub>3</sub> and SO<sub>4</sub><sup>-</sup> using pulsed laser photolysis coupled with LPA detection have demonstrated significant improvements in selectivity of radical production and sensitivity of radical detection compared with more conventional techniques.<sup>9-11</sup>

In this paper we report data on the  $Cl_2^-$  radical anion obtained using pulsed laser photolysis as our radical source and TR<sup>3</sup> as the detection technique. The sensitivity of the TR<sup>3</sup> technique does not appear to be comparable to that which can be attained using LPA detection. However, TR<sup>3</sup> detection offers potential improvements over LPA in both time resolution and detection selectivity. Also, much more structural information is attainable from TR<sup>3</sup> spectra than from LPA spectra. While TR<sup>3</sup> has been finding increasing use as a technique for monitoring transient species in solution,<sup>12</sup> the majority of studies have involved large organic molecules and have been spectroscopic in nature. Little quantitative kinetic data has been reported. There have been two previous studies of the TR<sup>3</sup> spectrum of  $Cl_2^-$ , both of which utilized pulse radiolysis as the radical source.<sup>13,14</sup> Relatively small discrepancies in the positions of the fundamental and overtone bands reported in the two studies have produced a major discrepancy in the calculated anharmonicity of the ground state potential of  $Cl_2^-$ , and hence in the  $Cl_2^$ dissociation energy. This work resolves this discrepancy and also presents sensitivity limits and preliminary kinetic data demonstrating the potential utility of TR<sup>3</sup> for aqueous phase kinetic studies of small inorganic radicals.

#### **EXPERIMENTAL TECHNIQUE**

Our basic experimental approach was similar to that reported in a number of  $TR^3$  studies.<sup>12</sup> We employed both a two-laser photolysis-probe configuration, and also a single-laser configuration with the single laser serving as both the photolysis and resonance Raman excitation source.

The basic configuration for the two-laser experiments is shown schematically in Fig. 1. It consists of (1) a quartz sample cell, (2) a photolysis laser, (3) a probe laser, and (4)a detection system composed of collection optics, a triple spectrograph, a gated, intensified reticon detector, and an optical multichannel analyzer.

Two different sample cells were employed. One was a



FIG. 1. Schematic of the PLP-TR<sup>3</sup> apparatus: EX—excimer laser; GID gated intensified diode array detector; HYP—high voltage gate pulser; L lens; M—mirror; OMA—optical multichannel analyzer; P—peristaltic pump; S—sample; T—trigger line; TM—triplemate spectrograph.

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flow cell designed for dye laser operation (NSG Precision Cells) while the other was a length of 2 mm i.d. quartz tubing. Reaction mixtures were circulated through the cells using a peristaltic pump and viton tubing. For some experiments a static cell was used which consisted of a length of the quartz tubing.

The photolysis laser was a KrF excimer laser (Lambda Physik EMG200E;  $\lambda = 248$  nm; pulse width = 25 ns). The photolysis beam was focused into the reaction mixture using a 1 m focal length quartz lens. Typical photolysis energies at the cell were 150 mJ in an area  $\approx 0.3$  cm<sup>2</sup>.

The probe laser was a frequency tripled Nd-Yag laser (Quanta Ray DCR-2). The 355 nm output, typically 5-10 mJ/pulse, 5 ns pulse width, was focused into the reaction mixture using a 35 cm focal length lens. The photolysis and probe lasers operated at 10 Hz and were triggered by two channels of a digital delay generator, thus allowing the delay between the photolysis and probe pulses to be varied in kinetic runs.

Laser energies were measured using a Scientech disk calorimeter and the area of the photolysis beam was estimated from burn patterns on thermal paper.

The experiments utilized a 90° scattering configuration with the scattered Raman light being collected by two 80 mm diameter glass lenses and focused into the triple spectrograph (SPEX triplemate). The spectrograph stage was equipped with an 1800 lines/mm holographic grating; the instrumental dispersion was 0.023 nm/optical channel. The reticon detector (EG&G PARC 1420) had 700 active elements and was operated in a gated mode using a fast highvoltage pulser (EG&G PARC 1302) with a 10 ns gate width. Signals were processed by an optical multichannel analyzer (EG&G PARC 1460).

Since the discrepancies in the two previous studies<sup>13,14</sup> are the result of relatively small differences in the frequency assignments of the fundamental and overtone bands of  $Cl_2^-$ , and since this work represents our first study using TR<sup>3</sup>, we took great care to establish the accuracy of our frequency calibration. The spontaneous Raman spectra of carbon tetrachloride  $(CCl_4)$ , chloroform  $(CHCl_3)$ , acetonitrile  $(CH_3CN)$ , benzene  $(C_6H_6)$ , and toluene  $(C_6H_5CH_3)$  were obtained under identical conditions. Literature values<sup>15</sup> for the Raman lines of CHCl<sub>3</sub>, CCl<sub>4</sub>, CH<sub>3</sub>CN, and C<sub>6</sub>H<sub>6</sub> were used to calibrate the diode array using the OMA calibration software. Both a nonlinear calibration in wave numbers and a linear calibration in wavelength relative to an excitation wavelength  $\lambda_{\rm vac} = 354.81 \text{ nm}^{16}$  were used. Toluene was treated as an unknown and its line positions determined using both calibrations. The results, shown in Table I, demonstrate that both procedures give excellent results and indicate a calibration accuracy of better than  $\pm 2 \text{ cm}^{-1}$ /optical channel. A calibration spectrum was obtained after all runs on Cl<sub>2</sub> without altering the spectrometer, cell position, or excitation beam. Frequency assignments were made relative to the calibration spectrum.

The salts used in this study were obtained from Aesar and had the following stated minimum purities: potassium peroxydisulfate,  $K_2S_2O_8$ , 99%; potassium chloride, KCl, 99%. Water was purified by a Millipore Milli-Q system

TABLE I. Comparison of observed toluene frequencies  $(cm^{-1})$  with literature values.

Literature value	Nonlinear calibration	Linear calibration
217ª	216.1	216.8
346ª	345.7	345.2
521ª	521.5	520.8
623ª	620.6	619.9
786, <sup>6</sup> 784*	785.1	785.3
1004 <sup>a,b</sup>	1002.9	1003.5
1030,° 1029 <sup>b</sup>	1028.7	1029.4
1211ª	1210.2	1209.6
1380 <sup>a</sup>	1380.6	1378.8
1605ª	1604.8	1604.6

\*Reference 15(a).

<sup>b</sup>Reference 15(b).

equipped with filters for removing particulates, ions, and organics.  $D_2O$  (Bio-Rad 99.8 mol %  $D_2O$ ) was used as supplied. Chlorine gas,  $Cl_2$ , was high purity grade, minimum purity 99%.

#### **RESULTS AND DISCUSSION**

#### Spectroscopy of Cl<sub>2</sub>

Our initial attempts at generating  $Cl_2^-$  utilized the 248 nm photolysis of the persulfate radical  $(S_2O_8^{2-})$  to produce  $SO_4^-$  in the presence of chloride  $(Cl^-)$ :

$$S_2 O_8^{2-} + h\nu \to 2SO_4^-,$$
 (1)

$$SO_4^- + Cl^- \to SO_4^{2-} + Cl,$$
 (2)

$$Cl + Cl^{-} \rightarrow Cl_{2}^{-}.$$
 (3)

Figure 2 shows a plot of the spectrum observed in the  $400-1200 \text{ cm}^{-1}$  region with the 355 nm probe laser firing 50 ns after photolysis of a solution containing  $S_2O_8^{2-}$  (5×10<sup>-2</sup> M) and  $Cl^{-}$  (0.5 M). The spectrum was obtained by averaging 800 shots with both lasers firing and then subtracting a "background" with only the probe laser firing. Both the "signal" and background spectra contained a broad nonresonant feature as a result of scattering from the cell walls. Since the background solution did not contain the strongly absorbing  $Cl_2^-$ , the nonresonant feature was considerably larger than in the signal spectrum; it was normalized to corresponding nonresonant points before subtraction. Under these conditions the 1/e times for reactions (2) ( $k_2$ =  $3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) and (3)  $(k_3 = 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})$ are 10 and 0.1 ns, respectively.<sup>11,17</sup> The spectrum in Fig. 2 shows the first three overtones of  $Cl_2^-$ ; however, the second and third overtones are distorted by the incomplete subtraction of the spontaneous Raman scattering from the  $S_2O_8^2$ ion (833,  $1081 \text{ cm}^{-1}$ <sup>18</sup>), which complicates an accurate assignment of their positions. We therefore attempted an alternate Cl<sub>2</sub><sup>-</sup> production scheme using 355 nm photolysis of chlorine saturated water in the presence of chloride ion,

$$Cl_2 + h\nu \rightarrow 2Cl,$$
 (4)

followed by reaction (3). As noted previously, with  $[Cl^-] = 0.5$  M the 1/e time for reaction (3) is 0.1 ns. Hence,  $Cl_2^-$  is formed rapidly within the 5 ns time period of



FIG. 2. First three overtone bands of  $Cl_2^-$  obtained using excimer laser photolysis of persulphate as the initial radical source.

the laser pulse, which then also serves as the Raman excitation source. Figure 3 shows a resonance Raman spectrum of  $Cl_2^-$  in the region 200–2600 cm<sup>-1</sup> obtained using the singlelaser configuration. The spectrum is a composite of several different spectral scans, each containing an overlapping band which was used to normalize the intensities. For the 200-1200  $\text{cm}^{-1}$  region, which contains the fundamental and first three overtone bands, spectra were obtained by averaging 5000 laser shots and then subtracting a background spectrum of water. The background spectrum was again normalized to corresponding nonresonant features in the signal spectrum before subtraction. At higher frequencies this procedure was not possible since a broad nonresonant background was present which was larger in  $Cl_2^-$  spectra than in the water background. This was the case for both  $S_2O_8^{2-}/$ Cl<sup>-</sup> and Cl<sub>2</sub>/Cl<sup>-</sup> solutions. As an additional complication, a Raman line of water at  $\approx 1650 \text{ cm}^{-1}$  (the  $v_2$  bending



FIG. 3. Resonance Raman spectrum of  $Cl_2^-$  obtained using 355 nm photolysis of  $Cl_2/H_2O$  solution.

mode) overlaps the fifth overtone of  $Cl_2^-$  and distorts its shape. A series of experiments using  $Cl_2/Cl^-/D_2O$  in a static cell were performed after establishing that the flowing and static systems gave identical results for  $Cl_2/Cl^-/H_2O$  solutions. These spectra, shown in Fig. 4, were used to obtain accurate frequency assignments for the fifth overtone. The band centers and bandwidths in Table II were obtained by simulating the band shapes with a Gaussian function and visually obtaining the best fit. A Gaussian was found to give a rather better approximation to the actual band shapes than a Lorentzian. Figure 4 includes the simulated band shapes for these bands.

The frequency of the  $Cl_2^-$  vibration is such that the v = 1 level is significantly populated at room temperature. Hence, observed spectra contain some contributions from "hot bands" which result in a small shift in band positions. Tripathi *et al.*<sup>14</sup> have estimated that the contribution of the 2–1 and higher overtones results in the observed frequency of the fundamental being shifted 0.8 cm<sup>-1</sup> below that of the 1–0 band. This effect is smaller than the uncertainty in our band positions and we made no attempt to correct for it.

Taking the equation<sup>19</sup> for the observed frequency,  $\tilde{\nu}_{v}$  of a transition of an anharmonic oscillator, and ignoring anharmonic constants higher than quadratic, gives

$$\frac{\tilde{\nu}(v)}{v} = (\omega_e - \omega_e \chi_e) - \omega_e \chi_e v.$$
(I)

A plot of  $\tilde{\nu}(v)/v$  vs v, constructed using our observed frequencies for the  $\text{Cl}_2^-$  fundamental and overtone bands, is shown in Fig. 5. We obtain the linear relationship predicted by Eq. (I) for v = 1-8; the points from the eighth and ninth overtones appear to show the effects of anharmonic terms higher than quadratic; however, the problems of obtaining background subtraction and the broad bandwidths of these bands results in a considerable uncertainty in their position. An unweighted least-squares analysis of the data for v = 1-8in Table II gives the harmonic frequency constant  $\omega_e \chi_e$  $= 277.0 \pm 0.3 \text{ cm}^{-1}$  and the anharmonic constant  $\omega_e \chi_e$  $= 1.83 \pm 0.05$  (errors are  $1\sigma$  and refer to precision only). Assuming all higher order anharmonicity terms are negligible, the  $\text{Cl}_2^-$  dissociation energy can be calculated from the following relationship<sup>19</sup>:

$$D_e = \omega_e^2 / 4 \omega_e \chi_e. \tag{II}$$

The result is  $D_e = 1.3 \pm 0.1$  eV. Since higher order anharmonicity terms may become important near the dissociation limit, the value for  $D_e$  calculated from Eq. (II) should be considered only an upper limit for the true dissociation energy.

#### Comparisons with previous work

The resonance Raman spectrum of  $Cl_2^-$  has previously been observed in a low-temperature matrix<sup>20</sup> and in aqueous solution.<sup>13,14</sup> Both of the aqueous phase studies were similar in approach to the present work with the most significant difference being that they utilized pulse radiolysis of acidic  $(pH \approx 1)$  chloride solutions to generate  $Cl_2^-$  via the reaction sequence

$$OH + Cl^{-} \rightarrow ClOH^{-}, \tag{5}$$



FIG. 4. Overtone bands of  $Cl_2^-$  in the 900–2000 cm<sup>-1</sup> region. (a)  $D_2O$ ; (b) simulated; (c)  $H_2O$ .

$$ClOH^{-} + H^{+} \rightarrow Cl + H_{2}O, \tag{6}$$

$$Cl + Cl^{-} \rightarrow Cl_{2}^{-} . \tag{3}$$

In this work  $Cl_2^-$  was produced in neutral solution. Table II contains a comparison of the observed frequencies reported in each study together with calculated frequencies based on the reported harmonic and anharmonic frequency constants. Our observed frequencies are in excellent agreement with those of Tripathi *et al.* and lie 6 cm<sup>-1</sup> below those reported for the fundamental and first two overtones by Wilbrandt *et al.* Table III contains a comparison of the reported harmonic frequency constants and anharmonic frequency constants and the corresponding upper limit estimates of the dissociation energy,

together with values obtained in matrix isolation studies and calculated gas phase values.

The dissociation energy obtained in this work,  $1.3 \pm 0.1$  eV, is in good agreement with the average value obtained in matrix isolation experiments,  $1.28 \pm 0.10$  eV.<sup>20</sup> It also agrees well with the values  $1.28^{21}$  and 1.24 eV<sup>22</sup> obtained from theoretical calculations of  $Cl_2^-$  potential curves, and with the values  $1.26 \pm 0.1^{21}$  and  $1.25 \pm 0.11$  eV<sup>20</sup> obtained from thermodynamic calculations. While somewhat lower, our result also agrees within combined error limits with the aqueous phase value obtained by Tripathi *et al.*,  $1.6 \pm 0.2$  eV.<sup>14</sup> In fact, the fundamental and anharmonic constants obtained in this work appear to reproduce the observed fre-

TABLE II. Experimental and calculated frequencies  $(cm^{-1})$  for the fundamental and overtone bands of  $Cl_2^{-1}$  in aqueous solution.

	This work		Tripathi et al. (Ref. 14)		Wilbrandt et al. (Ref. 13)		
	$\tilde{\nu}_{obs}$	$\Delta \tilde{\nu}_{1/2}^{a}$	$\tilde{\nu}_{\mathrm{calc}}$	$\tilde{v}_{obs}$	$\tilde{\nu}_{ m calc}$	$\tilde{\nu}_{\rm obs}$	$\tilde{\nu}_{\mathrm{calc}}$
1←0	$273 \pm 2$	30	273.3	271	270.1	279	278.8
2 ← 0	$543 \pm 2$	50	543.0	542	537.3	549	549.9
3⊷0	809 ± 2	70	809.0	808	801.6	814	813.3
4⊷0	$1071 \pm 2$	90	1071.4	1070	1063		
5 ←0	$1333 \pm 3$	110	1330.1	1333	1321.5		
6⊷0	$1585 \pm 10$	115	1585.1	1582	1577.1		
7⊷0	$1836 \pm 10$	150	1836.5	1836	1829.8		
8⊷0	2081 + 10	190	2084.2	2088	2079		
9⊷0	$2305 \pm 10$		2328.3				
10←0	$2545 \pm 10$		2568.7				

\*Uncertainty is  $\pm 5 \text{ cm}^{-1}$ .

(



FIG. 5. Plot of  $\tilde{v}(v)$  vs v. The solid line is obtained from a linear least squares analysis of the data up to v = 8. The vibrational constants  $\omega_e$  and  $\omega_e \chi_e$  are obtained from the slope and intercept of the solid line.

quencies of Tripathi *et al.* rather more closely than the constants which they estimated, indicating that their anharmonic constant may be a little too low. In contrast, as a result of a relatively small shift in their frequency assignments of the fundamental and first two overtones, Wilbrandt *et al.* obtained a significantly higher anharmonicity and lower dissociation energy than other studies.<sup>13</sup> They rationalized this difference by considering dissociation in terms of the process

$$\operatorname{Cl}_{2}^{-}(\operatorname{aq}) \to \operatorname{Cl}(\operatorname{aq}) + \operatorname{Cl}^{-}(\operatorname{aq})$$
 (7)

and ascribing the reduction in dissociation energy to the energies of hydration of Cl and Cl<sup>-</sup>. However, Tripathi *et al.*<sup>14</sup> have pointed out that solvation is unlikely to occur on the very fast time scale of dissociation.

Our results indicate that solution hydration has no ef-

fect on the electronic structure of  $Cl_2^-$ , a conclusion that is supported by the fact that  $Cl_2^-$  absorption spectra in the gas phase and in aqueous solution are almost identical. In the gas phase, Lee *et al.* obtain a  $Cl_2^-$  absorption cross section of  $(3.5 \pm 0.3) \times 10^{-17}$  cm<sup>2</sup> averaged over the wavelength range 350.7-356.9 nm,<sup>23</sup> while Jayson *et al.* obtain a cross section of  $(3.4 \pm 0.2) \times 10^{-17}$  cm<sup>2</sup> at 340.0 nm in aqueous solution.<sup>24</sup> As noted by Lee *et al.*, the potential curves for  $Cl_2^-$  in alkali halide crystals resemble those in the gas phase; it appears that this conclusion can be extended to the aqueous phase as well. Similar findings have been reported in resonance Raman studies of  $MnO_4^-$ ,<sup>25</sup> where the fundamental and anharmonic constants are almost identical in the solid and aqueous phase. In resonance Raman studies of  $I_{22}^{-26}$ the fundamental and anharmonic constants in the gas phase and a number of solvents were found to be almost identical.

One possible explanation of the results of Wilbrandt *et al.*<sup>13</sup> is a miscalibration of their detector by one optical channel. Since their dispersion was  $4 \text{ cm}^{-1}$ /optical channel, this would be consistent with the  $\approx 6 \text{ cm}^{-1}$  difference between their assignments of the fundamental and first two overtones and those obtained in this work.

#### Overtone bandwidths

Table II contains our estimates of the half-bandwidth of the fundamental and first seven overtones; these estimates were obtained by simulating the band shapes with a Gaussian function. We made no attempt to account for the fact that the lines are composites of the transitions of the three isotopic species  ${}^{35}Cl_2^{-}$ ,  ${}^{37}Cl_2^{-}$ , and  ${}^{35}Cl^{37}Cl^{-}$ . Isotopic splittings are known from matrix isolation studies<sup>20</sup> to be much smaller than the observed bandwidths. The eighth and ninth overtones appear to overlap each other to such an extent that estimates of their bandwidths were not possible. Our estimate of the fundamental bandwidth,  $30 \pm 5$  cm<sup>-1</sup>, agrees reasonably well with that obtained by Tripathi *et al.*, 23 cm<sup>-1</sup>.<sup>14</sup>

Overtone broadening appears to be characteristic of resonance Raman spectra in solution and has also been observed in the gas and solid phases. There appear to be few detailed studies of overtone broadening as a function of vi-

$\omega_e (\mathrm{cm}^{-1})$	$\omega_e \chi_e (\text{cm}^{-1})$	$D_e(ev)$	Phase	Reference
277.0 ± 0.3	1.83 ± 0.05	$1.3 \pm 0.2$	Aqueous	This work
286.4	3.83	0.66	Aqueous	13
273	1.45	$1.6 \pm 0.2$	Aqueous	14
263.7 ± 0.6	$1.71 \pm 0.12$	$1.26 \pm 0.09$	Low temperature matrix <sup>a</sup>	20
_		$1.28 \pm 0.10$	Low temperature matrix <sup>b</sup>	20
260		1.28	Self-consistent-field calculation of gas phase potential energy curves	21
258	1.5	1.24	Calculation of gas phase potential energy curves	22
		$1.26 \pm 0.1$	Thermodynamic estimate	21
		$1.25 \pm 0.11$	Thermodynamic estimate	20

TABLE III. Spectroscopic constants for  $Cl_2^-$  ( ${}^{2}\Sigma_{\mu}^+$ ).

 ${}^{*}Rb^{+35}Cl_{2}^{-}.$   ${}^{b}Average of M^{+}Cl_{2}^{-} (M = Li,Rb,Cs).$ 

brational quantum number, and no theoretical studies of this phenomenon. Our measured bandwidths increase linearly as a function of vibrational quantum number; a similar dependence was also noted by Tripathi *et al.* although they do not report overtone bandwidths. Overtone bandwidths have been reported for IBr<sup>27</sup> and  $MOS_4^{-28}$ ; they also show a linear dependence on v. Kiefer and Bernstein studied the bandwidth variation of  $MnO_4^{-}$  resonance Raman spectra in solution and in solid  $KMnO_4$ .<sup>25</sup> They observed an overtone broadening which was nonlinear as a function of vibrational quantum number and slightly different in the solid and liquid phases. The origin of the broadening is unclear. Interestingly, broadening is not observed in the resonance Raman spectra of  $Cl_2^{-}$  and  $O_3^{-}$  in low temperature matrices.<sup>20,29</sup>

#### Kinetics of Cl<sub>2</sub> disproportionation

A study of the kinetics of  $Cl_2^-$  disproportionation was undertaken in order to test the feasibility of employing the PLP-TR<sup>3</sup> technique to study the aqueous phase kinetics of small inorganic radicals and to establish sensitivity limits for TR<sup>3</sup> detection of  $Cl_2^-$  under "kinetic" conditions.

The  $Cl_2^-$  disproportionation reaction

$$Cl_{2}^{-} + Cl_{2}^{-} \rightarrow Cl_{3}^{-} + Cl^{-}$$
 (4)

is a second order process whose kinetics are described by Eq. (III):

$$\frac{-d\left[\mathrm{Cl}_{2}^{-}\right]}{dt} = 2k_{4}\left[\mathrm{Cl}_{2}^{-}\right]^{2}.$$
 (III)

If  $Cl_2^-$  is produced on a time scale which is very rapid compared with loss processes, and if reaction (4) is the only significant loss process, then the  $Cl_2^-$  temporal profile is governed by Eq. (IV):

$$[Cl_2^-]_t^{-1} - [Cl_2^-]_0^{-1} = 2k_4t.$$
 (IV)

Observation of a linear  $[Cl_2^-]_{,}^{-1}$  vs t dependence gives a strong indication that secondary kinetic complications are absent and that any first order component in the  $Cl_2^-$  decay is negligible. The bimolecular rate coefficient  $2k_4$  is obtained from the slope and intercept of a  $[Cl_2^-]_{,}^{-1}$  vs t plot. Consequently, it is necessary to relate the observed  $Cl_2^-$  TR<sup>3</sup> signal to the absolute  $Cl_2^-$  concentration.

Analysis of the concentration dependence of the TR<sup>3</sup> signal is complicated by the fact that the species under study absorbs both the excitation source and the scattered resonance Raman signal. As a consequence the scattered resonance Raman signal does not vary linearly with concentration. Atkinson et al.<sup>30</sup> have shown that the TR<sup>3</sup> signal can be normalized to the normal Raman scattering of a solvent band to give a quantity which is proportional to the concentration of the resonance Raman scatterer, and therefore useful for kinetic analysis. We were unable to use this procedure since water does not have a suitable Raman band. However, as noted previously, the 273 cm<sup>-1</sup> Cl<sub>2</sub><sup>-1</sup> fundamental signal was superimposed on a broad nonresonant background which appeared to originate from scattering from the cell walls. This background was reduced in the presence of  $Cl_2^{-1}$ and so the Cl<sub>2</sub><sup>-</sup> signal was normalized to off-resonance portions of the background to give a quantity proportional to  $[Cl_2^-]$ . As noted previously, at  $[Cl^-] = 0.5$  M, the reaction sequence (1)–(3) converts the SO<sub>4</sub><sup>-</sup> produced by S<sub>2</sub>O<sub>8</sub><sup>2-</sup> photolysis to Cl<sub>2</sub><sup>-</sup> with a l/e time of 10 ns. The only potential competing SO<sub>4</sub><sup>-</sup> loss process is

$$SO_4^- + SO_4^- \to S_2O_8^{2-}$$
 (5)

Reaction (5) is approximately 1000 times slower than reaction (2) at the SO<sub>4</sub><sup>-</sup> concentration levels ( $<10^{-4}$  M) used in kinetic runs ( $2k_5 = 1 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> at  $\mu \approx 0.25$  M<sup>10</sup>). Hence, the initially produced SO<sub>4</sub><sup>-</sup> is quantitatively converted to Cl<sub>2</sub><sup>-</sup>.

In the absence of saturation effects, the fractional dissociation D of  $S_2O_8^{2-}$  produced by the photolysis laser is given by

$$D = \rho \sigma, \tag{V}$$

where  $\rho$  is the photolysis laser fluence in photons/cm<sup>2</sup> and  $\sigma$  is the S<sub>2</sub>O<sub>8</sub><sup>2-</sup> absorption cross section at 248 nm.  $\sigma$  was measured and found to be  $9.5 \times 10^{-20}$  cm<sup>2</sup>. Assuming  $\Phi = 2$  for reaction (1), the concentration of photolytically produced SO<sub>4</sub><sup>-</sup> is

$$[SO_4^-] = 2D [S_2O_8^{2-}].$$
(VI)

The initial  $Cl_2^- TR^3$  signal, obtained 50 ns after the photolysis laser pulse, is then assumed equal to the calculated  $SO_4^$ concentration.

Figure 6 shows plots of  $[Cl_2^-]_t^{-1}$  vs t with initial concentrations of 1.1 and  $0.52 \times 10^{-4}$  M. The plots show the



FIG. 6. Second-order decay plots of  $Cl_2^-$  with initial concentrations of (a)  $0.52 \times 10^{-4}$  M, (b)  $1.1 \times 10^{-4}$  M. Linear least squares analyses of the plots gives (a)  $2k_4 = (8.2 \pm 0.5) \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, (b)  $2k_4 = (6.2 \pm 0.3) \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> (errors are  $1\sigma$ ).

Photolysis fluence 10 <sup>17</sup> photons cm <sup>-2</sup>	$\frac{[S_2O_8^{2-}]}{10^{-3}}M$	[SO <sub>4</sub> <sup>-</sup> ] <sub>0</sub> 10 <sup>-4</sup> M	Reaction half-lives followed	$\frac{2k_4 \pm 1\sigma}{10^9 \mathrm{M}^{-1} \mathrm{s}^{-1}}$
5.25	1.1	1.1	4	6.2 + 0.3
2.5	1.1	0.52	4	8.3 + 0.5
5.25	0.31	0.31	3	16.2 + 1.0
2.5	0.31	0.15	2	12.4 + 1.7

TABLE IV. Kinetic data for Cl<sub>2</sub><sup>-</sup> disproportionation.

linear dependence predicted by Eq. (IV) for four reaction half-lives. Table IV gives the bimolecular rate coefficient obtained from linear least squares analyses of this data and two other kinetic runs with lower initial  $[Cl_2^-]$ . Also tabulated are the photolysis fluence  $[S_2O_8^{2^-}]$ , calculated initial  $[SO_4^-]$ , and the number of reaction half-lives over which the  $Cl_2^-$  decay was followed. The average of the four measurements gives  $2k_4 = (11 \pm 4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (error is  $1\sigma$  and represents precision only).

In assessing the overall accuracy of the measurement, the three most potentially significant sources of uncertainty in the rate coefficient which we can identify are the calculation of laser fluence, our procedure for normalizing the TR<sup>3</sup> signal, and the assumption that  $\Phi(S_2O_8^{2^-}) = 2$ .

The use of a segmented aperture optical integrator (SAOI) to obtain spatially homogeneous photolysis beams and accurately known fluences has been described previously.9 The SAOI was not available for this exploratory study, so fluences were calculated from the total beam energy and an estimate of beam area obtained from burn patterns on thermal paper. The nonlinear response of the termal paper could mask beam inhomogeneity and lead to errors in the measurement of beam dimensions.<sup>31</sup> The sensitivity of the thermal paper used was such that the measurement gave an upper limit on the beam area. The accuracy of our power meter contributes an uncertainty of  $\pm 10\%$  and our estimate of beam area  $\frac{+15\%}{-0}$  giving a potential uncertainty of  $^{+\,25\%}_{-\,10}$  in the laser fluence. An underestimate of the fluence would lead to an overestimate of the bimolecular rate coefficient.

Errors caused by a failure of our normalization procedure to compensate for the differing degrees of absorption of the probe and scattered light as the  $Cl_2^-$  concentration varies would result in an underestimate of the rate coefficient. The importance of this effect decreases as the concentration decreases. The fact that our rate coefficient determinations in Table IV show an increase as the initial  $Cl_2^-$  concentration decreases, may be an indication that our normalization procedure is inadequate. An accurate assessment of the potential magnitude of this error requires knowledge of the distances the probe and scattered light travel through  $Cl_2^$ solution. To obtain a rough estimate we assume that the signal originates from a point at the center of the 0.2 cm diameter cell and that all the solution undergoes photolysis. Both the probe and scattered light would then pass through 0.1 cm of a solution containing  $Cl_2^-$ . Under these conditions and in the absence of any normalization, the observed rate coefficient would be underestimated by 50% when  $[Cl_2^-]_0$  $= 10^{-4}$  M and by 10% when  $[Cl_2^-]_0 = 10^{-5}$  M. Further

work on the kinetics of  $Cl_2^-$  with organics may offer the possibility of normalizing TR<sup>3</sup> signals to the normal Raman scattering of a reactant, thus allowing direct comparison of normalization procedures. Ultimately, our aim is to achieve a level of sensitivity where this correction becomes unimportant.

The assumption that  $\Phi(S_2O_8^{2-}) = 2$  is supported by the results of Tang *et al.*,<sup>10</sup> who obtained a value of  $\epsilon \Phi$  for reaction (1) using PLP-LPA. An assumption of  $\Phi = 2$  gave a value of  $\epsilon$  in good agreement with previous determinations. In this work a value of  $\Phi < 2$  would lead to an overestimate of  $[Cl_2^-]_0$  and hence to an underestimte of the rate coefficient.

#### Comparison with previous work

Table V contains a comparison of our rate coefficient  $2k_4$  with nine previous studies which used broad band flash photolysis or pulse radiolysis as a radical source and optical absorption for  $Cl_2^-$  detection. A number of these studies used  $\epsilon$ (340 nm) = 1.25×10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> reported by Arbor and Thomas.<sup>32</sup> As we have noted above, there is excellent agreement between Cl<sub>2</sub><sup>-</sup> absorption cross sections determined in the gas phase by Lee et al.<sup>23</sup> and in solution by Jayson et al.<sup>24</sup> We have recalculated rate coefficients which used  $\epsilon(340 \text{ nm}) = 1.25 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  using  $\epsilon(340 \text{ mm}) = 1.25 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$ nm) =  $8.8 \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup> as determined by Jayson *et al.* There is reasonable agreement between the previous studies, and the corrected average of the nine reported rate coefficients is  $9.7 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. This is in good agreement with our value,  $(11 \pm 7) \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, which is, of course, independent of any determination of the Cl<sub>2</sub><sup>-</sup> extinction coefficient. This agreement with previous studies indicates that our experimental approach and assumptions are basically sound.

TABLE V. Comparison of rate coefficients for  $Cl_2^-$  disproportionation.

$\frac{2k_4}{10^9 \mathrm{M}^{-1} \mathrm{s}^{-1}}$	pН	Ionic strength	Experimental technique	Reference
11 ± 7	5.5	0.25	PLP-TR <sup>3</sup>	This work
$10 \pm 2^{a}$	1.1,6	0.5	FP	34
$10 \pm 3^{*}$	3.1		PR	35
$8.4 \pm 2.1$	1.9	0.1	PR	36
7.3ª	1	0.2	FP	37
$13 \pm 4^{a}$	•••	~1	PR	38
$10.6 \pm 0.7$	•••	1–10	PR	39
$5.4 + 1.0^{*}$	7	1.5-14	PR	40
$9 + 4^{*}$	• • •	•••	PR	41
12 <sup>a</sup>	7	0.2	PR	42

<sup>a</sup>Recalculated using  $\epsilon = 8.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  (see Ref. 20). PLP-TR<sup>3</sup>: pulsed laser photolysis—time resolved resonance Raman spectroscopy; FP: flash photolysis; PR: pulse radiolysis.

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As pointed out above, the kinetics portion of this work is a preliminary study aimed at establishing sensitivity limits and determining the feasibility of using TR<sup>3</sup> to study the aqueous phase kinetics of small inorganic radicals. As noted by Hub et al.<sup>33</sup> there have been relatively few examples of quantitative kinetic data being derived from TR<sup>3</sup> measurements and very little opportunity to directly compare TR<sup>3</sup> kinetic data with results obtained by different techniques. In this work we have achieved a detection limit of  $\approx 5 \times 10^{-6}$ M, which is comparable with that achieved for large organic molecules.<sup>12</sup> Further improvements in experimental design offer a possibility of perhaps an order of magnitude increase in sensitivity. We have obtained kinetic data, which, while preliminary in nature and of rather low precision, is in good agreement with results obtained using broad band flash photolysis or pulse radiolysis coupled with optical absorption detection. We intend to incorporate the SAOI into the apparatus allowing a more accurate calculation of photolysis beam fluence and hence initial radical concentration. This should also eliminate problems associated with beam inhomogeneity. Under these conditions it should be possible to achieve levels of precision and accuracy currently attainable using PLP-LPA.9-11

#### CONCLUSION

We have employed pulsed laser photolysis-TR<sup>3</sup> techniques to obtain the resonance Raman spectrum of  $Cl_2^-$  in aqueous solution. Observation of the fundamental and nine overtone bands has enabled us to determine harmonic and anharmonic vibrational constants and hence an estimate of the  $Cl_2^-$  dissociation energy,  $1.3 \pm 0.1$  eV. This result is in good agreement with values obtained from studies in low temperature matrices, theoretical calculations, and thermodynamic estimates, and indicates that solvation has little effect on the  $Cl_2^-(^2\Sigma_u^+)$  ground state potential.

Preliminary kinetic studies of  $Cl_2^-$  disproportionation give a rate coefficient  $2k_4 = (11 \pm 7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , in good agreement with previous studies. We obtain a  $Cl_2^-$  detection sensitivity of  $5 \times 10^{-6}$  M, which is comparable to that reported in TR<sup>3</sup> studies of large organic molecules. This work indicates that TR<sup>3</sup> shows the sensitivity necessary to establish it as a powerful tool in the study of the kinetics and structure of small aqueous phase inorganic radicals. The TR<sup>3</sup> technique will be particularly useful in kinetics studies where selective UV-visible absorption detection of a single transient species is not possible due to overlapping spectra, and/or where the species of interest absorb only in the deep ultraviolet.

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