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Photoionization Mass Spectrometric Study of HOCl: Photoionization Efficiency Spectrum and Ionization Energy

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The photoionization efficiency (PIE) spectrum of HOCl was measured over the wavelength range $\lambda = 102-115$ nm, using a discharge flow-photoionization mass spectrometer (DF-PIMS) apparatus coupled to a synchrotron radiation source. The PIE spectra displayed steplike behavior near threshold. This study represents the first determination of the HOCl photoionization efficiency spectrum and the photoionization threshold. A value of $11.12_3 \pm 0.01_8$ eV was obtained for the adiabatic ionization energy (IE) of HOCl from analysis of photoion thresholds, corresponding to the $HOCl^+(X^2A'') \leftarrow HOCl(X^1A'')$ transition. Our PIMS result is identical to the only previous experimental measurement and in good agreement with a recent ab initio calculation. From our result for IE(HOCl), a value of 999.4 ± 3.6 kJ mol^{-1} was calculated for $\Delta_f H^o{}_0(HOCl^+)$, and from the latter, the proton affinity of ClO at $T = 0$ K, $PA_0(ClO)$, was determined to be 629.6 ± 3.6 kJ mol^{-1}. At 298 K, the computed values for $\Delta_f H^o{}_{298}(HOCl^+)$ and $PA_{298}(ClO)$ are 996.5 ± 3.6 and 635.1 ± 3.6 kJ mol^{-1}, respectively.

Introduction

Hypochlorous acid, HOCl, and chlorine nitrate, $ClONO_2$, are temporary chlorine reservoir species in the Earth's stratosphere.[1−4] As such, they sequester free-radical chlorine which catalyzes ozone depletion. During daylight, photolysis of HOCl and $ClONO_2$ releases Cl, enabling the catalytic cycles that destroy ozone.[3,4] Within the chemically perturbed region of the Antarctic stratosphere, HOCl is generated from heterogeneous reactions involving $ClONO_2$ on the surface of polar stratospheric clouds (PSCs).[5−7]

A simple triatomic molecule having C_S symmetry, HOCl is probably the most extensively studied hypohalous acid. Numerous vibration−rotation studies have determined the molecule's geometry and fundamental frequencies.[8−15] Other previous studies have included UV−visible spectroscopy in solution[16−18] and in the gas phase[17,19−21] as well as ab initio calculations.[22,23] There have been several determinations of the heat of formation of gas-phase HOCl which are summarized and compared in our recent study[24] reporting values for $\Delta_f H°_{298}$ of Cl_2O and HOCl. However, there has only been one reported experimental determination of the adiabatic ionization energy (IE) of HOCl.[25] This study employed photoelectron spectroscopy (PES) and was complicated by the presence of features due to Cl_2O, Cl_2, and H_2O in addition to HOCl. Colbourne et al.[25] argue persuasively that the additional peaks observed at 11.2 and 12.3 eV are to be identified with "the previously undetected species HOCl." This identification is based on the expected composition of the vapor, the observed known features due to Cl_2O, Cl_2, and H_2O, and the agreement between calculated HOCl values of Chong et al.[26] and the additional experimental peaks attributed to HOCl. Despite the consistency of the argument, the identification of the new features with HOCl is indirect. An independent determination of IE(HOCl) is desirable, especially if the identification of the observed signal with HOCl is direct, as in the case of mass spectrometry. In this study, we present the first determination of the HOCl photoionization efficiency (PIE) spectrum and the photoionization threshold from which the adiabatic ionization energy (IE) may be determined.

Experimental Section

Experiments were performed by employing a discharge flow-photoionization mass spectrometer (DF-PIMS) apparatus coupled to beamline U11 at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. In the present study, the microwave discharge was not employed. The apparatus and experimental procedures have been described in detail in previous publications.[24, 27−35]

HOCl was generated within a 2 L glass sample bulb from the following sequence of reactions: (1) the heterogeneous reaction of molecular chlorine on solid mercuric oxide to yield $Cl_2O(g)$ as described in detail in a previous publication,[24] and (2) the equilibrium of Cl_2O and water adsorbed on the HgO sample with HOCl:

$$2\,Cl_2 + HgO(s) \rightarrow Cl_2O + HgCl_2(s) \qquad (1)$$

$$Cl_2O + H_2O \leftrightarrow 2\,HOCl \qquad (2)$$

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The resulting $HOCl/Cl_2O/Cl_2/He$ mixture was analyzed via photoionization mass spectrometry. Mass spectrometric analysis indicated that about 95% of the initial [Cl_2] was consumed after addition to the bulb containing HgO. Typical residual [Cl_2] in the flow tube was about 6×10^{12} molecules cm^{-3} and the signals due to Cl_2 and Cl_2O were comparable. Also, we estimate roughly that only a few percent of the consumed Cl_2 ended up as Cl_2O and HOCl in the flow tube; loss of Cl_2O and HOCl in the transfer lines and in the flow controller was probably severe. Based on these considerations, a very rough estimate of [Cl_2O] in the flow tube would be of the order of 10^{13} molecules cm^{-3}. Based on an average value of K_{eq} for reaction 2 equal to $(8.2 \pm 1.0) \times 10^{-2}$ at $T = 298$ K as evaluated previously,[24] the estimated [HOCl] is of the order of 10^{12} molecules cm^{-3}.

For all measurements, the $HOCl/Cl_2O/ Cl_2/He$ mixture was introduced through the tip of the movable injector at a distance of 5−10 cm from the sampling nozzle. All experiments were conducted at ambient temperature ($T = 298 \pm 2$ K) and at a flow reactor pressure of about 4.3 ± 0.1 Torr with helium carrier gas. Flow velocities were in the range of 780−830 cm s^{-1}.

A monochromator with a normal incidence grating (1200 lines/mm) was used to disperse the VUV light[35] and a LiF filter ($\lambda > 105$ nm) was used to eliminate second- and higher-order radiation. For photoionization experiments performed at $\lambda <$ 105 nm, it was necessary to correct the PIE data for signal due to ionization by second-order light.[34,35] The intensity of the dispersed VUV light was monitored via a sodium salicylate coated window with an attached photomultiplier tube.

The helium (MG Industries, scientific grade, 99.9999%) and chlorine (MG Industries, 99.99% purity, 5.0% in He) were used directly from cylinders. The mercuric oxide (Aldrich Chemical Co., HgO, yellow, 99+%, ACS Reagent) was used without further purification.

Results and Discussion

As an example of the PIMS experiment, the PIE spectrum of the precursor species Cl_2 ($m/z = 70$) was measured over the wavelength range of $\lambda = 102-111$ nm at a nominal resolution of 0.18 nm (fwhm) and at 0.05 nm intervals. As shown in Figure 1, the onset of ionization at $\lambda = 108.00$ nm, taken as the half-rise point of the first step, corresponds to an adiabatic ionization energy of $11.48_0 \pm 0.01_9$ eV. This result is in good agreement with the recommended value of 11.48_0 eV,[36] and it demonstrates that the wavelength calibration, established by the location of zero order, is excellent.[34] In addition to the onset, the PIE spectrum of Cl_2 displays the vibrational steps ($\nu' = 0-3$) in the cation although the spectrum is perturbed by spin−orbit splitting and autoionization. There is generally good agreement with results from an earlier PIMS study[37] and two photoelectron spectroscopy (PES) studies.[38] Furthermore, through analysis of the signal levels that correspond to the hot band ($0 \leftarrow 1$ transition, at $\lambda \sim 108.6$ nm) and the ionization threshold ($0 \leftarrow 0$ transition, at $\lambda \sim 108.0$ nm), we estimate a vibrational temperature of about 298 K.[37]

The PIE spectrum for $HO^{35}Cl$ at $m/z = 52$ is shown in Figure 2 over the wavelength range of $\lambda = 102-115$ nm at 0.20 nm (fwhm) resolution and at 0.2 nm intervals. The peak signal to background is more than 100:1. The cationic state assignment is $^2A''$.[26] Thus the threshold transition is $HOCl^+(X^2A'') \leftarrow HOCl(X^1A')$, where the highest energy occupied orbital in the neutral is antibonding between the π-type atomic orbitals of chlorine and oxygen. Considerable structure is observed above the onset in the PIE spectrum (Figure 2) similar to that observed in the HOBr PIE spectrum.[31] This structure is the result of the Cl−O vibrational progression (steps) in the cation overlaid with features (peaks) that are characteristic of an autoionizing electronic state or series of states.

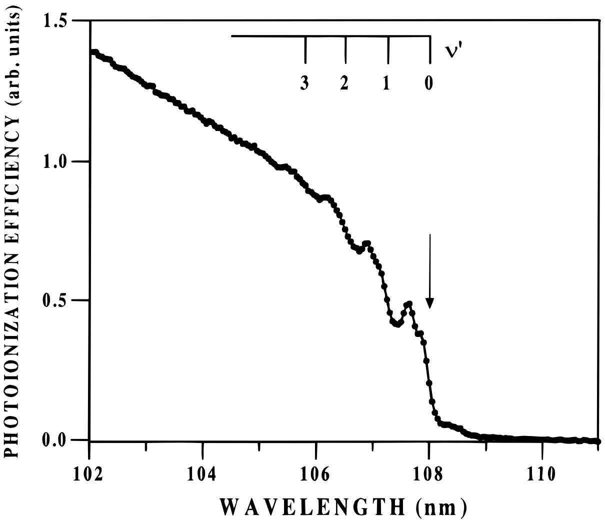

Figure 1. Photoionization efficiency spectrum of Cl_2 ($m/z = 70$) between $\lambda = 102$ and 111 nm at a nominal resolution of 0.18 nm and with 0.05 nm step. Photoionization efficiency is ion counts divided by light intensity in arbitrary units. The arrow indicates the onset of ionization at $\lambda = 108$ nm (IE = $11.48_0 \pm 0.01_9$ eV). The superposed lines (at 108.00, 107.25, 106.50, and 105.80 nm, which are taken from ref 38b) indicate the vibrational steps ($\nu' = 0-3$) in the Cl_2 cation ground, spin−orbit state ($^2X_{g,3/2}$).

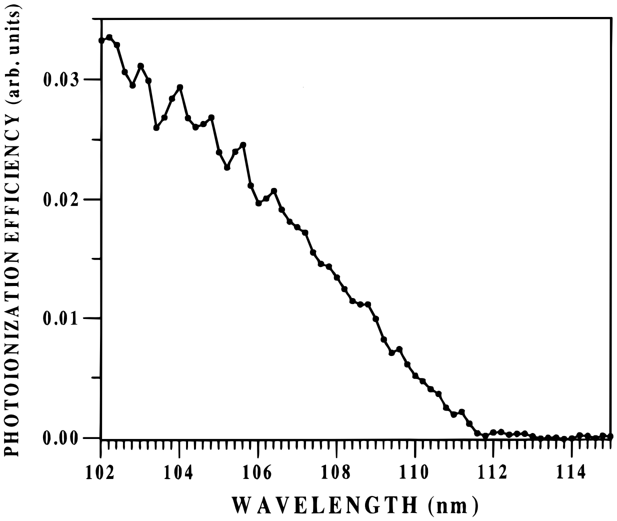

Figure 2. Photoionization efficiency spectrum of HOCl ($m/z = 52$) between $\lambda = 102$ and 115 nm at a nominal resolution of 0.20 and 0.2 nm steps.

To better determine the ionization energy, detailed examinations near the threshold were carried out, and an example is plotted in Figure 3. The spectrum for $HO^{35}Cl$ was obtained in the wavelength region between $\lambda = 110$ and 114 nm at 0.1 nm steps and a nominal resolution of 0.18 nm (fwhm). The threshold was analyzed by taking the half-rise point of the step to derive the ionization energy. From Figure 3, a threshold wavelength of $\lambda = 111.5_0$ nm is obtained and therefore an IE of 11.12_0 eV. Table 1 lists seven independent determinations of IE(HOCl). From these, we obtain a simple average value of $11.12_3 \pm 0.01_8$ eV for IE(HOCl), where the error limit is at the 2σ level. No experiments were conducted to examine the difference in IE between $HO^{35}Cl$ and $HO^{37}Cl$. Nevertheless, there should be negligible variation in the IEs between the two isotopes.

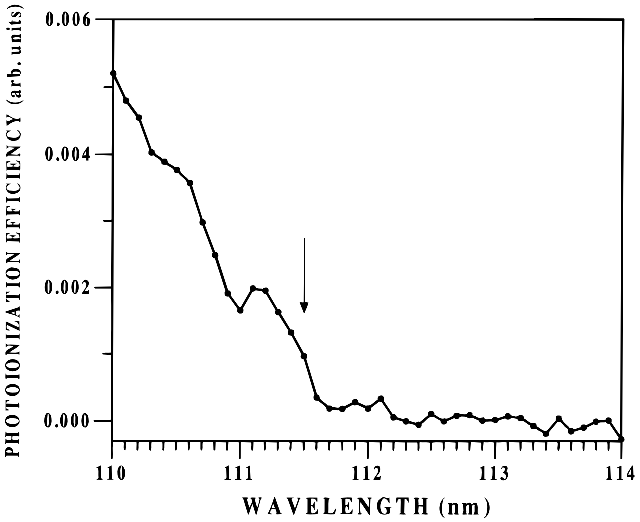

Figure 3. Photoionization threshold region of HOCl ($m/z = 52$) between $\lambda = 110$ and 114 nm at a nominal resolution of 0.18 and 0.1 nm steps. The arrow indicates the onset of ionization at $\lambda = 111.5_0$ nm (IE = $11.12_0 \pm 0.01_8$ eV).

TABLE 1: Threshold Wavelengths and Ionization Energies for HOCl

nominal step (nm)	fwhm (nm)	threshold (nm)	IE (eV)
0.1	0.20	111.55	11.115 ± 0.020
0.1	0.18	111.50	11.120 ± 0.018
0.1	0.18	111.50	11.120 ± 0.018
0.1	0.18	111.55	11.115 ± 0.018
0.2	0.20	111.5	$11.12_0 \pm 0.02_0$
0.2	0.20	111.4	$11.13_0 \pm 0.02_0$
0.2	0.20	111.3	$11.14_0 \pm 0.02_0$
		mean	$\langle 11.12_3 \pm 0.01_8 \rangle$[a]

[a] Uncertainty is precision only at the 2σ level.

TABLE 2: Ionization Energies for HOCl

IE(HOCl) (eV)	reference	method/comment
11.21	Chong et al. (1978)[26]	*ab initio* calculation/ vertical IE
11.12 ± 0.01[a]	Colbourne et al. (1978)[25]	HeI PES
11.08	Glukhovtsev et al. (1996)[39]	*ab initio* calculation (G2)
$11.12_3 \pm 0.01_8$	Present study	PIMS

[a] This value was selected in the critical evaluation of Lias et al.[40]

These PIMS results are in exact agreement with the only other experimental adiabatic IE determination: the aforementioned PES study[25] which reported an IE of 11.12 ± 0.01 eV. This agreement also confirms the identification[25] of the observed PES features with the HOCl species. As shown in Table 2, there is also good agreement with a recent G2 ab initio calculation[39] and with the recommended value of Lias et al.[40] The earlier ab initio calculation[26] refers to the vertical ionization energy.

The heat of formation of $HOCl^+$ may be computed readily from our IE value and our previous value for $\Delta_f H^o{}_0$(HOCl):[24,41-43]

$$\begin{aligned} \Delta_f H^o{}_0(\mathrm{HOCl}^+) &= \Delta_f H^o{}_0(\mathrm{HOCl}) + \mathrm{IE(HOCl)} \qquad (3) \\ &= (-73.8 + 1073.2)\ \mathrm{kJ\ mol^{-1}} \\ &= 999.4 \pm 3.6\ \mathrm{kJ\ mol^{-1}} \end{aligned}$$

where the uncertainties in $\Delta_f H$ and IE are 3.5 and 0.9 kJ mol^{-1}, respectively, and the combined uncertainty was derived from the square root of the sum of the squares.

Finally, by using our derived value for $\Delta_f H^o{}_0(\mathrm{HOCl}^+)$ and literature values for $\Delta_f H^o{}_0$ of ClO and H^+, the absolute proton affinity of ClO at $T = 0$ K may be determined via eq 4:

$$\mathrm{PA_0(ClO)} = \Delta_f H^o{}_0(\mathrm{ClO}) + \Delta_f H^o{}_0(\mathrm{H}^+) - \Delta_f H^o{}_0(\mathrm{HOCl}^+) \quad (4)$$

From $\Delta_f H^o{}_0(\mathrm{HOCl}^+) = 999.4 \pm 3.6$ kJ mol^{-1}, $\Delta_f H^o{}_0(\mathrm{ClO}) = 101.0 \pm 0.1$ kJ mol^{-1},[42] and $\Delta_f H^o{}_0(\mathrm{H}^+) = 1528.0$ kJ mol^{-1},[36] $\mathrm{PA_0(ClO)}$ at $T = 0$ K is calculated from eq 4 to be 629.6 ± 3.6 kJ mol^{-1} where the combined uncertainty is the square root of the sum of the squares of the individual uncertainties. The heat of formation of $HOCl^+$ at $T = 298$ K may be computed by correcting the zero K value for the heat capacity[42] of both $HOCl^+$ and the elements to obtain a value of 996.5 ± 3.6 kJ mol^{-1}. From this result, the value of the proton affinity at 298 K is readily computed via eq 5:

$$\mathrm{PA_{298}(ClO)} = \Delta_f H^o{}_{298}(\mathrm{ClO}) + \Delta_f H^o{}_{298}(\mathrm{H}^+) - \Delta_f H^o{}_{298}(\mathrm{HOCl}^+) \quad (5)$$

to obtain a value of 635.1 ± 3.6 kJ mol^{-1}.

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