Low Energy Photodissociation of HCl : Theoretical Analysis

Sungyul Lee

Department of Chemistry, Kyunghee University, Kyungki-do 449-701, Korea, and Center for Molecular Science, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea
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Photodissociation of hydrogen halides is quite interesting. Since the potential curves of the Born-Oppenheimer states correlating to the lowest electronic state of the halogen atom (^2P_j, j = 1/2, 3/2) are well known, comparison between theory and experiment is feasible. Numerous groups have studied photodissociation dynamics of HF,[1] HCl[2-4] and HI.[5] Careful theoretical analysis of the experimental data would give valuable information on the dynamics of these molecules. As a prelude to the full quantal analysis of the photodissociation dynamics of the hydrogen halides, we present the low-energy photodissociation of HCl in the present work. HCl was studied in a number of experimental and theoretical works. Givertz and Balint-Kurti,[3] and Alexander, Pouilly and Duhoo[2] (APD) calculated spin-orbit branching ratios of Cl atom produced from $A^1\Pi$- $X^1\Sigma$ transition. Neither of those calculations agreed well with measurements.[4] These inconsistencies are one of the motivations of the present work. Photodissociation of HCl is also intriguing, since the branching ratios of Cl(^2P_j, j = 1/2, 3/2) calculated by APD for photon energy between 50,000 and 80,000 cm^{-1} are different from the high recoil limit values.[6] We try to resolve and confirm these findings in the present work. We also treat the vector properties of Cl(^2P_j, j = 1/2, 3/2) in this work, and predict that they also do not approach the high energy recoil limit values in the energy range studied.

The theory employed here was developed by Singer *et al.*[6] The basic ingredient of the theory is the frame transformation matrix that connects the adiabatic Born-Oppenheimer (ABO) states to the atomic term. Two basis sets are employed to describe the dissociation dynamics in the molecular and asymptotic region, respectively. The first basis (ABO basis) is a space-fixed basis derived from Hund's coupling cases. Hund's case (a) basis is used here. The second basis set, which is called 'asymptotic' molecular basis, diagonalizes the total Hamiltonian at infinite internuclear distances. These two basis sets are related to each other by the r-independent transformation matrix. Close-coupled equations are solved for the continuum wave function. Photodissociation amplitudes to a specific fine structure component of the chlorine atom are computed by the Golden Rule. The potential curves, transition dipole moments and the spin-orbit couplings employed in the present calculation are those calculated by APD in Reference 2.

The potential curves of the electronic states included in the present calculations are depicted in Figure 1. The $X^1\Sigma^+$, $a^3\Pi$, $A^1\Pi$ and $1^3\Sigma^+$ states all correlate with Cl(^2P). There are two fine structure states of Cl, $^2P_{1/2}$ and $^2P_{3/2}$. Of these two levels, Cl($^2P_{1/2}$) is of higher in energy by 882.36 cm^{-1}. Since the latter three states are repulsive, the photodissociation is direct. Only the $A^1\Pi$ state carries oscillator strength from the ground $X^1\Sigma^+$ state, and no significant effects of the quantum interference[7-10] are expected on the dynamics. However, the interactions among the dissociative states ($X^1\Sigma^+$, $a^3\Pi$, $A^1\Pi$ and $1^3\Sigma^+$) in the recoupling region can complicate the dynamics, as we show below. Figure 2 depicts the total absorption cross section. The spectrum is structureless and broad, typical of the direct dissociation process, and peaks at 62500 cm^{-1}. The computed ratios $\sigma(^2P_{1/2})$ / $\sigma(^2P_{3/2})$ are presented in Figure 3 for photon energy of 50,000-80,000 cm^{-1}. Agreement with the predictions[2] by Alexander, Pouilly and Duhoo is excellent except near 80,000 cm^{-1}. However, our

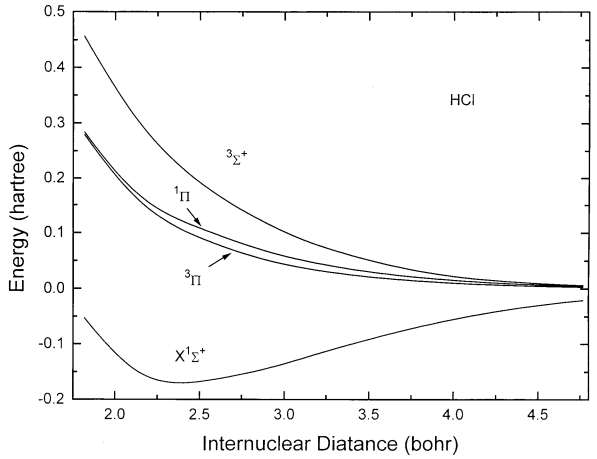

Figure 1. Potential curves of HCl. The zero of energy is defined as the statistical average of the energies of Cl(^2P_j, j = 1/2, 3/2).

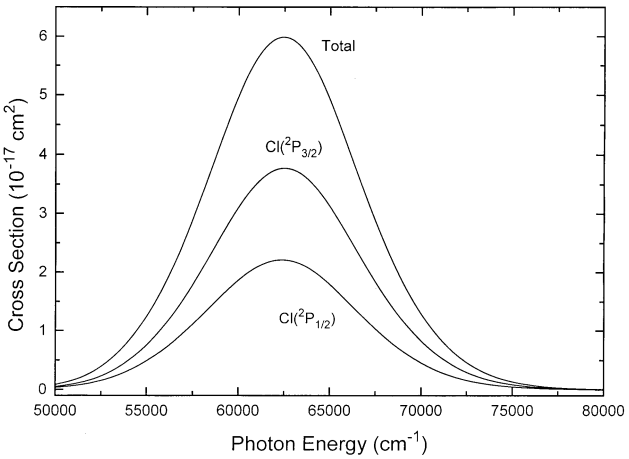

Figure 2. Total cross section from $A^1\Pi$-$X^1\Sigma$ (v_i = 0, J_i = 2) photoexcitation.

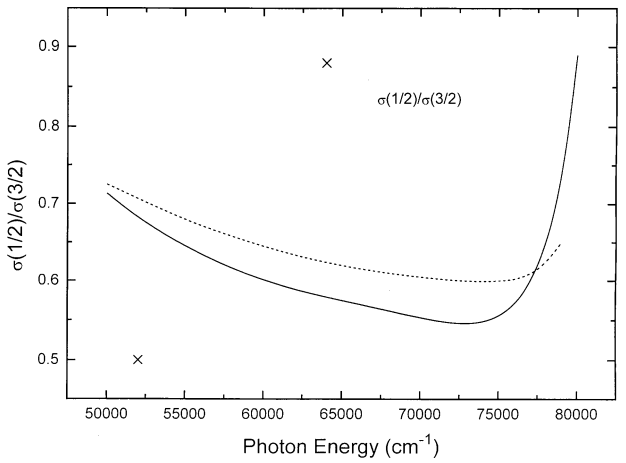

Figure 3. The ratios ($\sigma(^2P_{1/2})$ / $\sigma(^2P_{3/2})$) for photon energy 50,000-80,000 cm^{-1}. v_i = 0 and J_i = 2. Solid line: present results; Dotted line: theoretical results by APD, Ref. 2; Crosses: experimental results, Ref. 4.

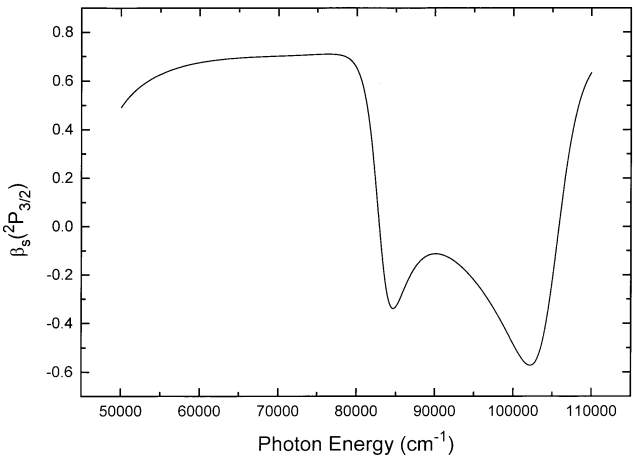

Figure 4. The β_S parameters of $Cl(^2P_j, j = 1/2, 3/2)$. v_i = 0 and J_i = 2.

computed results did not compare well with the experimental observations, as discussed by APD.[2] Since the non-Born-Oppenheimer interactions at large internuclear distance can profoundly affect the dynamics in the present case, the values of the branching ratios will also be very sensitive to the details of the topology of the potential curves at long range. However, good agreement of our present results with those by APD seems to suggest that further experimental study is clearly needed.

It should be noted that the computed ratio $\sigma(^2P_{1/2})/\sigma(^2P_{3/2})$ is different from the high-energy recoil limit value of 1/2. The ratio tends to approach 1/2 up to the photon energy of 75000 cm^{-1}, but deviates more beyond that energy. This indicates that the kinetic energy of the atoms is not enough for recoil limit behavior. Due to the low kinetic energy of the atomic fragments, couplings among the electronic states are comparable in magnitude with the differences between the potential energies of these states at large internuclear distance. Therefore, a part of the quantum flux switches to the "dark" triplet states ($a^3\Pi$ and $1^3\Sigma^+$), which do not carry oscillator strengths from the ground $X^1\Sigma^+$ state, and the dynamics deviates from the simple $A^1\Pi$ - $X^1\Sigma^+$ photoabsorption. Figure 4 show the fluorescence anisotropy parameters β_S indicating the distributions of the magnetic sublevels of $Cl(^2P_{j,j} = 1/2, 3/2)$. Again, the values of the vector property deviate highly from the high-energy recoil limit value for the (perpendicular) $A^1\Pi$ - $X^1\Sigma^+$ transition, indicating the importance of the interactions in the recoupling region between the singlet and the (dark) triplet states.

An interesting experimental work related to the present study was carried out by Gordon *et al*.[12] for the HCl molecule at higher energy regime, involving higher electronic states of HCl and electronically excited states of Cl. They found that the spin-orbit branching ratios do not approach the higher energy limit, and that the branching ratios exhibit a variety of patterns (adiabatic, diabatic and intermediate cases), depending on the states involved. We suggested by simulated computations[12] on OH molecule that these diverse patterns may be the results of the interactions between the repulsive states. The theoretical analysis of the interesting experimental observations on HCl by Gordon *et al*. will need the construction of numerous transformation matrices, as in OH predissociation. We are currently planning such analysis.

Large deviations of the branching ratios and the fluorescence anisotropy parameters of the Cl atoms from the recoil limit values in the energy range studied in the present work are the results of the rather large spin-orbit couplings, which will be similar in magnitude to the energy difference (882.36 cm^{-1}) between the two spin orbit states, $Cl(^2P_{1/2})$ and $Cl(^2P_{3/2})$. Experimental studies on these findings will be highly desirable.

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