

Photodissociation of HCl at 193.3 nm: Spin-orbit branching ratio

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HCl was photodissociated by ultraviolet (uv) radiation at 193.3 nm. Time-of-flight spectra of the hydrogen atom fragment provided the spin-orbit state distribution of the chlorine fragment, $[\text{Cl}(^2P_{1/2})]/[\text{Cl}(^2P_{3/2})]=0.69\pm 0.02$, in excellent agreement with recent theoretical studies. The H atom angular distribution studied by changing the uv photolysis laser polarization confirmed a dominant $A\ ^1\Pi\leftarrow X\ ^1\Sigma^+$ electronic transition in the photoexcitation process ($\beta=-1.01\pm 0.04$ and $\beta^*=-0.94\pm 0.07$). © 1997 American Institute of Physics. [S0021-9606(97)01629-2]

Hydrogen chloride is one of the simplest model systems for studying photophysics and photochemistry.¹⁻¹⁰ Its first uv absorption bands are assigned to $\sigma^*\leftarrow np\pi$ transitions; among the electronically excited repulsive states ($A\ ^1\Pi$, $a\ ^3\Pi_2$, $a\ ^3\Pi_1$, $a\ ^3\Pi_0+$, and $a\ ^3\Pi_0-$), the allowed perpendicular transitions ($\Delta\Omega=\pm 1$) are from the $X\ ^1\Sigma^+$ ground state to the $A\ ^1\Pi$ and $a\ ^3\Pi_1$ states, and the allowed parallel transition ($\Delta\Omega=0$) is to $a\ ^3\Pi_0+$.^{1,2,5} At higher energy, the $t\ ^3\Sigma^+$ state can be accessed via a $\sigma^*\leftarrow\sigma$ transition.^{1,2,5} Dissociation of HCl on the excited surfaces into atomic fragments $\text{H}(^2S)$ and $\text{Cl}(^2P_j)$ occurs with the spin-orbit electronic excitation of the Cl atom as the only internal energy, aside from the hydrogen and chlorine hyperfine levels. Besides the $X\ ^1\Sigma^+$ ground state, four excited electronic surfaces ($A\ ^1\Pi$, $a\ ^3\Pi_2$, $a\ ^3\Pi_1$, and $a\ ^3\Pi_0-$) correlate adiabatically with $\text{H}(^2S)+\text{Cl}(^2P_{3/2})$; while the $a\ ^3\Pi_0+$ and $t\ ^3\Sigma^+$ states correlate with $\text{H}(^2S)+\text{Cl}(^2P_{1/2})$.^{1,2,5} It is noteworthy that in small light-atom molecules, such as HF and HCl, the spin-orbit interaction is very small compared to that in HI; therefore, the photoexcitation is restricted primarily to spin-conserving transitions, i.e., the $X\ ^1\Sigma^+$ to $A\ ^1\Pi$ transition is much more important than those to $a\ ^3\Pi_1$, $a\ ^3\Pi_0+$ and $t\ ^3\Sigma^+$.^{1,2,5-8} Though the HCl molecule is excited predominantly to a single electronic surface $A\ ^1\Pi$ in the Franck-Condon region, nonadiabatic couplings between the excited surfaces may nevertheless occur at long range and can redistribute the photodissociation flux as the fragments recoil. The multiple-surface environment of the excited states provides a means for studying nonadiabatic couplings between the excited electronic states. A strong indication of such couplings can be observed via the spin-orbit branching ratio, and its measurement can provide insight into dissociation mechanisms.²⁻¹⁰

Despite extensive experimental and theoretical studies on HCl photochemistry,¹⁻¹⁰ the spin-orbit branching ratio of the Cl product from photodissociation of HCl in the ground vibrational state is still subject to controversy. The measured spin-orbit branching ratio $[\text{Cl}(^2P_{1/2})]/[\text{Cl}(^2P_{3/2})]$ was 0.50 ± 0.05 at 193.3 nm and 0.88 ± 0.13 at 157 nm,²⁻⁵ and it was shown that the electronic transition at these wavelengths is

primarily perpendicular ($A\ ^1\Pi\leftarrow X\ ^1\Sigma^+$).²⁻⁵ Recently, the ratio has also been measured between 193.3 and 119.3 nm.⁶ Givertz *et al.*⁷ and Alexander *et al.*⁸ used *ab initio* methods to calculate the branching ratio; however, the results differed from each other, as well as from the early experimental data.^{5,8} These discrepancies prompted two more theoretical studies,^{9,10} and it was shown that the branching ratio is very sensitive to details of the nonadiabatic coupling. The primary goal of this article is to provide a new, accurate experimental measurement of the spin-orbit branching ratio at 193.3 nm.

In this study, the high- n Rydberg time-of-flight (HRTOF) technique was utilized to record the H atom product TOF spectra and to obtain center-of-mass (c.m.) translational energy distributions.¹¹⁻¹³ The apparatus has been described previously.^{12,13} A pulsed HCl molecular beam was produced by expanding 1% HCl in Ar or 5% HCl in He at a total pressure of ~ 760 Torr. HCl was excited with 193.3 nm radiation from an ArF excimer laser (4–15 mJ). This radiation could be polarized with an eight-plate stack of quartz slides placed at the Brewster angle, resulting in $85\%\pm 2\%$ polarization.¹⁴ H atoms from HCl photodissociation were excited to radiatively metastable high- n Rydberg states by sequential absorption of 121.6 and 366 nm photons. A small fraction of these excited atoms drifted with their nascent velocities to a microchannel plate detector, where they were detected as ions after being field ionized in front of the detector. The flight path is 110.6 cm. TOF spectra were recorded by using a transient digitizer; spectra usually represent $3-10\times 10^3$ laser firings.

Figure 1 shows the c.m. translational energy and angular distributions for 193.3 nm photolysis of HCl; they were obtained from a direct conversion of the TOF spectra taken at different polarization conditions of the photolysis radiation. The two peaks correspond to the two spin-orbit states of the Cl atom product, and their relative probabilities reflect the relative differential cross sections for these two product channels and can reveal the relative total cross sections, i.e., spin-orbit branching ratio. Both the $\text{Cl}(^2P_{1/2})$ energy and $D_0(\text{H}-\text{Cl})$ agree with literature values.^{15,16} The resolution, i.e., width of the peaks, is limited by the excimer laser line-width. As shown in Fig. 1, when the uv laser radiation is horizontally polarized, i.e., perpendicular to the flight path, $\theta=90^\circ$, the H atom signal is a maximum, whereas the signal with the uv polarization parallel to the flight path ($\theta=0^\circ$) is

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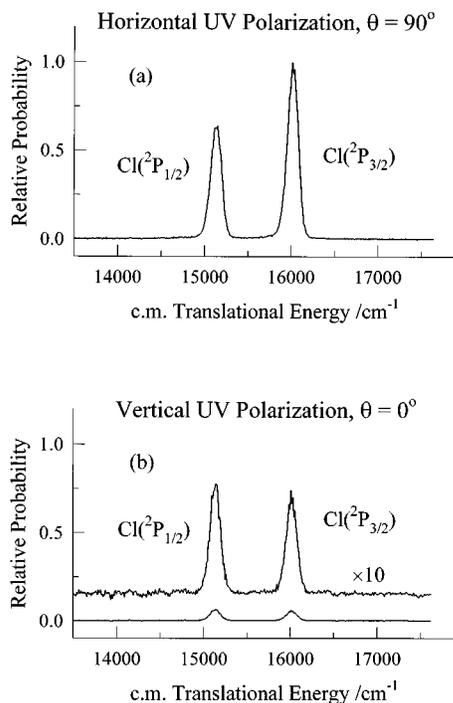


FIG. 1. c.m. translational energy distributions. Conditions: 1% HCl/Ar, total stagnation pressure 760 Torr. Spectra are normalized to the laser energy and number of laser shots. Signals at vertical polarization are mainly due to the imperfect polarization of the stacked-plate polarizer.

a minimum. The signal observed with vertically polarized uv radiation ($\theta=0^\circ$) is largely a result of imperfect polarization from the stacked quartz-plate polarizer. Since HCl dissociates on a time scale much faster than its molecular rotation period (fs vs ps), the H atom will recoil along the original HCl molecular bond and it is obvious that the electronic transition dipole moment of HCl is perpendicular to its molecular axis. Both Cl^* and Cl peaks have nearly the same uv polarization dependence, and it appears that both channels derive predominantly from the perpendicular transition $A\ ^1\Pi \leftarrow X\ ^1\Sigma^+$.

For one-photon, electric-dipole-allowed photodissociation of randomly oriented molecules, the fragment angular distribution is described by¹⁷

$$I(\theta) = \frac{\sigma}{4\pi} [1 + \beta P_2(\cos \theta)], \quad (1)$$

where β ($-1 \leq \beta \leq 2$) is the asymmetry parameter, θ is the polar angle between the electric vector of the polarized radiation and the final photofragment recoil direction, and $P_2(\cos \theta)$ is the second-order Legendre polynomial. For a perpendicular transition ($\Delta\Omega = \pm 1$), $\beta = -1$ and for a parallel transition ($\Delta\Omega = 0$), $\beta = 2$. Based on Eq. (1), the β parameters can be calculated from the measured product angular distributions, i.e., the relative probabilities of the Cl peaks at different uv polarizations. The Cl^* and Cl atom peaks in the c.m. translational energy spectra are fitted to Voigt functions and the relative peak areas are used. Correction for imperfect polarization is also taken into account.^{14,18} The resulting β parameters for the two product channels are:

$\beta(\text{Cl}^*) = -0.94 \pm 0.07$ and $\beta(\text{Cl}) = -1.01 \pm 0.04$. The statistical error limits reflect a 95% confidence level. If A is the percentage of parallel and B is the percentage of perpendicular character, one finds that $A = (\beta + 1)/3$ and $B = (2 - \beta)/3$.¹⁹ For the photodissociation of HCl at 193.3 nm, the Cl channel has 100% perpendicular character, while the Cl^* channel has 98% perpendicular and 2% parallel characters. The minor parallel character should come from the singlet-triplet transition ($a\ ^3\Pi_0 \leftarrow X\ ^1\Sigma^+$). This differs from uv photodissociation of HF in which both F^* and F have 100% perpendicular character.¹³ It seems that as the molecule gets larger, besides the dominant singlet-singlet ($A\ ^1\Pi \leftarrow X\ ^1\Sigma^+$, perpendicular) transition, a minor singlet-triplet transition ($a\ ^3\Pi_0 \leftarrow X\ ^1\Sigma^+$, parallel) starts to become noticeable, to a small extent in HCl and to a much larger extent in HI.

Two approaches are taken to calculate the spin-orbit branching ratio $[\text{Cl}^*]/[\text{Cl}]$. The first is to use the integrated peak areas in the translational energy spectra obtained by using unpolarized radiation and to include a weighting factor of $(1 + \beta/4)^{-1}$ for each peak.^{17,19} The second is to use the sum of the integrated areas from the horizontally and vertically polarized spectra and to include a weighting factor of 2 for the horizontally polarized data ($\theta=90^\circ$).^{17,19} These two sets of data increase the precision of the spin-orbit branching ratio measurement. Our best estimate is $[\text{Cl}^*]/[\text{Cl}] = 0.69 \pm 0.02$. The statistical error reflects a 95% confidence level. This result is in excellent agreement with the recent theoretical value of 0.71 at 193.3 nm.⁸ Note that our experimental technique is independent of the detection efficiency of Cl and Cl^* atoms, as opposed to previous experimental studies. The photolysis and probe laser delay is checked to ensure that it does not affect the spin-orbit branching ratio measurements, i.e., it does not affect the collection efficiency.

Unlike HI, uv photoexcitation promotes HCl primarily to a single electronic state, $A\ ^1\Pi$, and complications from initial population of multiple zeroth-order electronic states is minimum. In the adiabatic limit, the atoms separate slowly and the initially populated molecular states correlate adiabatically with the atomic fragment spin-orbit states, i.e., the branching ratio $[\text{Cl}^*]/[\text{Cl}]$ should be 0.5.^{2,5,20} In the diabatic limit, separation occurs very fast, such that the formation probabilities of Cl^* and Cl are determined by the probabilities of projecting the molecular wave function onto the eigenstates of the separated atoms. In this case, the branching ratio in the diabatic limit is 0.5.^{2,5,20} Our measured branching ratio of 0.69 ± 0.02 corresponds to neither the adiabatic limit nor the diabatic limit, being higher than both.

Detailed theoretical studies of HCl have helped elucidate its photodissociation mechanisms.^{1,7-10} Since both spin-orbit channels derive predominantly from the $A\ ^1\Pi$ state which is accessed in the Franck-Condon region, it is the nonadiabatic couplings at large separation that determine the spin-orbit branching ratio. At large H-Cl distances where the spin-orbit energy becomes significant, couplings of the $A\ ^1\Pi$ state and the $\Omega=1$ components of the triplets $a\ ^3\Pi$ and $t\ ^3\Sigma^+$ will redistribute the photodissociation flux and

thus determine the product spin-orbit branching ratio.⁸ It is the coupling between the $A^1\Pi$ and $t^3\Sigma_1^+$ states that redistributes photodissociation flux into the $t^3\Sigma_1^+$ state which correlates with the Cl^* asymptote and therefore increases the population of the Cl^* channel above the statistical or diabatic limit. A complex spin-orbit coupling of the excited potentials is involved, and we hope this work will settle the controversy in the HCl spin-orbit branching ratio at 193.3 nm.

The minor $a^3\Pi_{0+}$ channel is not coupled to other optically active excited states, $A^1\Pi$, $a^3\Pi_1$, and $t^3\Sigma_1^+$, due to the conservation of the total electronic angular momentum.⁵ Therefore it will not redistribute photodissociation flux to other excited states, as $A^1\Pi$ does. In the adiabatic limit, all the $a^3\Pi_{0+}$ population will produce Cl^* and the oscillator strength carried by $a^3\Pi_{0+}$ is estimated to be 0.8% (2% $a^3\Pi_{0+}$ character in the Cl^* channel multiplied by $[Cl^*]/([Cl^*]+[Cl])$). Note that the theoretical value is $\leq 0.5\%$.⁸

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¹⁴The polarization of the polarizer at 193.3 nm was estimated by the following approaches: (a) our previous study on HF (Ref. 13); (b) a calculation based on discussions in Chapter 5, *Handbook of Optics*, edited by M. Bass *et al.* (McGraw-Hill, New York, 1995); (c) polarization measurement at 266 nm (polarized output from a Nd:YAG laser) and extrapolation to 193.3 nm.

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