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Photodissociation processes in the HCl molecule

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Various ab initio methods have been employed for the study of photodissociation processes in the HCl molecule. Potential curves for selected singlet and triplet states and dipole transition moments between singlet states have been calculated. The transition moments vary significantly with internuclear distance for all states studied. The lifetime of the B' \Sigma^+ state is predicted to be 3 ns. The calculations show that photodissociation of HCl occurs by absorption into the repulsive A'' state and by absorption into the bound C'' state, followed by predissociation. The theoretical photodissociation cross sections for the A'' state and oscillator strengths for the C'' state are in good agreement with experimental data. The contributions from other excited states are investigated. The photodissociation rate of HCl in diffuse interstellar clouds is computed.

I. INTRODUCTION

There have been numerous experimental and theoretical studies of the photodissociation of neutral diatomic molecules and positive molecular ions but it appears that for no neutral species has a quantitative comparison of the measured cross sections with theoretical predictions been possible. Except for processes leading to the production of excited atoms which can be detected by the resulting emission, the end products of the photodissociation processes are difficult to identify. Because many channels may contribute to the photodissociation process, the theoretical analysis often involves the study of many excited electronic states, both bound and repulsive, which must be described with comparable accuracy and for which there occurs a competition between radiative decay and dissociation.

The hydrogen chloride molecule HCl is a simple system for which reliable absorption cross section data exist\textsuperscript{4,5} and for which accurate calculations can be made. Theoretical studies of the excited electronic states\textsuperscript{4,5} have established that the observed absorption at 1400–1800 Å occurs by transitions from the ground X' \Sigma^+ state into the repulsive A'' state which dissociates directly into ground state products. The absorption spectra\textsuperscript{6,7} of the strong C'' state which dissociates by predissociation. The absorption oscillator strength for the C'' state has recently been determined experimentally.\textsuperscript{7} Numerous other excited states are known to exist in the 1350–1050 Å region, both from experiments\textsuperscript{8-10} and theoretical investigations,\textsuperscript{5} but the assignments of the observed bands are often uncertain. No calculations of the transition moments, absorption oscillator strengths or photodissociation cross sections, which would assist in clarifying the interpretation, have been reported.

Hydrogen chloride is a constituent of the terrestrial atmosphere and the atmosphere of Venus. It is predicted to exist in detectable amounts in interstellar clouds\textsuperscript{6,10} but searches for it have been able only to place upper limits on its abundance.\textsuperscript{11} Photodissociation of HCl is the principal destruction process in diffuse interstellar clouds and a better understanding of the details of the mechanism will help to locate the source of the discrepancy between the predicted abundances\textsuperscript{12} and the observed upper limits.

II. COMPUTATIONAL DETAILS

Two sets of calculations were performed, using completely different program packages. The calculations were of the type recently carried out for the OH molecule.\textsuperscript{13} The first set of calculations, which we will call the "Gaussian calculation," was carried out using a package of programs, consisting mainly of the IBMOL SCF program, interfaced with the Wuppertal–Bonn multireference single- and double-excitation configuration interaction (MRD-CI) program series including configuration selection and energy extrapolation.\textsuperscript{14,15} The Gaussian atomic orbital (AO) basis set employed for Cl was the [7\sigma,5\rho] basis of Dunning.\textsuperscript{16} To this set were added one d function with exponent \(\alpha = 0.6\), one negative ion \(p\) function with \(\alpha = 0.049\), and two \(s\) diffuse functions with \(\alpha = 0.025\) and \(0.015\), one \(p\) with \(\alpha = 0.020\), and one \(d\) with \(\alpha = 0.015\). For hydrogen, the \(5\sigma\) primitive set of Huzinaga\textsuperscript{17} contracted to [3\sigma] by Dunning\textsuperscript{18} was chosen, augmented by one \(p\) function with \(\alpha = 0.75\) and one Rydberg \(s\) function with \(\alpha = 0.03\). In order to calculate the transition moments between the various states it was necessary to use a common set of molecular orbitals (MO's) in all subsequent CI's. Several sets of MO's were investigated. CI calculations were carried out with a core consisting of five MO's, corresponding to the 1s, 2s, and 2p orbitals of Cl and 1s orbital of H, which were kept doubly occupied in all configurations. Some test calculations were performed with a core of only one MO, corresponding to the 1s orbital of Cl, to confirm the unimportance of configurations formed by excitations out of the 2s and 2p orbitals. Depending on the symmetry, the configuration selection threshold was set...
at 15 or 30 μH (1 μH = 2.72 × 10⁻⁵ eV) in the calculations, choices which resulted in CI matrices of the order of 3000 configurations. The set of reference configurations, typically eight in number, consisted of all configurations with final CI coefficients greater than 0.1 in any of the states. The calculations were performed in C₂v symmetry.

As an independent check on the reliability of the results a second set of calculations was performed using the ALCHEMY package of programs. These programs employ Slater-type AO's and we refer to the calculations as the "Slater calculations." For Cl, the [6s,5p] basis set of Cade and Huo was taken with the addition of two 3d functions with exponents 2.0 and 1.0, two more diffuse 4s and 4p functions with exponents 0.9 and 0.475, and one diffuse 4d function with exponent 0.45. For hydrogen, the basis used in the calculations on OH was employed. Again, several sets of MO's were examined for use in the subsequent CI's. CI matrices consisting of 950 configurations for 1Σ⁺ states and 1273 configurations for 1Π states were constructed by partitioning the MO's into core (1a, 2a, 3a, 1s), internal (4a-10a, 21T-31T) and external (11a-20a, 4a-10a, 15-26) orbitals. For each symmetry, a reference set was then chosen which included most of the configurations with a CI coefficient greater than 0.1 in the Gaussian calculation for the lowest two states at any internuclear distance. The reference set for the 1Π symmetry consists of

\[ \cdots \cdots 4\sigma^2 5\sigma^2 \cdots 2\pi^4 \]
\[ \cdots 4\sigma^2 5\sigma^6 \sigma \cdots 2\pi^1 \]
\[ \cdots 4\sigma^3 6\sigma^3 \cdots 2\pi^4 \]
\[ \cdots 4\sigma^3 5\sigma^2 \cdots 2\pi^3 3\pi \]
\[ \cdots 4\sigma^3 5\sigma^6 \sigma \cdots 2\pi^3 3\pi \]
\[ \cdots 4\sigma^3 5\sigma^7 \sigma \cdots 2\pi^1 \]
and for the 1Π symmetry of

\[ \cdots 4\sigma^5 5\sigma^6 \sigma \cdots 2\pi^3 \]
\[ \cdots 4\sigma^5 5\sigma^7 \sigma \cdots 2\pi^3 \]
\[ \cdots 4\sigma^5 5\sigma^8 \sigma \cdots 2\pi^3 \]
\[ \cdots 4\sigma^5 5\sigma^9 \sigma \cdots 2\pi^3 \]

TABLE I. SCF and CI energies in hartrees of the ground state at the equilibrium internuclear distance \( R_e = 2.409 \) bohr.

<table>
<thead>
<tr>
<th>Calculation</th>
<th>SCF</th>
<th>CI²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaussian</td>
<td>-460.0966</td>
<td>-460.2562⁰⁻⁶⁶⁶</td>
</tr>
<tr>
<td>Slater</td>
<td>-460.1088</td>
<td>-460.1397⁰⁻⁶⁶⁶</td>
</tr>
<tr>
<td>Ref. 4</td>
<td>...</td>
<td>-460.2179</td>
</tr>
<tr>
<td>Ref. 5</td>
<td>...</td>
<td>-460.2259</td>
</tr>
</tbody>
</table>

⁰Extrapolated as described in the text.

²In all CI calculations a core of five MO's was employed.

In the CI calculations the MO's resulting from an \( a^2 \Pi \) SCF calculation were used.

III. POTENTIAL CURVES

In the calculations, emphasis was placed on the accurate determination of the transition moments. The SCF and CI energies for the ground \( X \Sigma^+ \) state at the equilibrium internuclear distance \( R_e = 2.409 \) bohr²¹ are presented in Table I. Because of the larger AO basis set the Gaussian calculation gives slightly lower energies compared with other calculations.⁴⁻⁵ The higher energy resulting from the Slater calculation is due mainly to the CI used.

The potential energy curves are similar to those found in other calculations.⁶ Those obtained from the Gaussian calculation are presented in Fig. 1 for the \( 1(\Xi) \Sigma^+ \), \( 2(\Pi) \Sigma^+ \) and \( 1(\Delta) \Pi \) singlet states and in Fig. 2 for the \( 1(\Pi) \Pi \), \( 2(\Delta) \Xi \) 1(\( \Pi \))Σ⁺, \( 1(\Xi) \Pi \), \( 1(\Delta) \Pi \) and \( 1(\Delta) \Sigma \) triplet states of HCl (see Ref. 5 for the nomenclature). The potential curves were obtained using the MO's re-

FIG. 1. Calculated (extrapolated) MRD-CI potential energy curves for singlet states of HCl.
resulting from the $a\ ^1\Pi(1\sigma^22\sigma^23\sigma^24\sigma^25\sigma^26\sigma^12\pi^2)$ SCF calculation. The energies changed by less than 0.2 eV when the MO’s resulting from the $A\ ^1\Pi(1\sigma^22\sigma^23\sigma^24\sigma^25\sigma^26\sigma^12\pi^2)$ or $b\ ^3\Sigma^+(1\sigma^22\sigma^23\sigma^24\sigma^25\sigma^26\sigma^12\pi^2)$ SCF calculation were employed. The character of the MO’s is similar to that found in earlier studies. The $5\sigma$ MO changes from a HCl bonding orbital at $R_0$ to a $3\pi$ orbital on CI at large $R$, while the $6\sigma$ MO changes from a HCl antibonding orbital to a hydrogen $s$ orbital. The $2\pi$ MO is mainly a Cl $3p$ orbital, the $7\sigma$ MO corresponds to a diffuse Cl $s$ orbital, while the $8\sigma$ and $3\pi$ MO’s have large diffuse CI $p$ orbital contributions. The leading configurations for the singlet states at $R_0$ and the most important changes in configurations at larger internuclear distances are shown in Table II. The $A\ ^1\Pi$ and $a\ ^3\Pi$ states can be described by a single configuration, with a CI coefficient greater than 0.97, at all bond lengths. The vertical excitation energies are within 0.2 eV of those obtained by Bettendorf et al. except for the $2\ ^1\Sigma^+$ state. Our calculations place the $2\ ^1\Sigma^+$ state 0.2 eV below the experimental value of 10.3 eV, while the calculations of Bettendorf et al. place it 0.2 eV above the experimental value.

The potential curves for the $^1\Sigma^+$ and $^1\Pi$ states resulting from the Slater calculation differ slightly from those obtained from the Gaussian calculation. Because of the smaller CI representation, the vertical excitation energies are too small, especially for states with diffuse character. Similar trends occurred in the computations of the excited states of OH. The computed dissociation energy for the $X^1\Sigma^+$ state is 4.2 eV for the Gaussian calculation and 3.9 eV for the Slater calculation. The discrepancies with the experimental value of 4.62 eV are in the expected range. The equilibrium bond length of the $X^1\Sigma^+$ state obtained from the Slater calculation is 2.50 bohr and from the Gaussian calculation 2.43 bohr. The measured value is 2.409 bohr. The equilibrium bond length for the $C\ ^1\Pi$ state resulting from the Slater calculation is 2.62 bohr and from the Gaussian calculation 2.68 bohr. The experimental value is 2.55 bohr. Similar discrepancies were found in other theoretical studies.

### Table II. Principal configurations as functions of internuclear distance.

<table>
<thead>
<tr>
<th>State at $R = 2.409$ bohr</th>
<th>Leading configuration</th>
<th>Leading configuration at larger distances</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^1\Sigma^+$</td>
<td>$\ldots, 4\sigma^5\delta^2, \ldots \rightarrow 2\sigma^4$</td>
<td>$4.00^a \ldots, 4\sigma^5\delta^0\gamma^0, \ldots, 2\sigma^4$</td>
</tr>
<tr>
<td>$2\ ^1\Sigma^+\ldots, 4\sigma^5\delta^2, \ldots \rightarrow 2\sigma^4\delta^2\gamma^2$</td>
<td>$4.25$</td>
<td>$4.00 \ldots, 4\sigma^5\delta^2, \ldots, 2\sigma^4$</td>
</tr>
<tr>
<td>$A\ ^1\Pi \ldots, 4\sigma^5\delta^0\gamma^0, \ldots, 2\sigma^4$</td>
<td>$4.00$</td>
<td>$4\sigma^5\delta^0\gamma^0, \ldots, 2\sigma^4$</td>
</tr>
<tr>
<td>$C\ ^1\Omega \ldots, 4\sigma^5\delta^2\gamma^2, \ldots, 2\sigma^4$</td>
<td>$4.75$</td>
<td>$4\sigma^5\delta^2\gamma^2, \ldots, 2\sigma^4$</td>
</tr>
<tr>
<td>$a\ ^1\Pi \ldots, 4\sigma^5\delta^0\gamma^2, \ldots, 2\sigma^4$</td>
<td>$1.25$</td>
<td>$4\sigma^5\delta^0\gamma^2, \ldots, 2\sigma^4$</td>
</tr>
<tr>
<td>$b\ ^1\Pi \ldots, 4\sigma^5\delta^2\gamma^0, \ldots, 2\sigma^4$</td>
<td>$2.75$</td>
<td>$4\sigma^5\delta^2\gamma^0, \ldots, 2\sigma^4$</td>
</tr>
</tbody>
</table>

$^a$A core of $1\sigma^22\sigma^23\sigma^1$ occurs in all configurations.

$^b$The notation indicates that the change in configuration takes place around 4.0 bohr.

$^c$The notation indicates that the configuration at infinite separation is not yet attained and further changes in configurations take place.

### Figure 2

Calculated (extrapolated) MRD-CI potential energy curves for triplet states of HCl.
TABLE III. SCF molecular orbitals used and dipole moments.\(^a\)

| State | Configuration | \(\mu_{SCF}(R=2,409)\)  |
|-------|---------------|----------------|---|
| \(a^3\Pi\) | 1s\(^2\)2s\(^2\)3s\(^2\)4s\(^2\)5s\(^2\)6s\(^4\)2p\(^3\) | -1.01 | |
| \(A^1\Pi\) | 5s\(^6\)6p\(^4\)2p\(^3\) | -1.31 | |
| \(2\Sigma^+\) | 5s\(^6\)6p\(^4\)2p\(^4\) | -0.47 | |
| \(X^1\Sigma^+\) | 5s\(^2\)2p\(^2\) | +0.47<sup>b</sup> | |

\(^a\)The plus sign indicates HCl polarity. The values correspond to the Gaussian calculation.  
\(^b\)The measured value is +0.43<sup>23</sup>.

TABLE IV. Transition moments at \(R_s=2,409\) bohr.

<table>
<thead>
<tr>
<th>Calculation</th>
<th>MO's used in CI</th>
<th>Size of CI</th>
<th>Transition moments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\sigma^3\Pi)</td>
<td>(\sigma\Pi) states</td>
<td>(X^1\Sigma^+) states</td>
</tr>
<tr>
<td>Gaussian</td>
<td>(a^3\Pi)</td>
<td>2346</td>
<td>2395</td>
</tr>
<tr>
<td></td>
<td>(A^1\Pi)</td>
<td>2346</td>
<td>3547</td>
</tr>
<tr>
<td></td>
<td>(2\Sigma^+)</td>
<td>2414</td>
<td>3377</td>
</tr>
<tr>
<td></td>
<td>(X^1\Sigma^+)</td>
<td>2512</td>
<td>3749</td>
</tr>
<tr>
<td>Slater</td>
<td>(a^3\Pi)</td>
<td>950</td>
<td>1273</td>
</tr>
<tr>
<td></td>
<td>(A^1\Pi)</td>
<td>950</td>
<td>1273</td>
</tr>
<tr>
<td></td>
<td>(2\Sigma^+)</td>
<td>950</td>
<td>1273</td>
</tr>
<tr>
<td></td>
<td>(X^1\Sigma^+)</td>
<td>950</td>
<td>1273</td>
</tr>
</tbody>
</table>

FIG. 3. The calculated transition moment between the \(X^1\Sigma^+\) state and the \(A^1\Pi\) state as a function of internuclear separation.  
Full line: Gaussian calculation; dotted line: Slater calculation.  
\(o\): Gaussian calculation, \(a^3\Pi\) MO's; \(a\): Gaussian calculation, \(A^1\Pi\) MO's; \(\Delta\): Slater calculation, \(a^3\Pi\) MO's; \(\nabla\): Slater calculation, \(A^1\Pi\) MO's.

Small molecules, such as CO<sub>24</sub>, C<sub>2</sub><sup>25</sup> and OH<sub>13</sub>,<sup>20</sup> For the \(A^1\Pi-X^1\Sigma^+\) transition in the CO molecule,\(^24\) the canonical \(X^1\Sigma^+\) MO's were also found to be inappropriate for determining the transition moment and differences of up to 30% in the CO transition moment were found if \(X^1\Sigma^+\) or \(A^1\Pi\) canonical MO's were used, even for CI wave functions containing 10,000 configurations. A transformation of the \(X^1\Sigma^+\) canonical MO's to internally-consistent SCF orbitals brought the values much closer together.\(^24\) For the Swan \(d^3\Pi_u-a^3\Pi_u\) system of C<sub>2</sub> the transition moment depends strongly on the size of the CI employed.\(^25\) For the OH molecule the transition mo-

FIG. 4. The calculated transition moment between the $X^1\Sigma^+$ state and the $C^1\Pi$ state as a function of internuclear separation. For explanation of the symbols see Fig. 3.

FIG. 5. The calculated transition moment between the $A^1\Pi$ state and the $C^1\Pi$ state as a function of internuclear separation. For explanation of the symbols see Fig. 3.

FIG. 6. The calculated transition moment between the $X^1\Sigma^+$ state and the $2^1\Sigma^+$ state as a function of internuclear separation. For explanation of the symbols see Fig. 3.

ments for the $3\Sigma^+$ states and other excited states, resulting from three separate calculations agreed within 20%, even though the MO's and the sizes of the CI used were quite different. Increasing the size of the CI in the present Gaussian calculation on HCl for the $A^\Pi$ states (see Table III) improves the results but still larger CI's are needed to remove the discrepancies resulting from the use of different MO's.

The transition moment connecting the $X^1\Sigma^+$ and $2^1\Sigma^+$ states is presented in Fig. 6. Small differences occur between the moments calculated using the $A^{3}\Pi$ and $a^2\Pi$ molecular orbitals. The transition moment is small in the Franck-Condon region of the $X^1\Sigma^+$ state but increases to a large value in the region of the minimum in the outer well near 4.75 bohr where an avoided crossing of the states occurs. The $2^1\Sigma^+$ state of HCl resembles the $C^3\Sigma^+$ and $3^2\Pi$ states of OH where at large distances a minimum in the potential and a peak in the transition moment coincide at an avoided crossing with a lower-lying state.

The transition moment between the excited $2^1\Sigma^+$ state and the excited $A^1\Pi$ state is shown in Fig. 7 as a function of $R$. The moment is very large in the Franck-Condon region of the ground state but decreases sharply for $R$ greater than about 2.7 bohr.

We do not have reliable estimates of the transition moments to higher-lying excited states. Preliminary studies suggest that the transition moments from the
PHOTODISSOCIATION OF HCl

The threshold for the photodissociation of HCl occurs at an energy of 4.62 eV or at a wavelength of 2683 Å. It is clear from Fig. 1 that photodissociation will occur following absorption into the low-lying repulsive $A^1\Pi$ state which is accessible at wavelengths shorter than 2683 Å by an electric dipole transition from the ground state.

The cross section for the photodissociation of HCl by the absorption of radiation of energy $E$ in hartrees is given by the expression

$$
\sigma_{\nu''}(E) = 1.225 \times 10^{-23} E E \left| \langle \chi_{\nu''}(R) \mid D(R) \mid \chi_{\nu'}(R) \rangle \right|^2 \text{ cm}^2,
$$

where $g$ is a degeneracy factor equal to unity for $\Sigma-\Sigma$ transitions and to two for $\Sigma-\Pi$ transitions and $\chi_{\nu'}(R)$ is the final continuum wave function normalized to the asymptotic form

$$
\chi_{\nu'}(R) \sim \left( \frac{2(2\mu)^{1/2}}{\pi R^2 \hbar^2} \right)^{1/2} \sin(k' R + \eta),
$$

in which $k' = (2\mu E)^{1/2}$ is the wave number, $\mu$ is the reduced mass of HCl measured in units of the electron mass, and $\eta$ is a scattering phase.

We obtained $\chi_{\nu''}$ and $\chi_{\nu'}$ by numerical integration of the vibrational wave equations with several versions of the potential functions. In the evaluation of the matrix element $[\chi_{\nu'} \mid D \mid \chi_{\nu''}]$, Gaussian and Slater dipole moments $D(R)$ were used. The photodissociation cross sections calculated from Gaussian potential energies and transition moments obtained with $a^3\Sigma$ and $A^1\Pi$ MO's and from Slater potential energies and transition moments obtained with $a^3\Pi$ or $A^1\Pi$ MO's are presented in Fig. 8. The cross sections differ by not more than 20%. They pass through a maximum value of $4 \times 10^{-16}$ cm$^2$ at a photon energy of 8 eV or a photon wavelength of 1550 Å and decrease rapidly at higher energies.
A discrepancy between theory and the experiment of
Inn\textsuperscript{2} appears above a photon energy of about 8.5 eV. Thus, the measured absorption can be definitely identified with a transition to the repulsive \( A \) \( ^{1} \Pi \) state which dissociates to ground state hydrogen and chlorine atoms.

A careful study of the uncertainties in the calculated potential energy curves and transition moments. The slightly large equilibrium bond length of the computed \( C \) \( ^{1} \Pi \) Gaussian curve may well be the cause of the low calculated oscillator strengths. Nevertheless the discrepancy with the value 0.185 is larger than expected and the theoretical results support a value nearer the lower limit of the experimental range.

For absorption in the 1-0 band, we obtain a value of \( f_{01} \) in the range 0.02-0.03 which is consistent with the measured value of 0.022 within the experimental uncertainty of a factor of two. Table VI lists the values of \( f_{0\nu} \) for \( \nu \leq 3 \) calculated with an RKR potential for the \( C \) \( ^{1} \Pi \) state, an empirical representation of the ground-state potential\textsuperscript{26} and the dipole moment obtained with a \( 3 \) \( ^{1} \Pi \) Slater MO's, shifted by \(-0.1 \Delta E\) (see the text).

is a scatter of 35\% in the various experiments above 8.5 eV.

Figure 9 presents the theoretical photodissociation cross sections for absorption from the \( \nu'' = 0, 1, \) and 2 vibrational levels of the \( X \) \( ^{1} \Sigma^+ \) state, calculated with the Gaussian potential energies and the transition moment obtained from the \( a \) \( ^{1} \Pi \) MO's. The different shapes reflect the structure of the initial eigenfunctions.

At higher energies, absorption bands of \( \text{HCl} \) have been observed.\textsuperscript{2,5,6,7,8} Price\textsuperscript{7} observed a sharp absorption band at 1330 Å, seen also by Myer and Samson\textsuperscript{5} and Tilford \textit{et al.}\textsuperscript{6} It has been attributed to a discrete transition into the lowest vibrational level of the \( b \) \( ^{1} \Pi \) state, which contains its intensity via spin-orbit coupling with the nearby \( C \) \( ^{1} \Pi \) state. We discuss first the allowed absorptions into the \( C \) \( ^{1} \Pi \) state. The very strong absorption bands from the lowest vibrational level of the \( X \) \( ^{1} \Sigma^+ \) state into the \( C \) \( ^{1} \Pi \) state are located in a progression beginning with the 0-0 band at 1291 Å. Their intensities may be characterized by the band absorption oscillator strengths

\[
f_{0\nu} = \frac{2}{3} g \Delta E \left| \langle \psi_{0} | \mathbf{D} | \psi_{\nu} \rangle \right|^{2},
\]

where \( \Delta E \) is the transition energy, all quantities are measured in atomic units and \( g \) is a degeneracy factor equal to two in this case. We have calculated \( f_{0\nu} \) using the various \textit{ab initio} potential energy curves and dipole moments and the resulting values of \( f_{0\nu} \) are presented in Table VI. They cluster in the range 0.12 ± 0.03 and are all smaller than the experimental value 0.185 ± 0.037.\textsuperscript{7} The \( C \) \( ^{1} \Pi - X \) \( ^{1} \Sigma^+ \) dipole moment is changing rapidly with \( R \) and the calculated oscillator strength is sensitive to small shifts of the potential energy curves and transition moment. The slightly large equilibrium bond length of the computed \( C \) \( ^{1} \Pi \) Gaussian curve may well be the cause of the low calculated oscillator strengths. Nevertheless the discrepancy with the value 0.185 is larger than expected and the theoretical results support a value nearer the lower limit of the experimental range.

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\begin{table}[h]
\centering
\begin{tabular}{llll}
\hline
\( \nu' \) & \( f_{0\nu'} \) & \( \lambda (\text{Å}) \) \\
\hline
0 & 1.5(-1) & 1290.3 \\
1 & 2.4(-2) & 1247.1 \\
2 & 2.4(-3) & 1290.6 \\
3 & 6.0(-5) & 1175.2 \\
\hline
\end{tabular}
\caption{Calculated oscillator strengths\textsuperscript{a} for the (0-\( \nu' \)) bands of the \( C \) \( ^{1} \Pi \to X \) \( ^{1} \Sigma^+ \) system.
}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{lll}
\hline
\( X \) \( ^{1} \Sigma^+ \) potential & \( C \) \( ^{1} \Pi \) potential & Transition moments \\
\hline
\( \text{Gaussian} \) & \( \text{Gaussian} \) & 0.10 \\
Gaussian & Gaussian & 0.09 \\
Slater & Slater & 0.13 \\
Slater & Slater & 0.14 \\
\hline
Experiment (Ref. 7) & (0.185 ± 0.037) \\
\hline
\end{tabular}
\caption{Oscillator strengths for the (0-0) band of the \( C \) \( ^{1} \Pi \to X \) \( ^{1} \Sigma^+ \) system.
}
\end{table}

the Slater A $^1 \Pi$ MO’s, shifted towards smaller $R$ by 0.1a$_0$ because of the difference in the empirical and Slater calculations of the equilibrium internuclear distance of the ground state. If the Slater potential energy curves and the Slater dipole moment are used without any empirical modifications, there results $f_0 = 0.14$, $f_0 = 0.022$, $f_0 = 2.8 \times 10^{-5}$, and $f_0 = 2.0 \times 10^{-4}$.

We estimate now the absorption oscillator strength of the forbidden transition into the $b^3 \Pi$ state. It is related to the allowed transition by the approximate formula

$$f(X \sim^1 \Sigma^+ - b^3 \Pi) = 1/\pi \Sigma f(X \sim^1 \Sigma^+ - C \sim^1 \Pi),$$

where $\pi$ is a measure of the interaction strength between the $b^3 \Pi$ and $C^1 \Pi$ states. The spectroscopic analysis of Tilford and Green晶体 yields a value of about 56 for $\pi$ so that with an oscillator strength of 0.17 for the transition into the $C^1 \Pi$ state, $f(X \sim^1 \Sigma^+ - b^3 \Pi) \approx 3 \times 10^{-5}$.

Photodissociation occurs following absorption into the $C^1 \Pi$ state. Superposing Fig. 1 and 2 shows that the $C^1 \Pi$ state is crossed by the repulsive $1^3 \Sigma^+$ state and it will undergo predissociation through spin-orbit coupling. Other triplet states may participate in the process. Experiments indicate that the predissociation of the $C^1 \Pi$ state is very efficient, the observed linewidths exceeding the radiative-damping widths. A theoretical estimate of the rate for predissociation by the $1^3 \Sigma^+$ state can be made from the Fermi Golden Rule. Using the calculated potential curves and an estimated spin-orbit interaction of 0.1 eV, a predissociation rate of $10^{15}$ s$^{-1}$ is obtained. The $C^1 \Pi$ state may also radiate into the lower lying repulsive $A^1 \Pi$ state. The probability for spontaneous emission into this continuum is calculated to be approximately $5 \times 10^4$ s$^{-1}$ with the theoretical potentials and transition moments, so the process contributes negligibly to dissociation of the $C^1 \Pi$ state. The $b^3 \Pi$ state may decay similarly by predissociations and by radiative transitions to the lower lying repulsive $1^3 \Sigma^+$ and $a^3 \Pi$ states.

Absorption bands at 1236 Å and at shorter wavelengths have been detected by Tilford and Green晶体 and by Douglas and Green晶体 and identified by them as a progression in the $2^1 \Sigma^+$ state. As Fig. 1 shows the $2^1 \Sigma^+$ state can be regarded as a single state with a double minimum or as two interacting states. The inner state is the spectroscopic $E^3 \Sigma^+$ state and the outer state the spectroscopic $V$ or $B^1 \Sigma^+$ state. The $E^3 \Sigma^+$ state has a progression of absorption bands beginning at 1194 Å. Absorption into the $V(B)^1 \Sigma^+$ state has been observed in a very weak progression beginning at 1236 Å corresponding to vibrational level $v' = 6$. The computed absorption oscillator strengths for the $0 \rightarrow 0$ band of the $X^1 \Sigma^+ - E^1 \Sigma^+$ transition range from 0.001–0.003. They are considerably smaller than the $C-X(0–0)$ band oscillator strength and photodissociation by absorption into the $E^1 \Sigma^+$ state is unimportant. Because of the large differences between the equilibrium separation of the ground state and the location of the minimum of the $B^1 \Sigma^+$ state, the absorption oscillator strengths into the vibrational levels of the $B^1 \Sigma^+$ state occupying the outer well of the $2^1 \Sigma^+$ state are extremely small and the bands with $v' \approx 5$ have not been detected in absorption.

Many other excited states are observed in experimental studies of absorption by HCl. They are mainly Rydberg in character, except for the lower $1\Sigma^+$ members where considerable Rydberg-valence mixing occurs. The Rydberg states include the $C^1 \Pi$ state which can be described approximately as the result of the excitation from the $2\sigma$ orbital to a $4s$ orbital, though to fit it into the Rydberg series a large quantum defect is needed. An estimate of the absorption oscillator strengths for pure Rydberg states can be derived from the photoionization cross section. The Hartree-Fock calculations of Faegri and Kelly give a cross section at the threshold energy of 12.8 eV of about $2.5 \times 10^{-15}$ cm$^2$. If $n$ is the principal quantum number of the Rydberg state, the discrete oscillator strength is approximately $6.2/n^2$, divided between the accessible Rydberg type $1\Sigma^+$ and $1\Pi$ excited states.

The total oscillator strength of the states lying above the $C^1 \Pi$ state may thus be as much as 0.2. The absorption, though strong, may not contribute significantly to the dissociation of the molecule. The excited states are bound and are not crossed by repulsive triplet states. They may decay predominantly in radiative transitions to discrete levels of low-lying electronic states.

Above 12.8 eV photoionization occurs and it is then the principal photodestruction process.

VI. THE RADIATIVE LIFETIME OF THE $2(\Sigma^+) \sim^1 \Sigma^+$ STATE

Absorptions into low-lying vibrational levels of the outer well of the $2^1 \Sigma^+$ state, or equivalently the $V$ or $B^1 \Sigma^+$ state, from the $v' = 0$ level are improbable but emissions from them to high vibrational levels of the $X^1 \Sigma^+$ state are not and they have been recorded in experiments with discharges through hydrogen chloride vapour.

The excited vibrational levels probably decay preferentially by radiating to the $X^1 \Sigma^+$ and $A^1 \Pi$ states. Because of the rapid decrease in the $2^1 \Sigma^+ - A^1 \Pi$ dipole moment, shown in Fig. 7, the probabilities of transition to the $A^1 \Pi$ state will be small and their lifetimes are determined by radiation to the $X^1 \Sigma^+$ state.

If $\chi_\nu(R)$ is the vibrational wave function in the $B^1 \Sigma^+$ state and $\chi_\nu(R)$ is the vibrational wave function in the $X^1 \Sigma^+$ state, both normalized to unity, the transition probability $A_{\nu'\nu}$ is given by

$$A_{\nu'\nu} = 2.03 \times 10^5 \nu_{\nu'\nu} \left| \chi_\nu(R) \right| D(R) \left| \chi_\nu(R) \right|^2 \text{s}^{-1},$$

where $\nu_{\nu'\nu}$ is the transition frequency in cm$^{-1}$. The lifetime of level $v'$ is given by the expression

$$\tau_{\nu'} = 1/2 \nu_{\nu'\nu} A_{\nu'\nu},$$

where the sum over $\nu'$ includes an integration over the continuum vibrational levels of the final electronic state.

We have calculated the radiative lifetime of the $v' = 0$ level of the $B^1 \Sigma^+$ state using both $ab initio$ potential energy curves in the nuclear wave equations. The $2^1 \Sigma^+ - X^1 \Sigma^+$ dipole moments, which are shown in Fig. 6, are very large in the region of the outer minimum of the
TABLE VII. Interstellar HCl photodissociation and photoionization rates in s⁻¹ for an optically thin cloud.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Rate (10⁻¹⁹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A ¹Σ⁺</td>
<td>2.1</td>
</tr>
<tr>
<td>C ¹Π</td>
<td>5.3</td>
</tr>
<tr>
<td>b ³Π</td>
<td>0.1</td>
</tr>
<tr>
<td>Higher lying states</td>
<td>2.3</td>
</tr>
<tr>
<td>Ionization</td>
<td>0.9</td>
</tr>
</tbody>
</table>

2 ¹Σ⁺ state so the calculated lifetimes τ₀ are short, ranging from 2–4 ns. The calculated lifetimes of those higher vibrational levels which are not greatly perturbed by interaction with the E ¹Σ⁺ levels are slightly longer. The contributions to the radiative lifetimes from transitions into the vibrational continuum of the X ¹Σ⁻ state are less than 1% for v' = 0, but as much as 20% for v' = 5.

VII. PHOTODESTRUCTION OF ATMOSPHERIC AND INTERSTELLAR HCl

Chlorine compounds play a central role in the chemistries of the stratospheres of the planets Earth and Venus and photodissociation of HCl is a critical process in the chemical sequences. Recent calculations assumed that photodissociation occurs only by absorption into the A ¹Π state of HCl and adopted the cross sections measured by Inm. Additional contributions to the photodissociation rate come from absorptions into the C ¹Π, b ³Π and possibly the Rydberg states, though the wavelengths of the transitions lie in a region where molecular oxygen is an effective absorber.

The calculated photodissociation rates in interstellar clouds also have assumed only transitions into the A ¹Π state. We present in Table VII the contributions to the photodissociation rate in optically thin interstellar clouds arising from the continuous absorption into the A ¹Π state and the discrete absorptions into the C ¹Π and b ³Π states. For oscillator strengths for the C ¹Π state we employed the values listed in Table VI and for the b ³Π state we employed an oscillator strength of 3 × 10⁻³.

The contributions to the higher lying states may contribute to the dissociation process. To obtain an upper limit to the possible rate, we adopted an effective oscillator strength of 0.2 for these states, and assumed a dissociation efficiency of unity. The photodissociation rate corresponding to the cross sections of Faegri and Kelly is included in the Table. In calculating the photodestruction rates we adopted the mean interstellar radiation field of Roberge et al.

The photodissociation rate is 7.5 × 10⁻¹⁹ s⁻¹ if the absorption into the higher lying states is excluded and is 9.8 × 10⁻¹⁹ s⁻¹ if the maximum possible contribution from the higher lying states is included. Previous studies of interstellar hydrogen chloride used a rate in the optically thin limit of 2.4 × 10⁻¹⁹ s⁻¹. The enhanced photodestruction rate obtained here diminishes substantially the discrepancy between observation and theory and in conjunction with other modifications to the chemistry may remove it.

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18The ALCHEM system of programs were developed by P. S. Bagus, B. Liu, A. D. McLean and M. Yoshimine.
3702 van Dishoeck, van Hemert, and Dalgarno: Photodissociation of HCl

29 K. Faegri and H. P. Kelly (in press).