

7 Anhang

7.1 Summary

In this work HCl and DCI were examined with the help of the predissociationspectroscopy. For this UV-UV double resonance method a new experimental setup was realised using two nanosecond dye lasers. The first step of the experiment, the resonance enhanced multiphoton ionisation (REMPI), was realised utilizing one dye laser. The REMPI process offers thereby the possibility to prepare state selected HCl^+ - and DCI^+ ions, with which the angular momentum can be tuned. These state selected molecular ions represent promising precursors for investigations of ion molecule reactions. Further the spectroscopy of the HCl - and DCI $f^3\Delta_2 \leftarrow X^1\Sigma^+$ transition is accessible by the REMPI step of the experiment. In the second part of the experiment the molecular ions are photoexcited into the $A^2\Sigma^+$ state with the help of the second laser system. Due to the fact, that the $A^2\Sigma^+$ state can predissociate, one receives the predissociation spectra (PD-spectra) of the HCl^+ - and DCI^+ $A^2\Sigma^+ \leftarrow X^2\Pi_{3/2}$ transitions. The photodissociation causes formation of Cl^+ ions, which can be detected using a time of flight mass spectrometer. Via the PD-spectra it was possible to determine the rotational state distribution of the $\text{DCI}^+/\text{HCl}^+$ ions formed in the REMPI step. In addition, the spectroscopic parameters of the HCl^+ - and DCI^+ $A^2\Sigma^+$ -states have been derived. Finally, through the analysis of the linewidth and lineprofile conclusions on the predissociationdynamics of HCl^+ and DCI^+ can be drawn. In particular, this yields in the exact determination of the predissociationthreshold.

New spectroscopic parameters v_0 , B, D and H for the HCl and DCI $f^3\Delta_2(v''=0)$ Rydberg state were achieved from the $f^3\Delta_2 \leftarrow X^1\Sigma$ REMPI spectra. So far, according to knowledge on available literature, this is the first time that these parameters for H^{37}Cl and D^{37}Cl were determined.

The PD spectra of the $\text{HCl}^+ A^2\Sigma^+(v' = 4-6) \leftarrow X^2\Pi_{3/2}(v'' = 0)$ - and $\text{DCI}^+ A^2\Sigma^+(v' = 6-9) \leftarrow X^2\Pi_{3/2}(v'' = 0)$ transitions result from a one color (1+1) photodissociation, whereas

the resonant states are below the predissociation threshold. As a result, the spectroscopic parameters of these states can be determined. Data from literature on emission spectroscopy experiments compares well with the DCI⁺ states, but not with the HCl⁺ states, observed in this study.

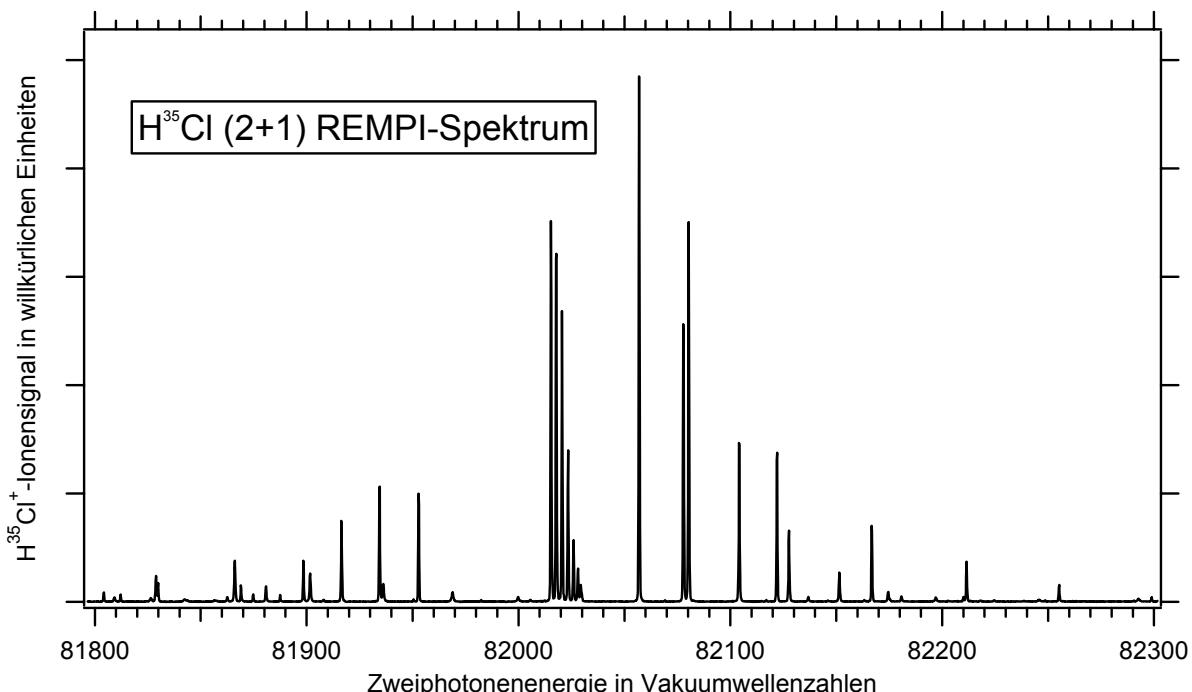
For the HCl⁺ A $^2\Sigma^+(v' = 7)$ - as well as the DCI⁺ A $^2\Sigma^+(v' = 10)$ state the rotational constants B, the γ -coupling constants and the transition energy T_v have been determined. Data for B and γ of these states were previously not available, since no rotational resolved spectra were accessible. From the HCl⁺ A $^2\Sigma^+(v' = 7)$ - and the DCI⁺ A $^2\Sigma^+(v' = 10)$ PD-spectra one derives the rotational state distribution of the ions formed via different pump lines in the REMPI process. It could be shown that the ionisation via the $f^3\Delta_2(v''=0)$ Rydberg state leads to a high rotational state selectivity and a narrow rotational state distribution of the ions in the X $^2\Pi_{3/2}$ state. Ions are formed in not more than four different rotational states, whereat about 70% of all ions are formed in just two rotational states. By proper choice of the pump line (tuning from R(1) to R(2)) in the REMPI spectrum the distribution in the HCl⁺/DCI⁺ X $^2\Pi_{3/2}$ state can be shifted from N'' = 0-1 to N'' = 4-5. A line profile analysis of a step in the HCl⁺ A $^2\Sigma^+(v' = 7)$ spectrum gave a new value for the dissociation energy of $D_0(\text{HCl}^+) = 37536,7 \pm 0,5 \text{ cm}^{-1}$. Combining this value with literature data on the ionisation energy of HCl and Cl, a new value for the dissociation energy of the neutral HCl have been derived as $D_0(\text{HCl}) = 35747,2 \pm 1,2 \text{ cm}^{-1}$.

Therefore in this work the predissociationspectra of the HCl⁺A $^2\Sigma^+(v' = 8-10)$ \leftarrow HCl⁺ X $^2\Pi_{1/2}(v'' = 0)$ - as well as the DCI⁺A $^2\Sigma^+(v' = 11,12)$ \leftarrow DCI⁺ X $^2\Pi_{1/2}(v'' = 0)$ transitions were obtained. For these states the predissociationlifetime as a function of the vibrational quantum number is observed. Within the HCl⁺ states the shortest lifetime of $\tau = 0.063(12) \text{ ps}$ was determined in the ($v' = 8$) state. For higher vibrational quantum numbers the predissociation lifetime increases again. This experimental finding shows a similar trend, as already available theoretical work.

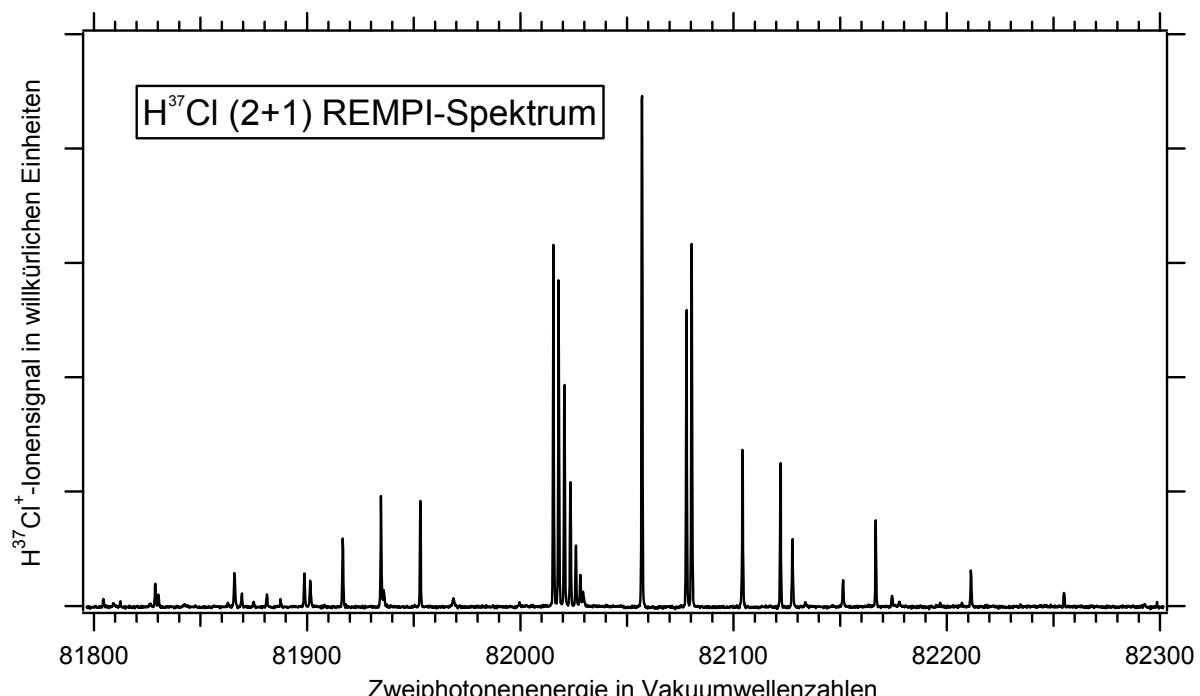
7.2 Spektrenverzeichnis

In diesem Abschnitt sind die REMPI-Spektren über den $f^3\Delta_2$ -Zustand sowie die PD-Spektren der $A^2\Sigma^+ \leftarrow X^2\Pi_{3/2}$ Übergänge, die im Rahmen dieser Arbeit aufgenommen wurden, zusammengesellt.

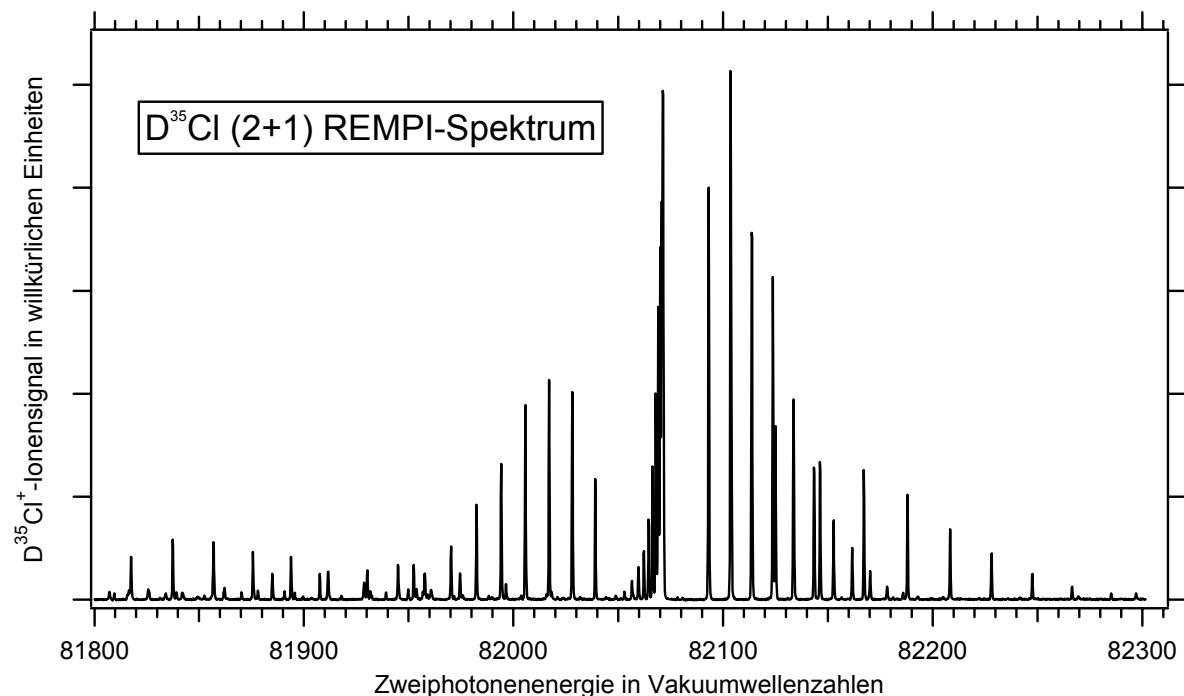
7.2.1 REMPI-Spektren über den $f^3\Delta_2$ -Zustand



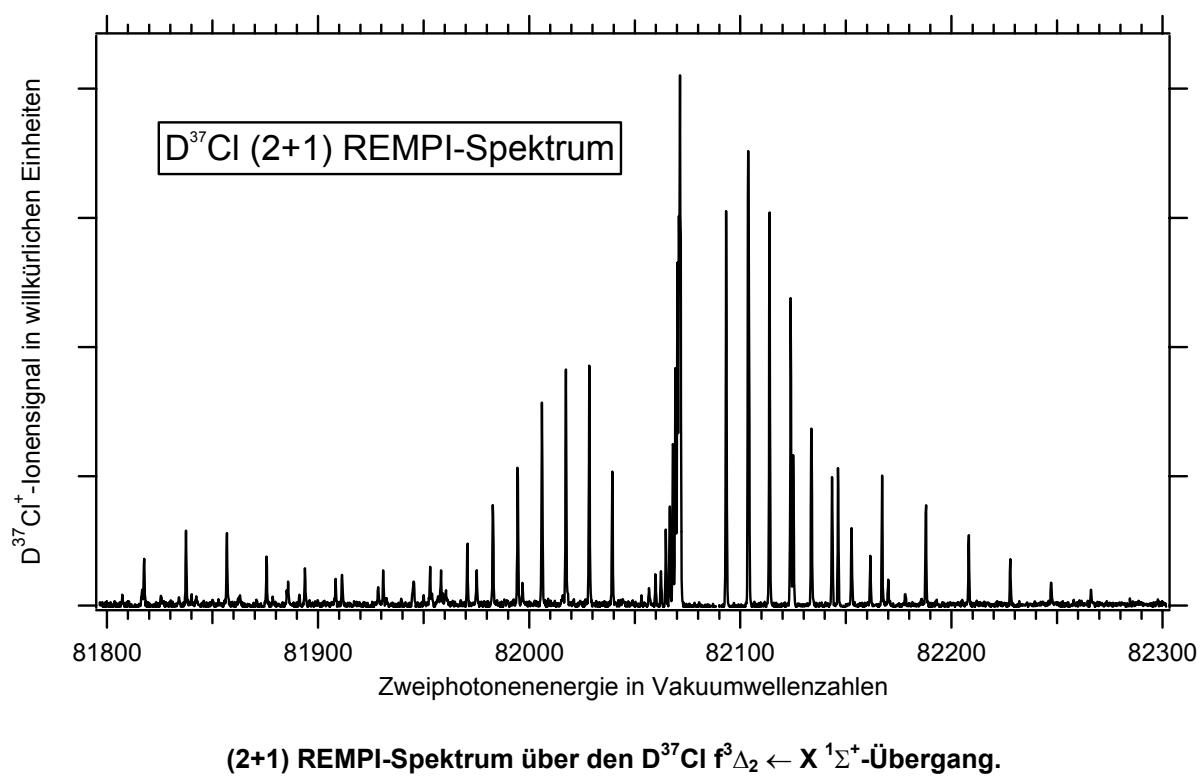
(2+1) REMPI-Spektrum über den $H^{35}Cl f^3\Delta_2 \leftarrow X^1\Sigma^+$ -Übergang.



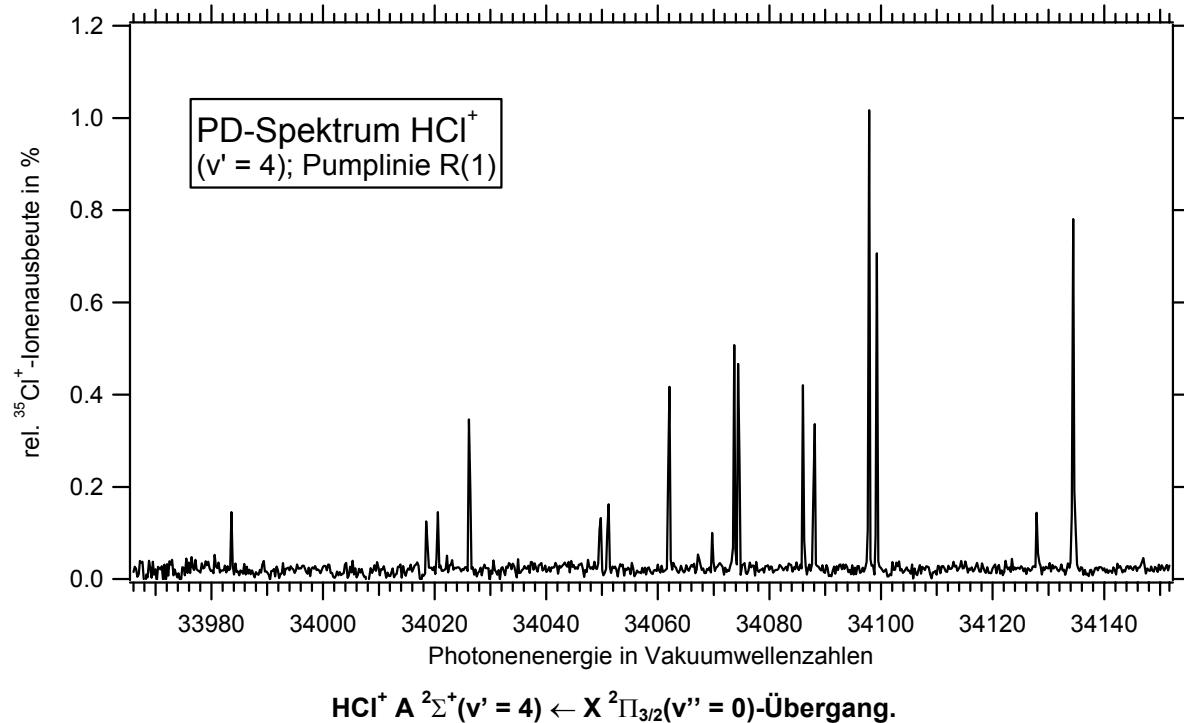
(2+1) REMPI-Spektrum über den H³⁷Cl f³Δ₂ ← X 1Σ⁺-Übergang.

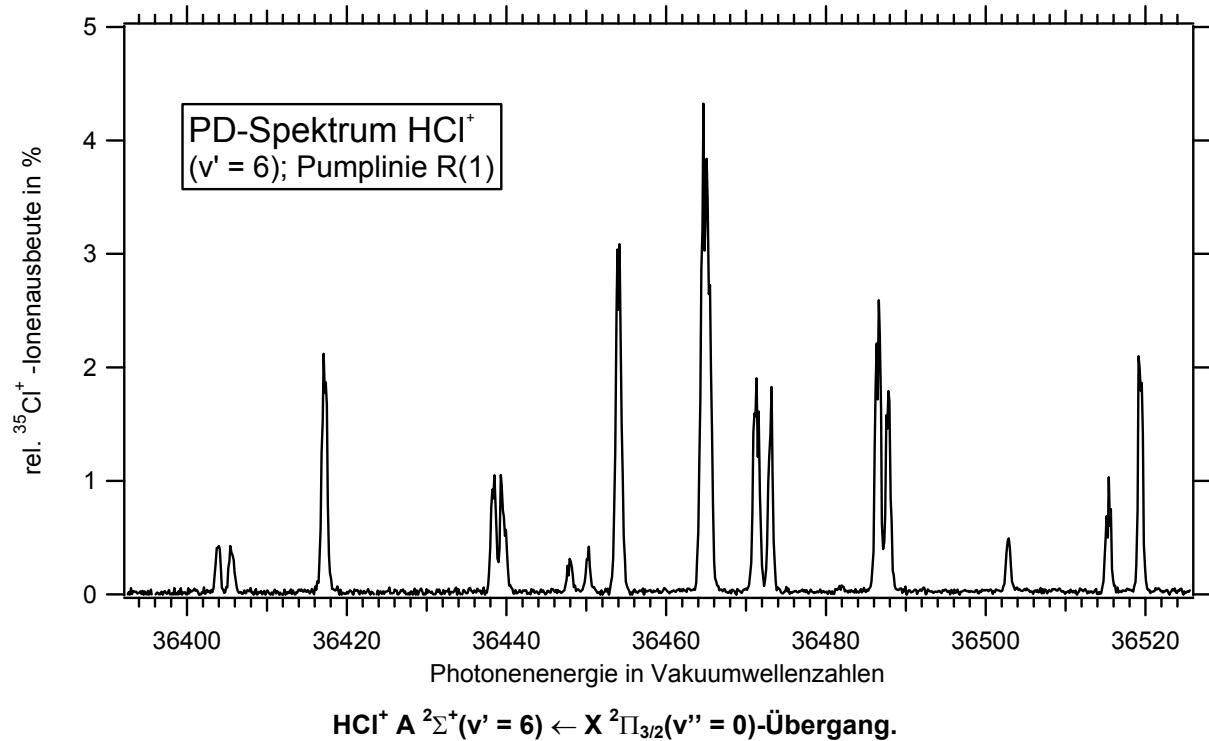
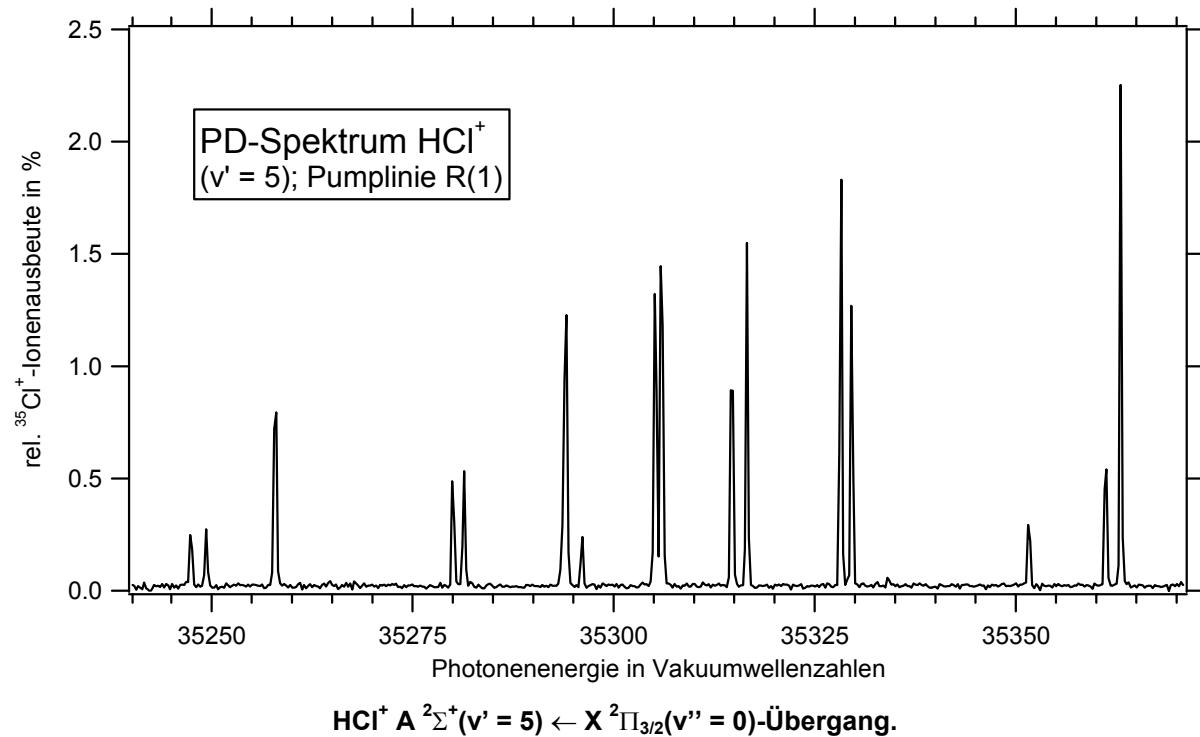


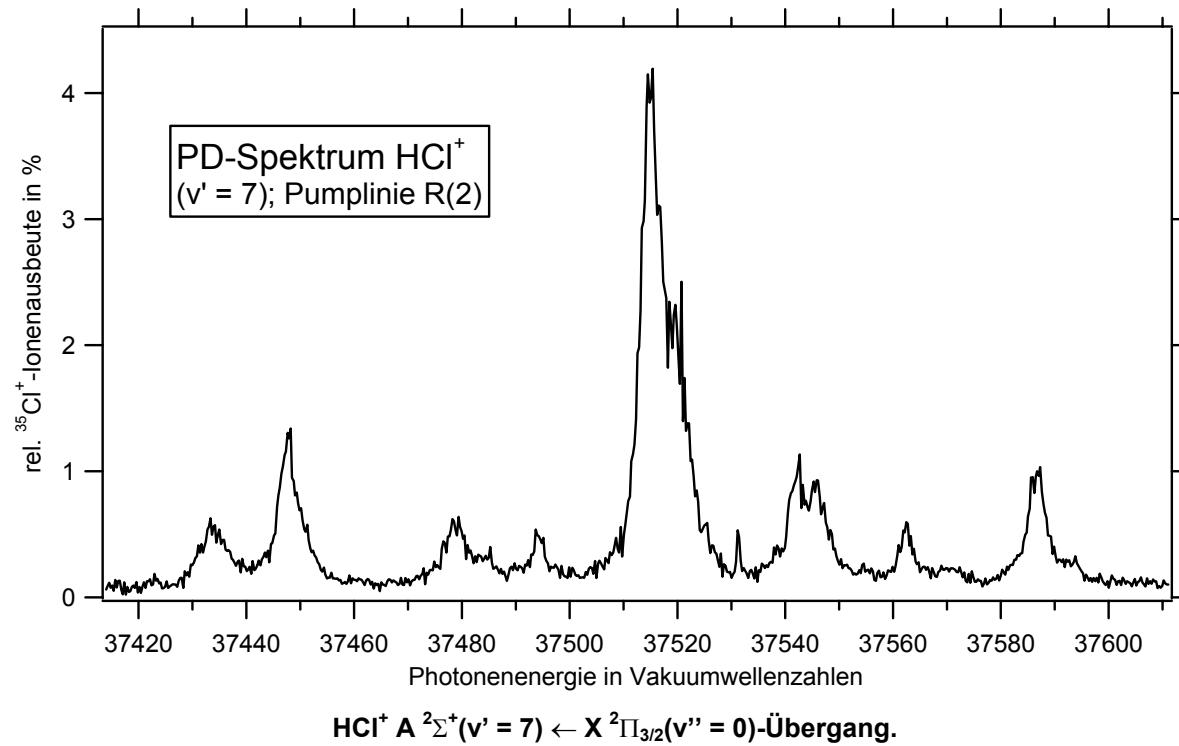
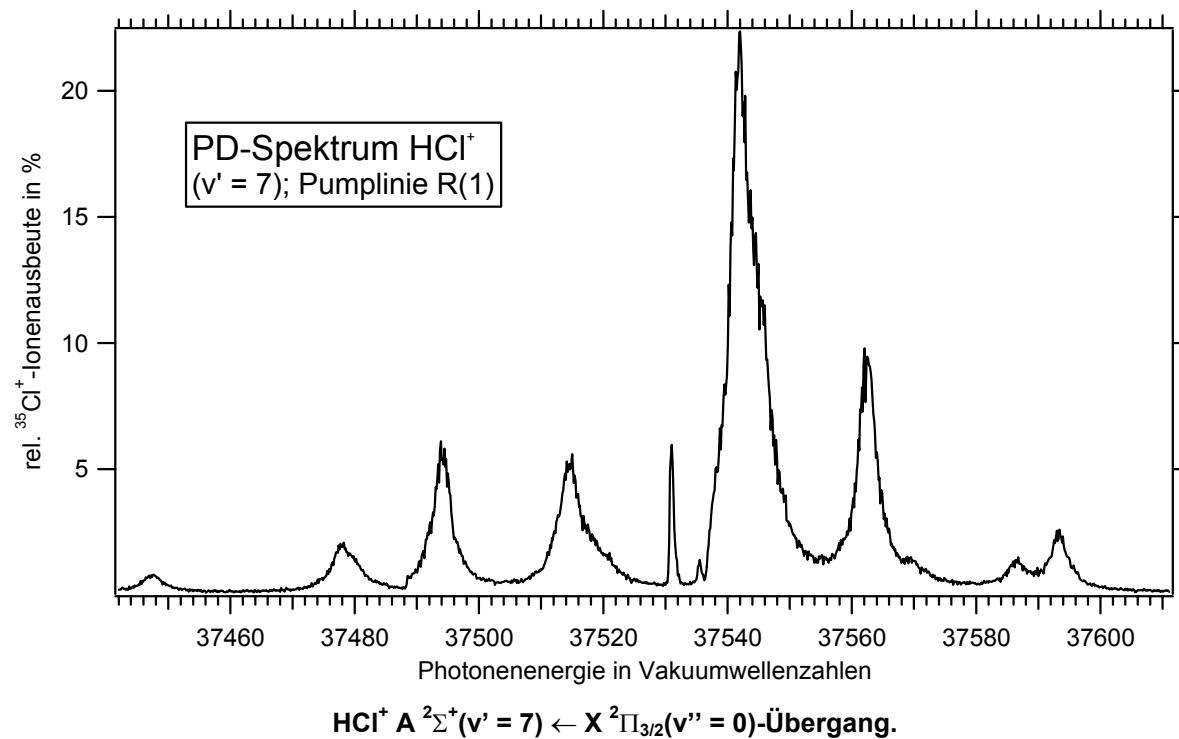
(2+1) REMPI-Spektrum über den D³⁵Cl f³Δ₂ ← X 1Σ⁺-Übergang.

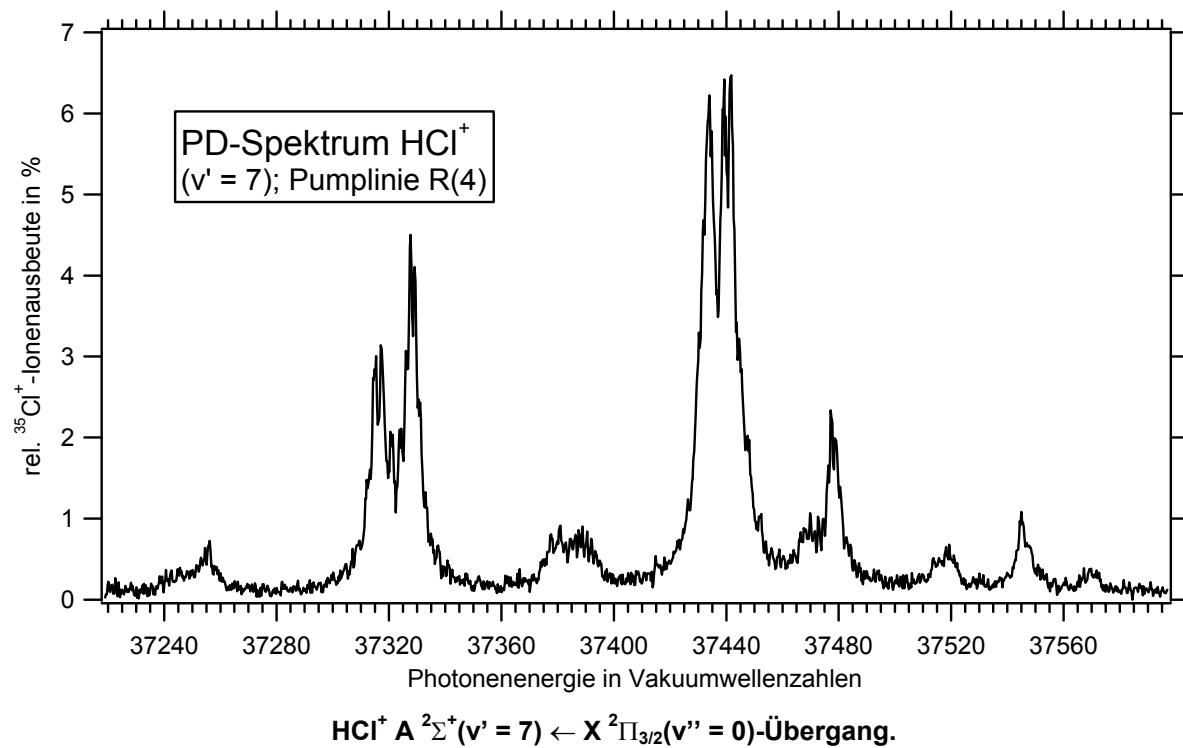
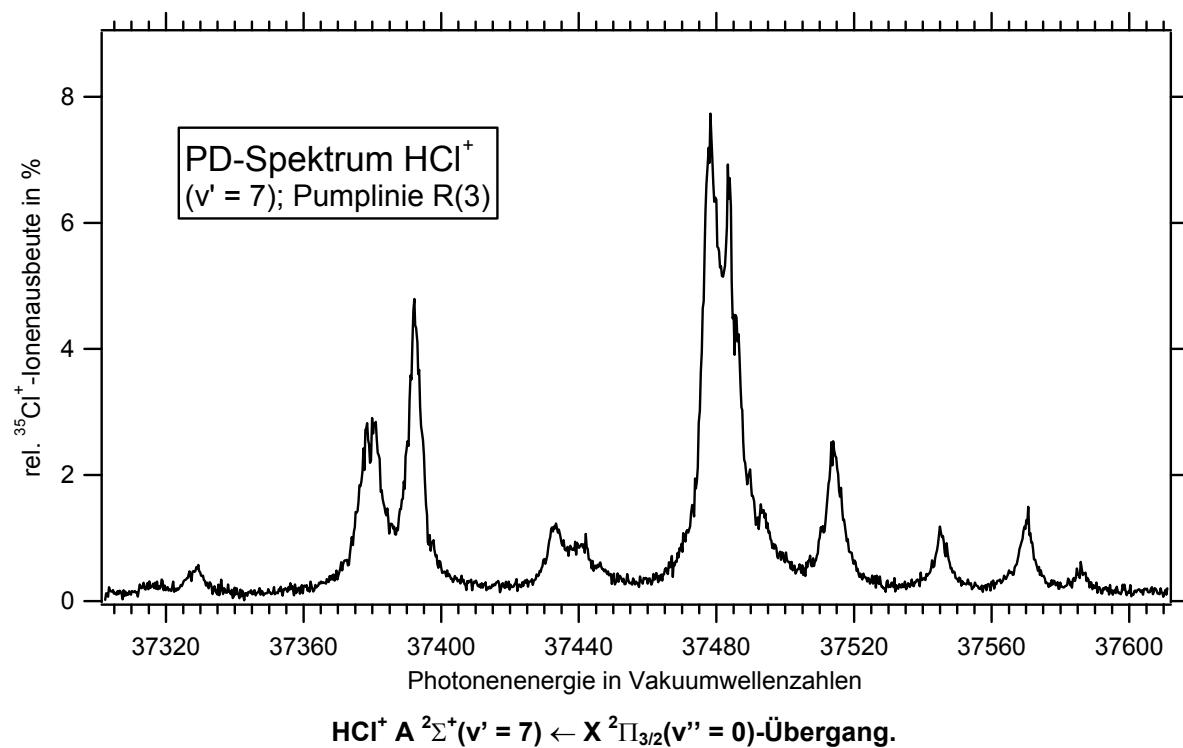


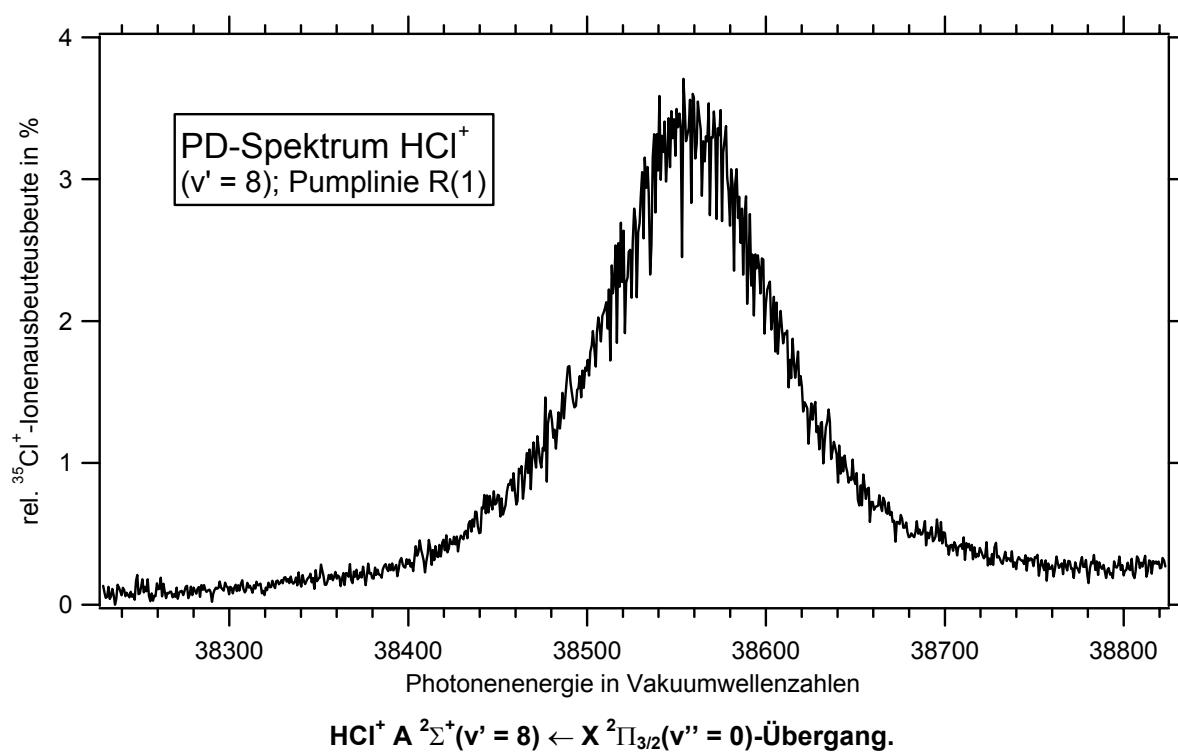
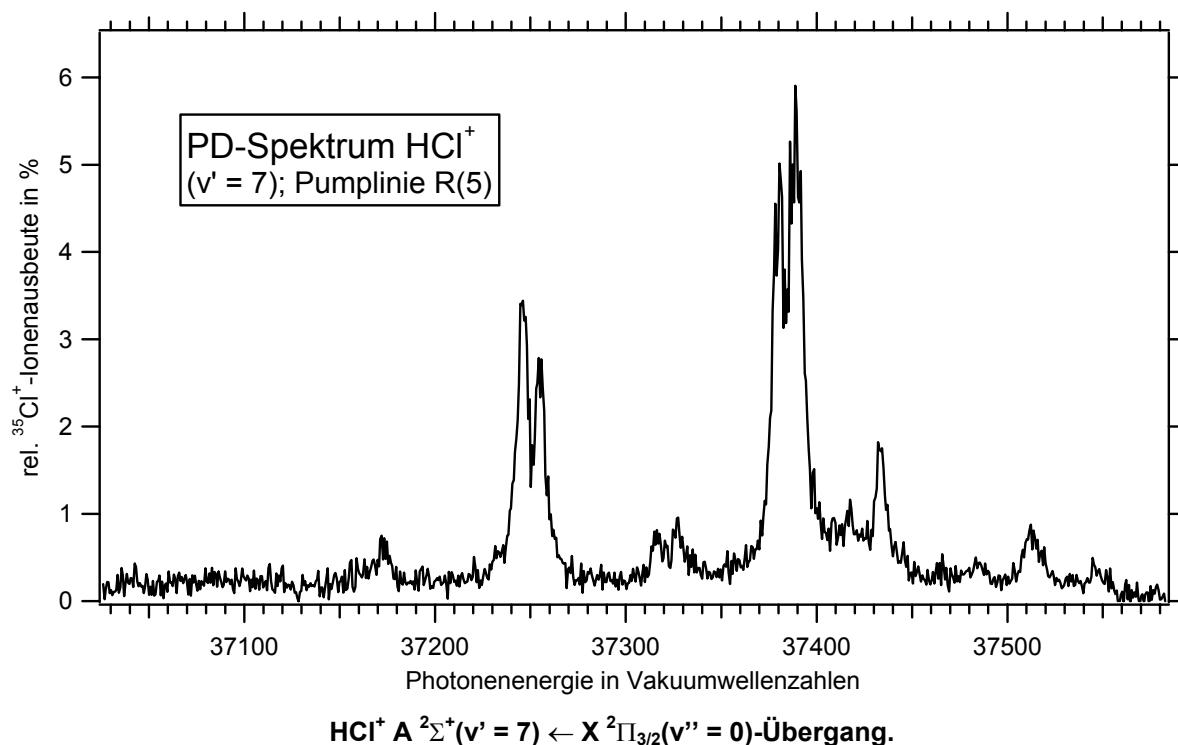
7.2.2 PD-Spektren der HCl⁺ A ²Σ⁺ ← X ²Π_{3/2}-Übergänge

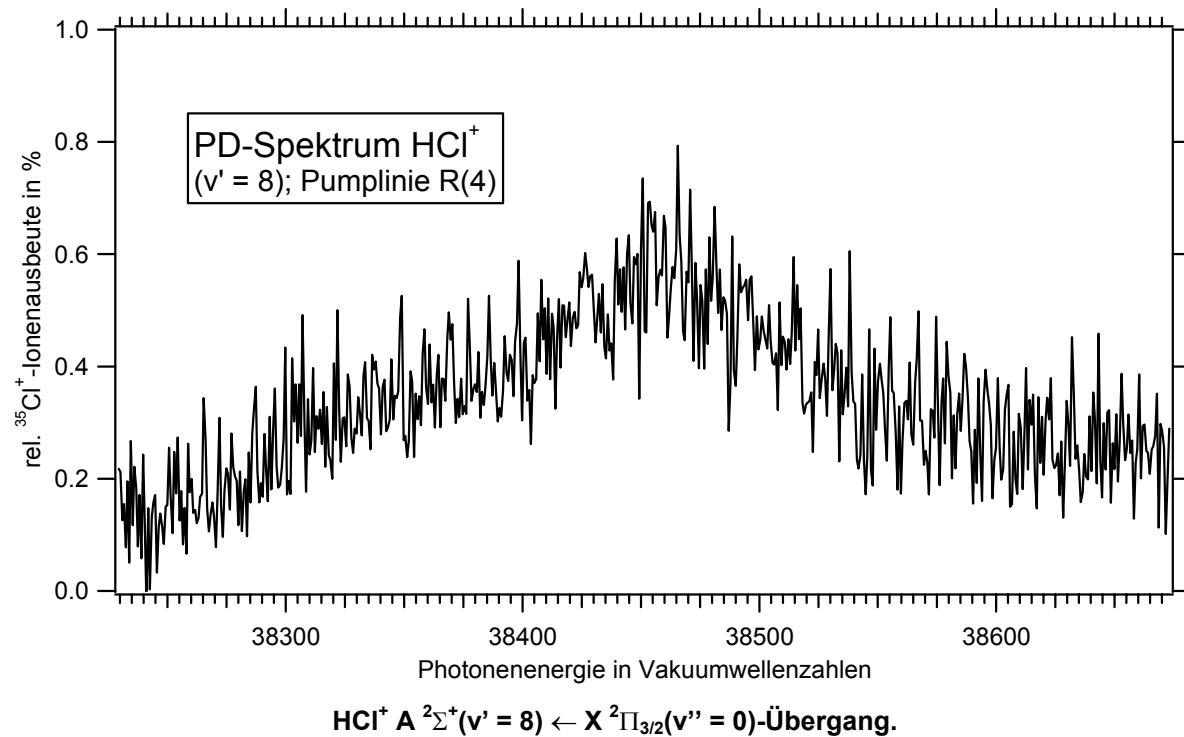
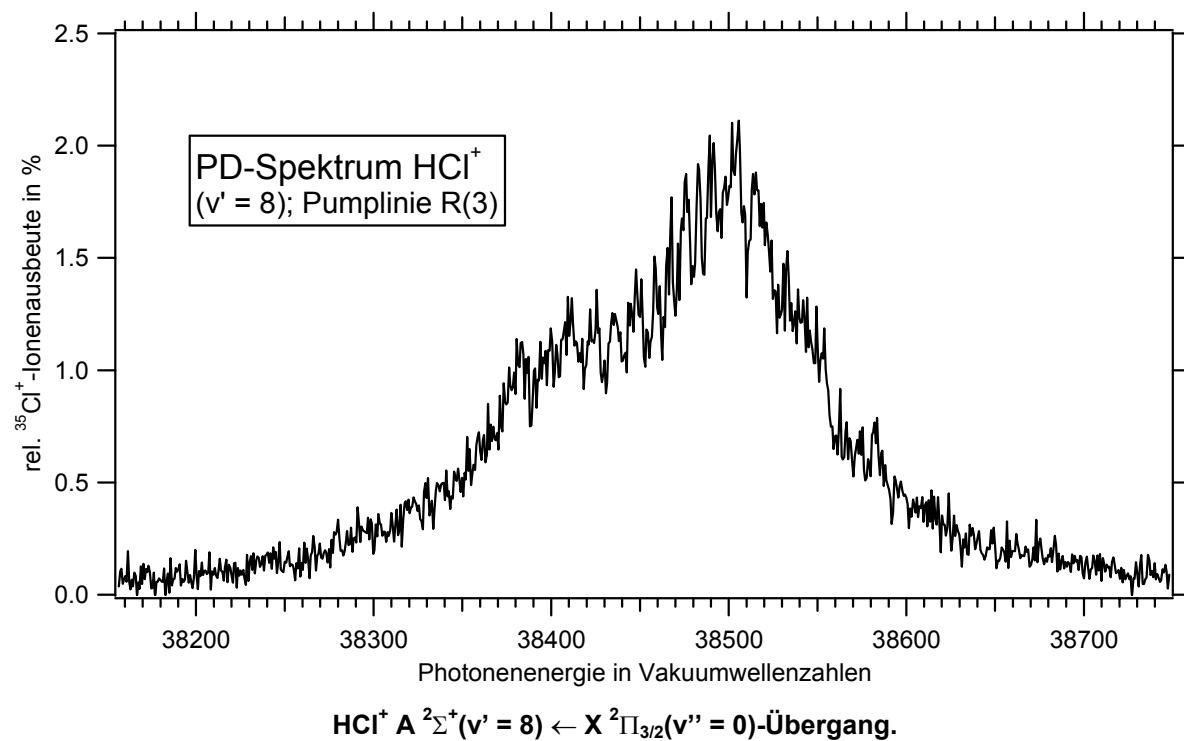


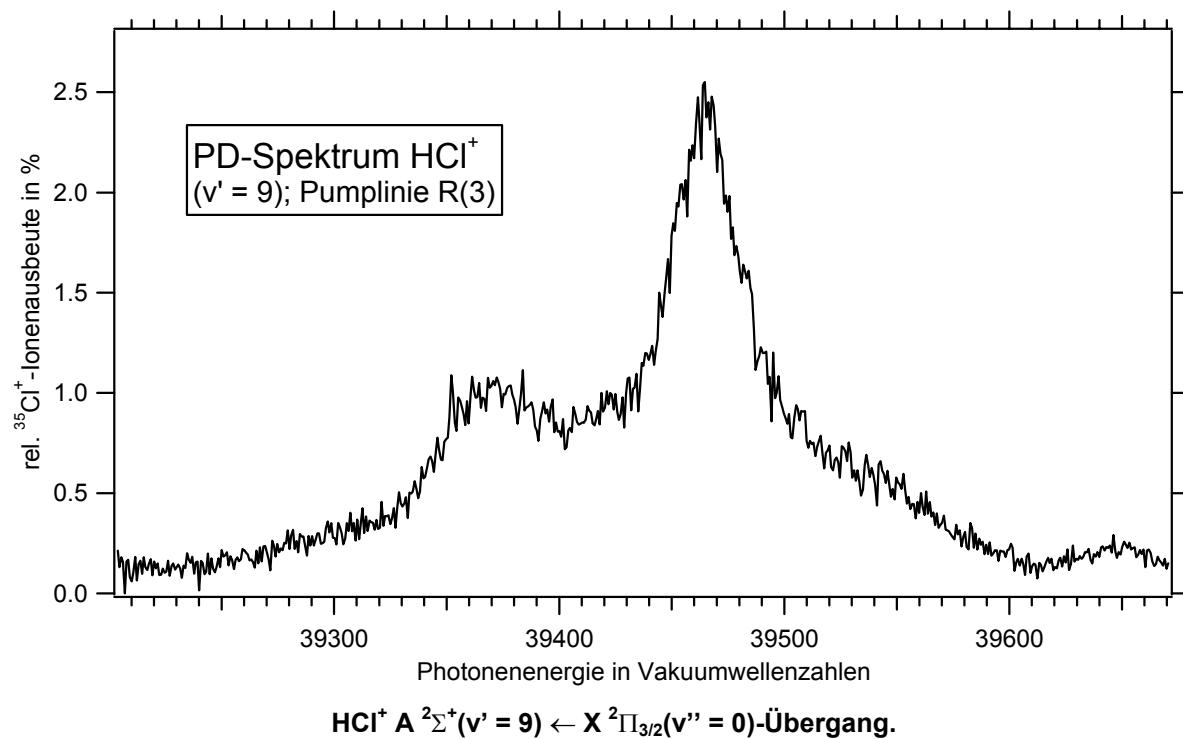
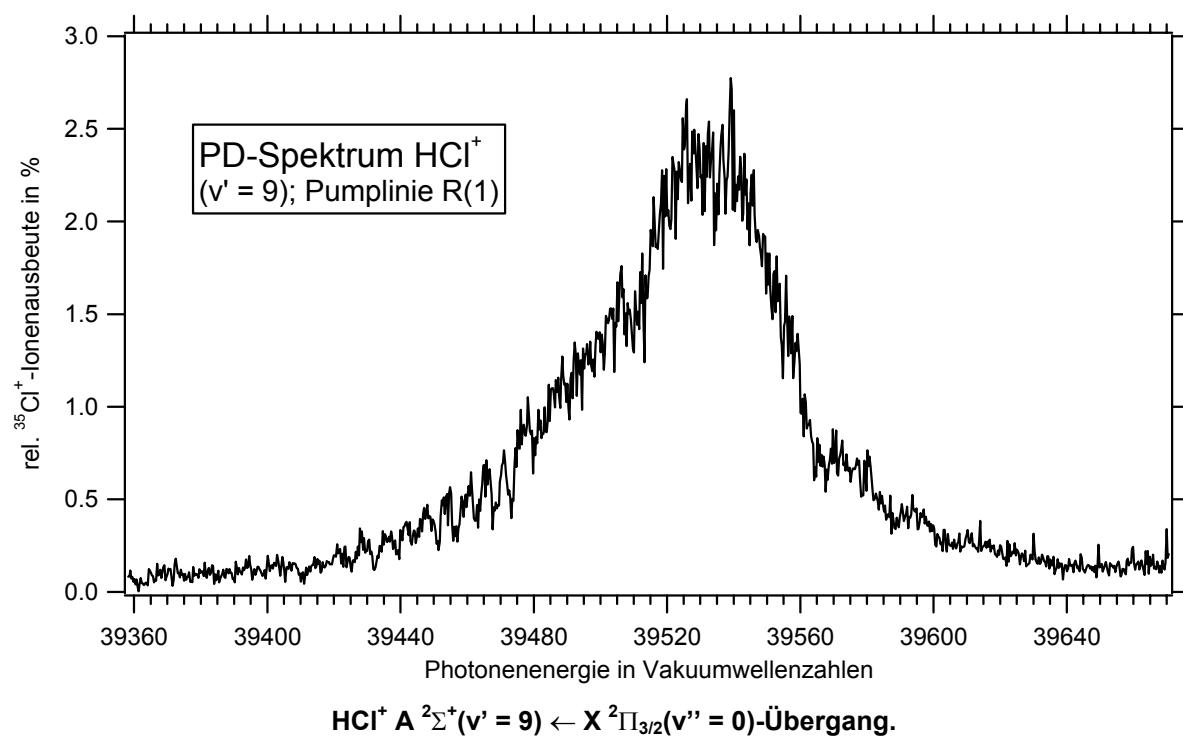


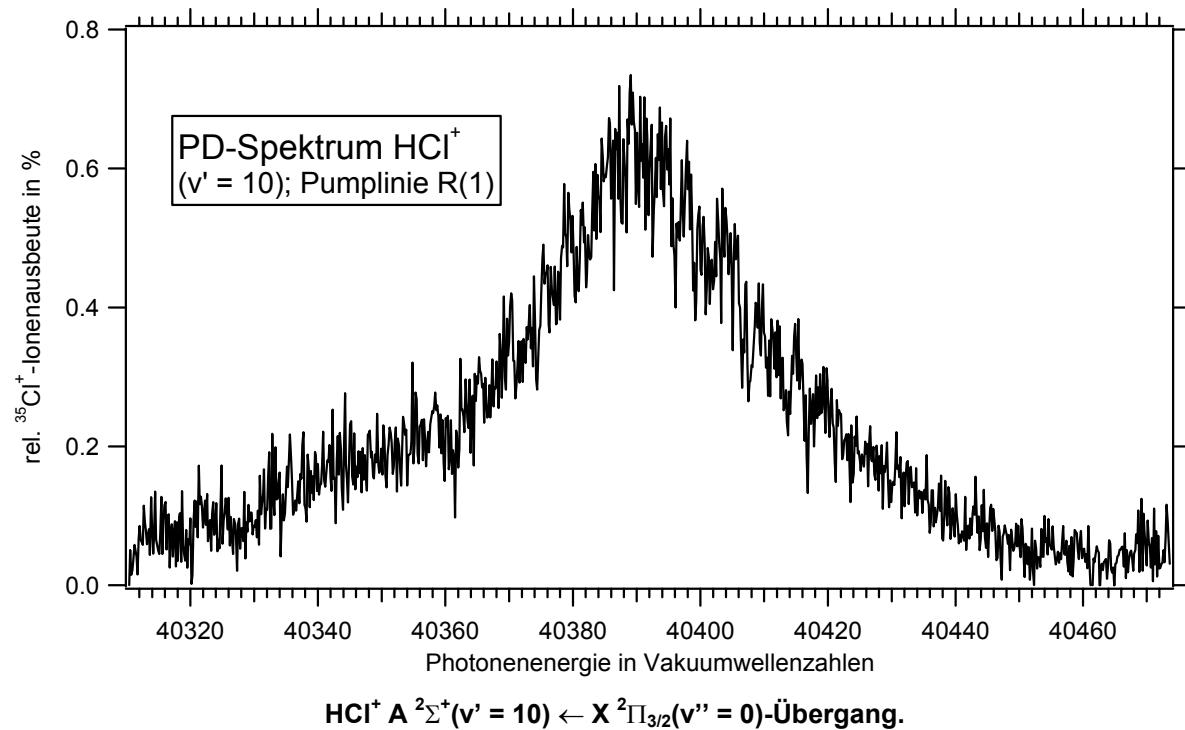
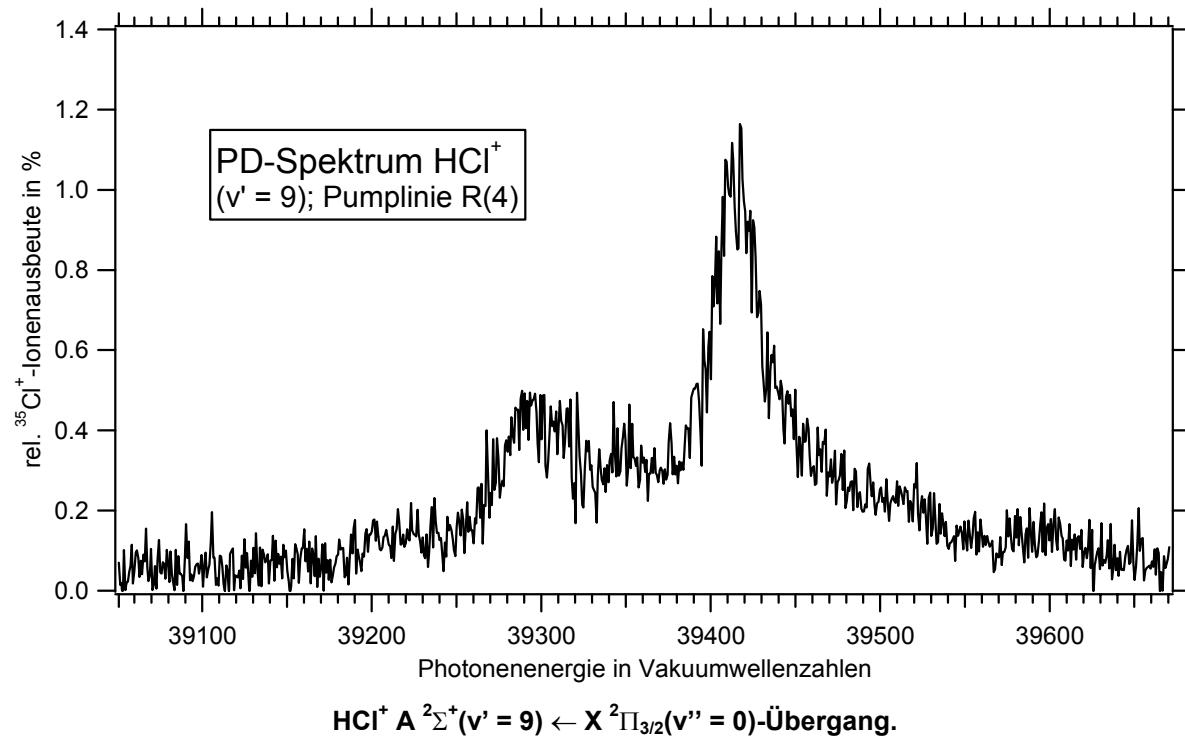


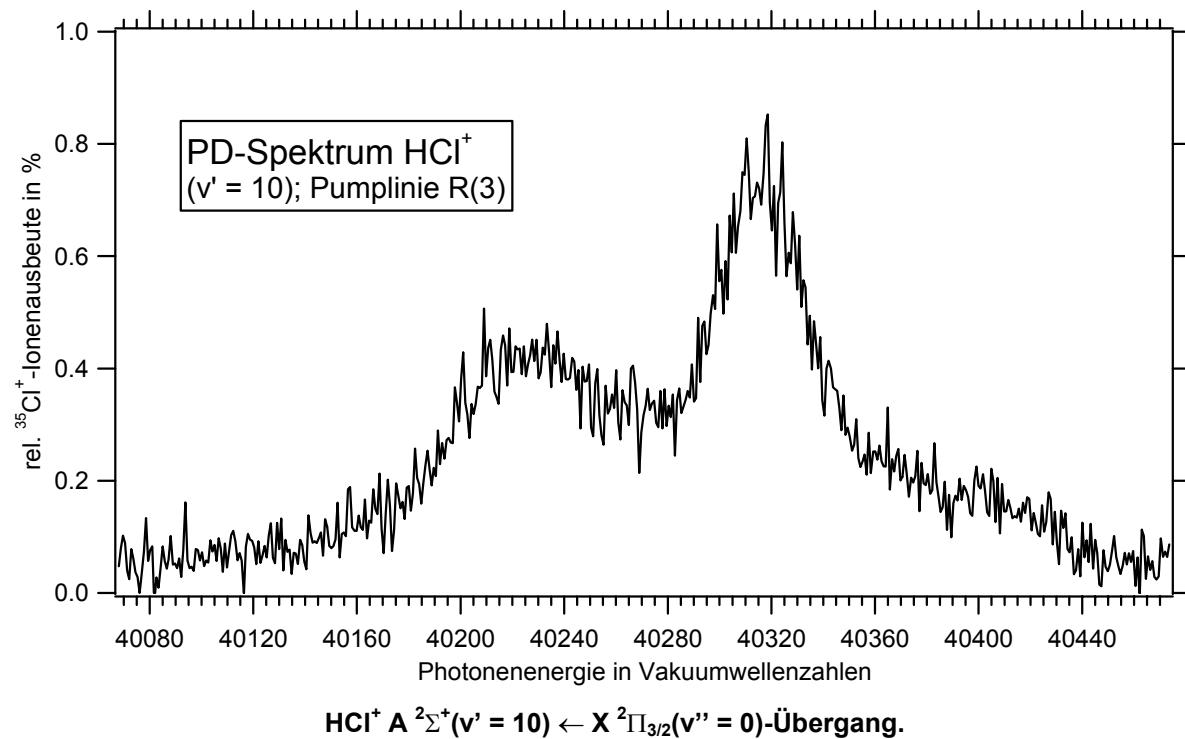
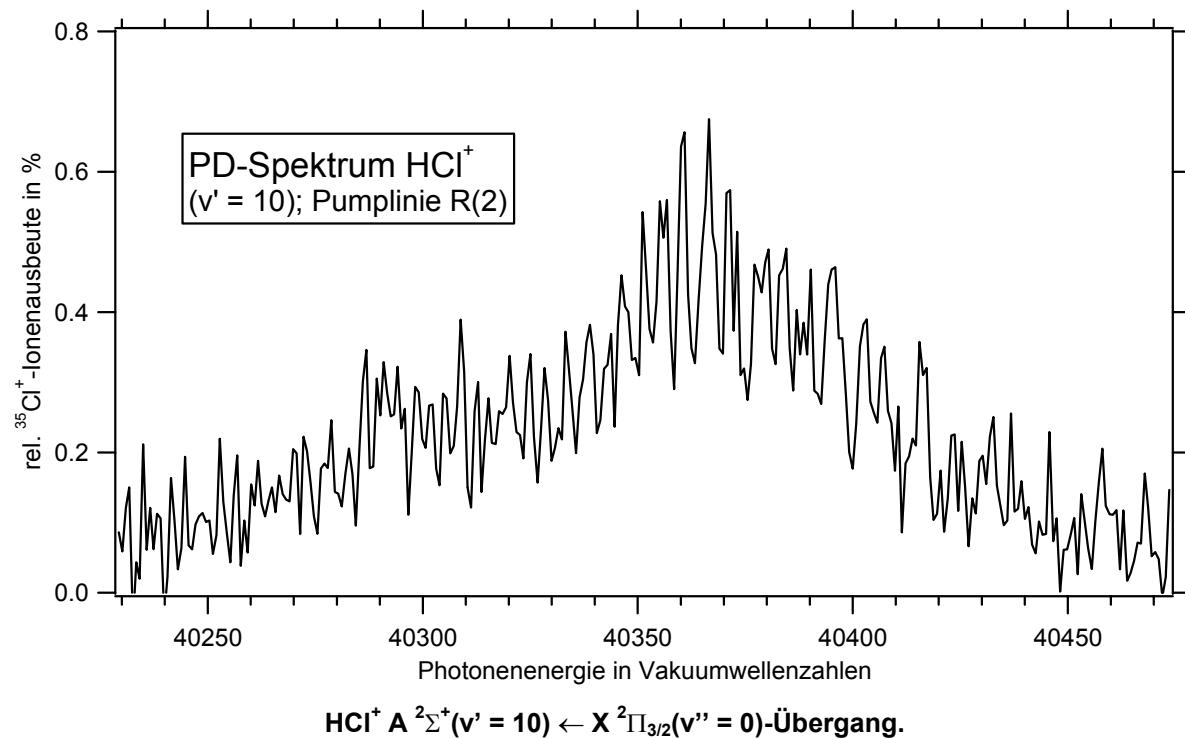


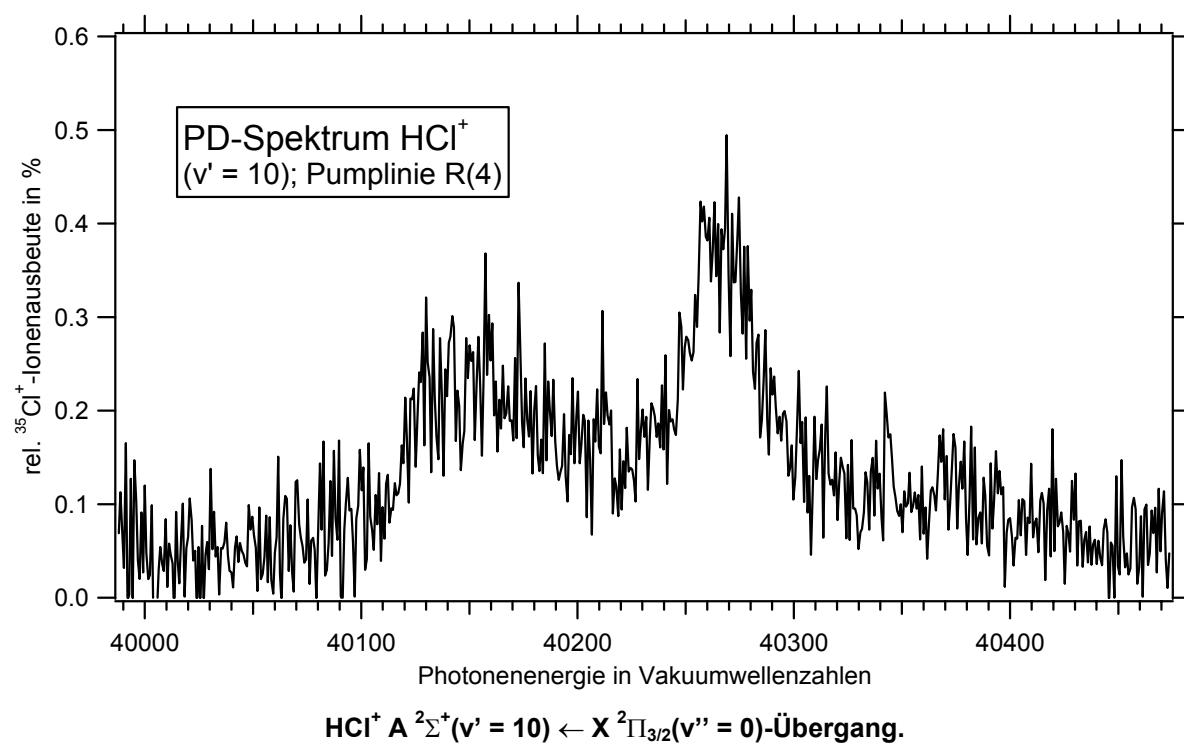




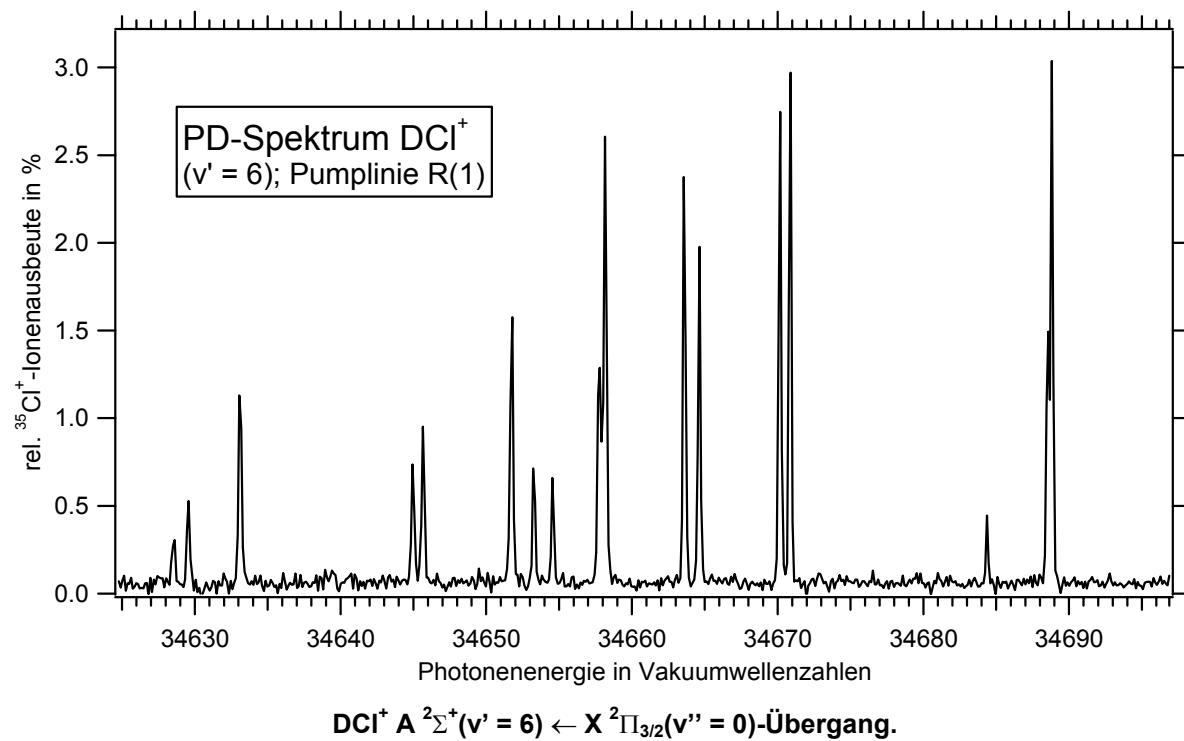


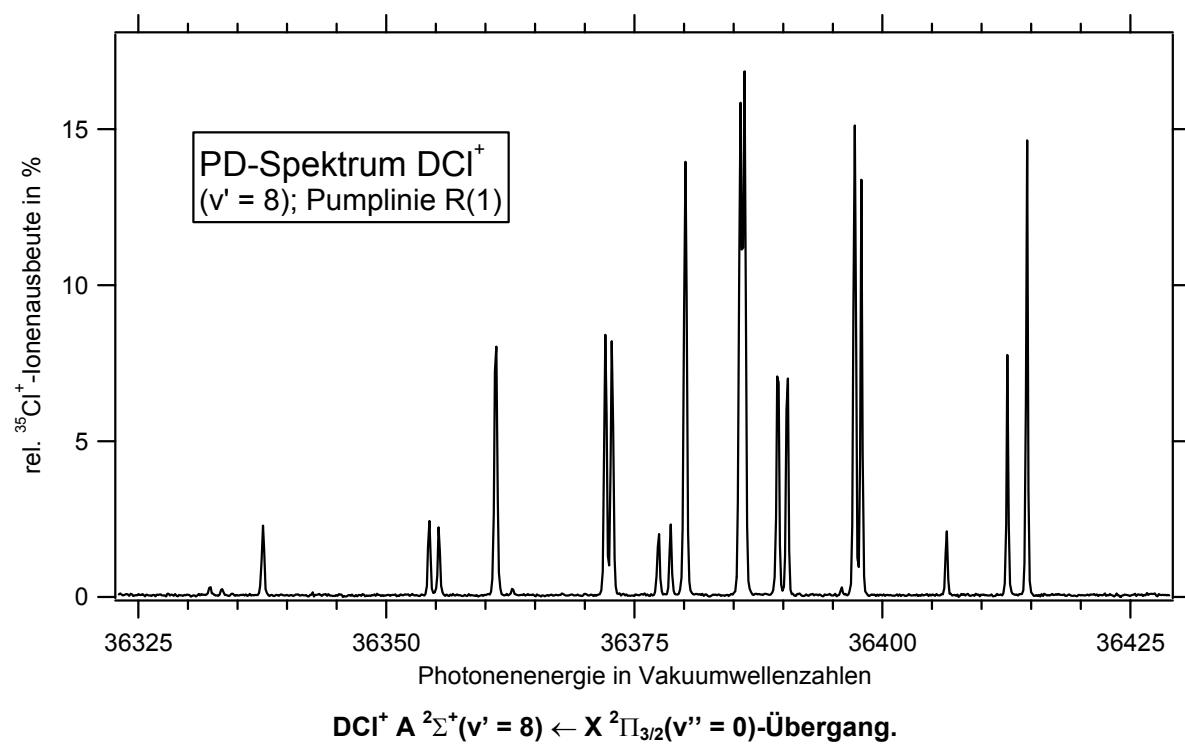
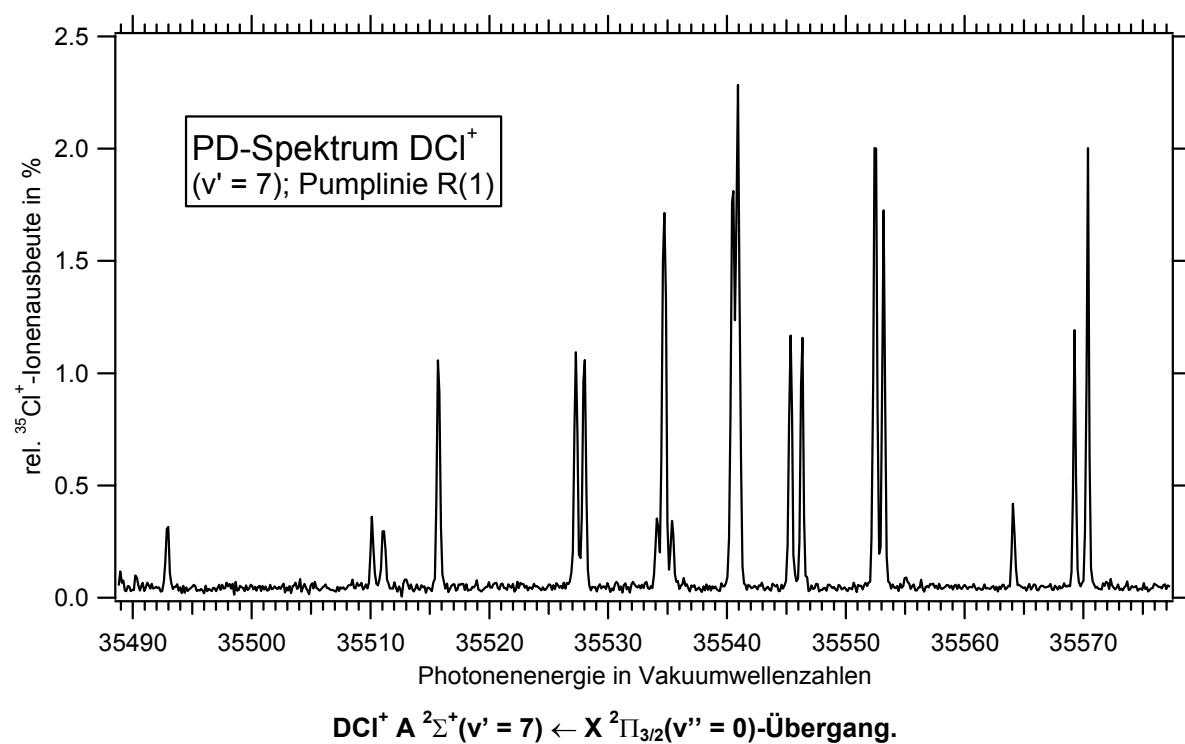


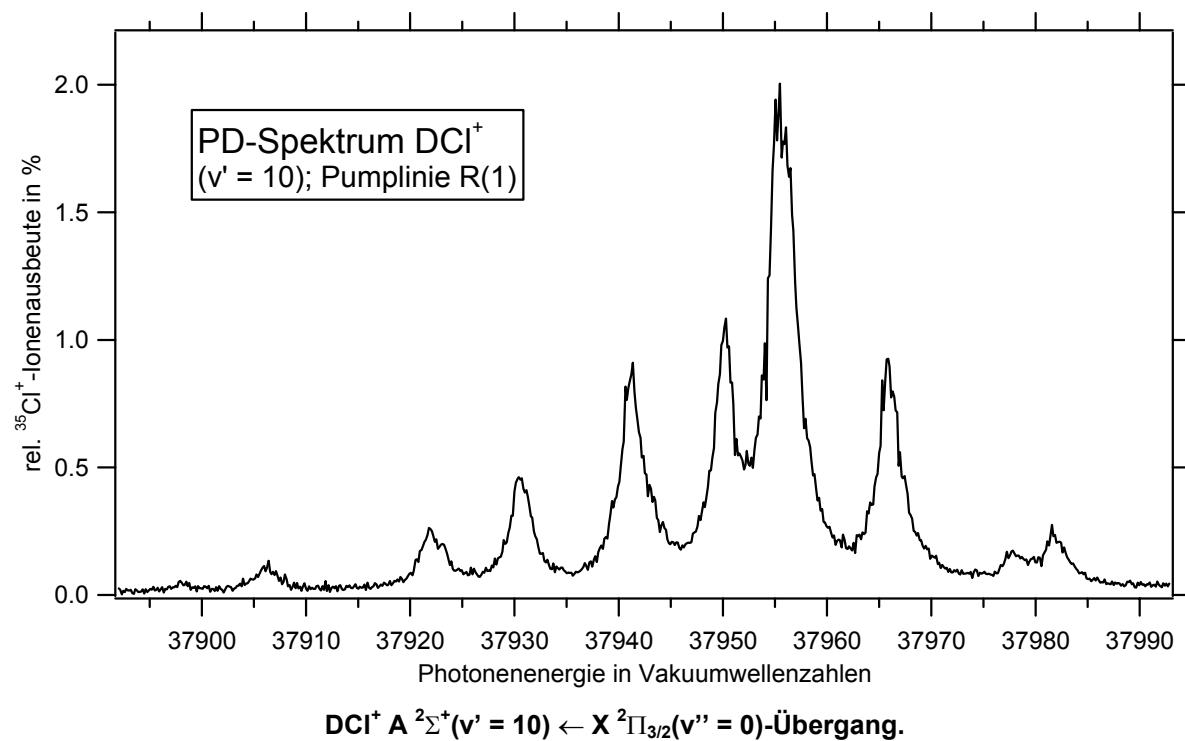
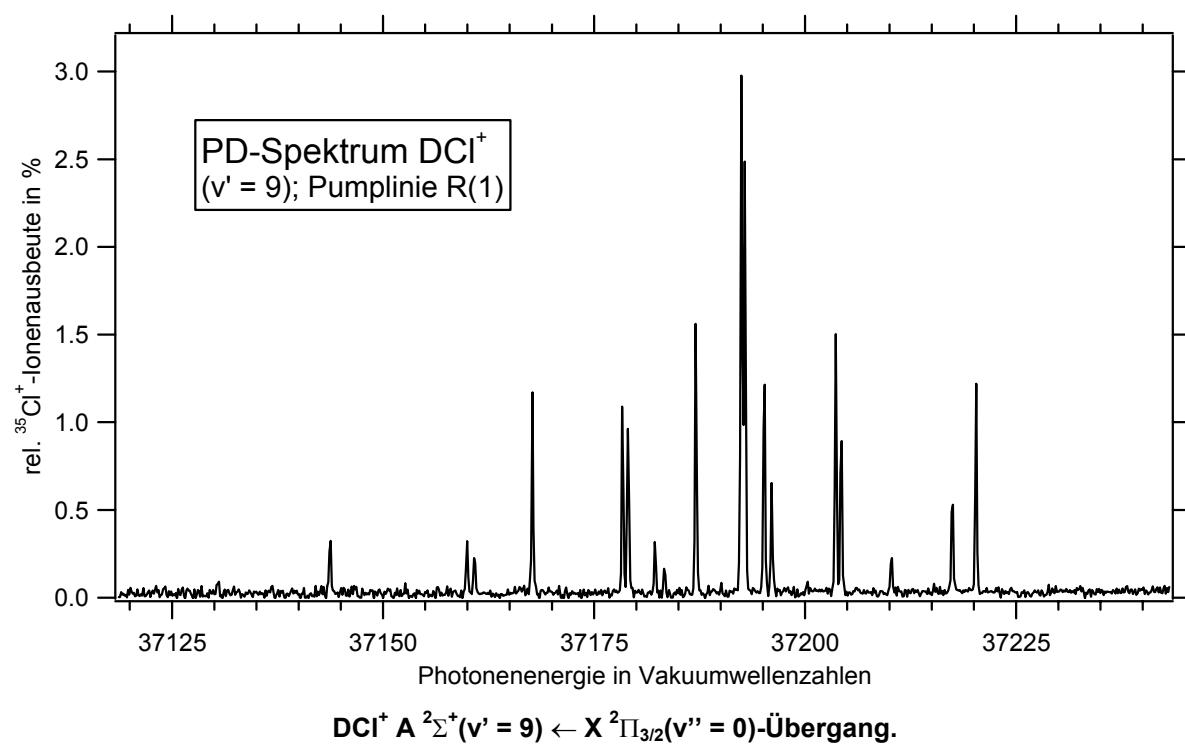


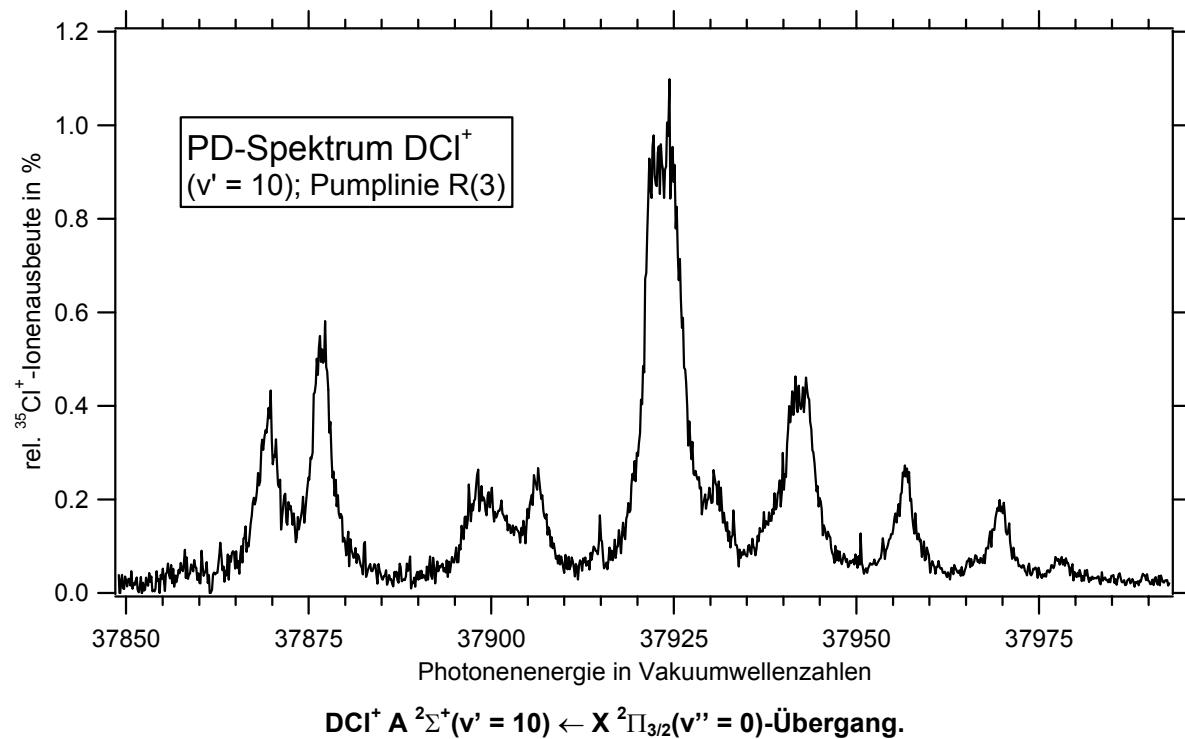
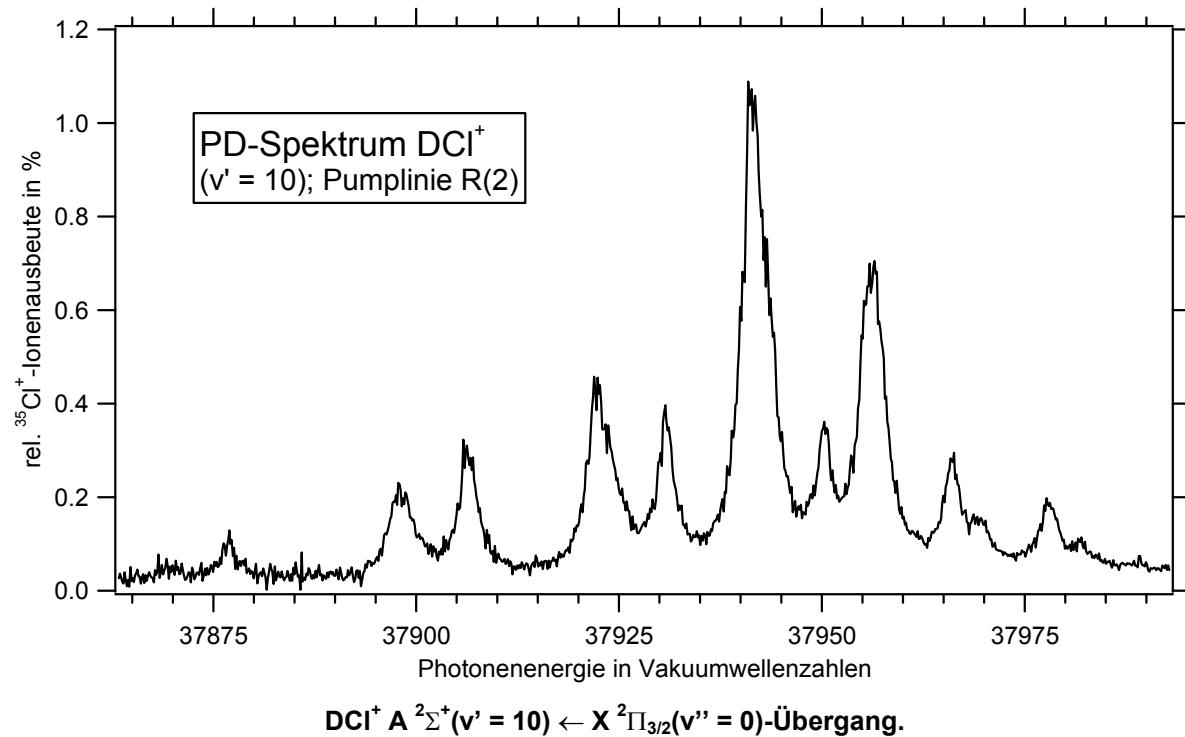


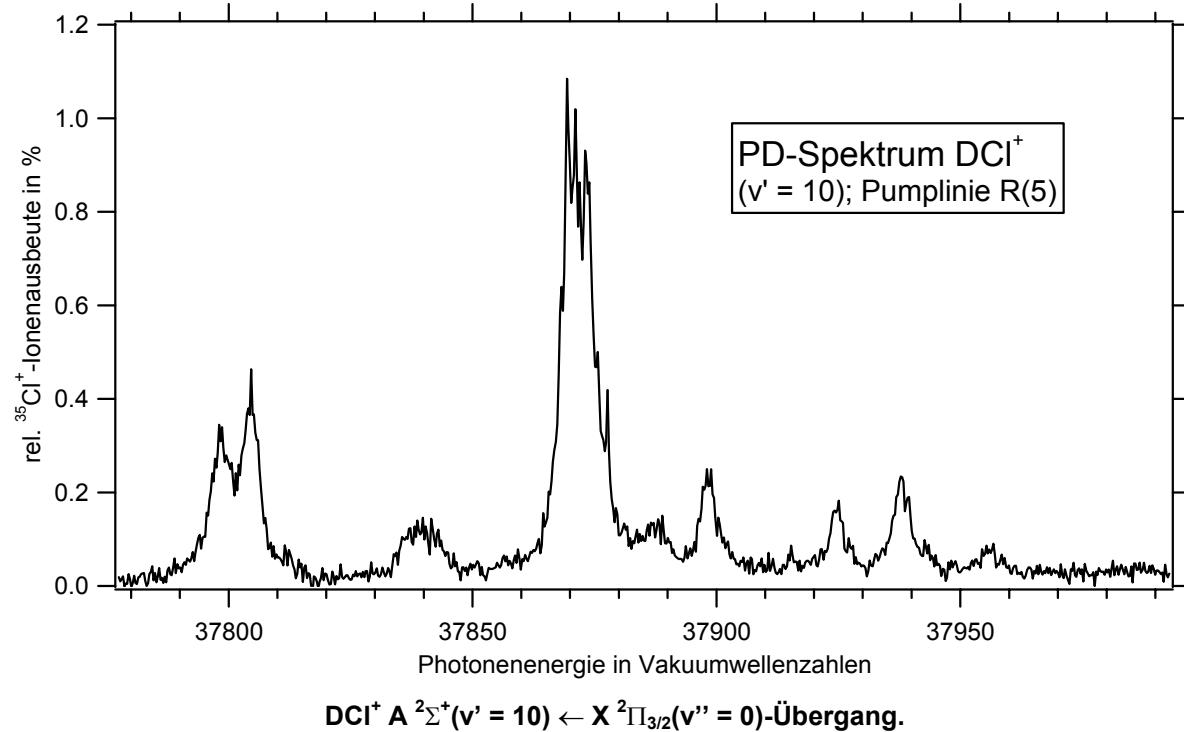
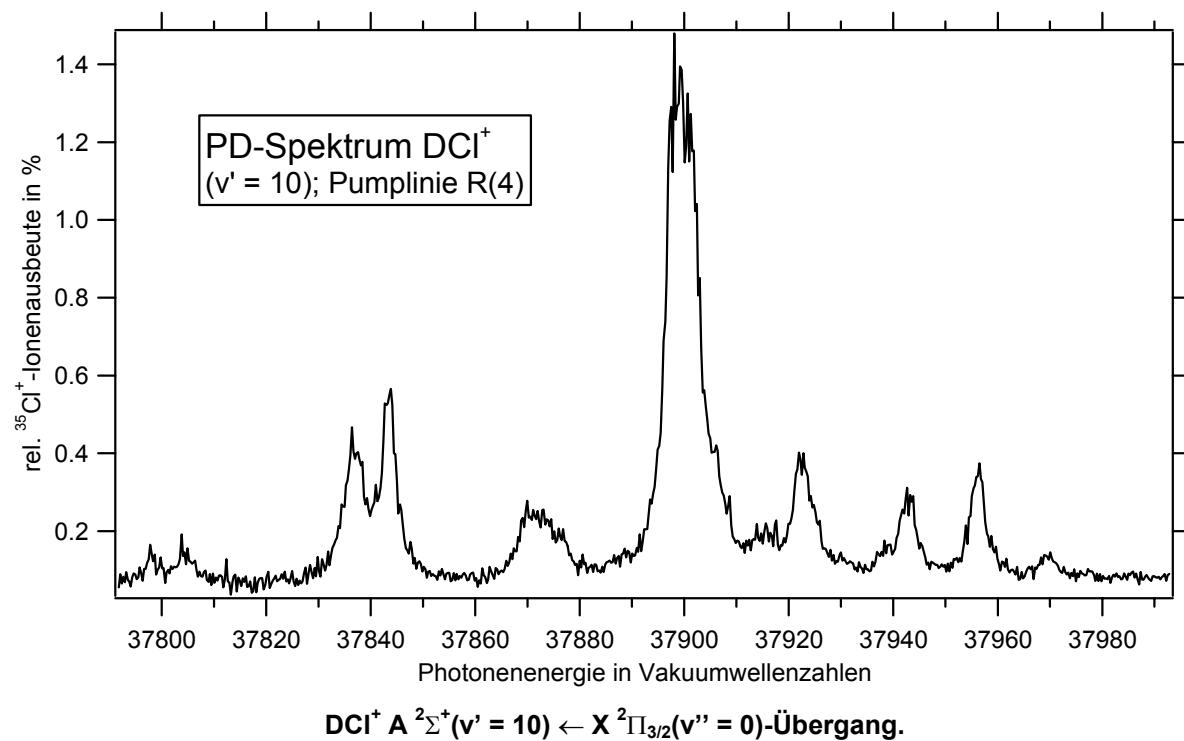
7.2.3 PD-Spektren der $\text{DCI}^+ \text{ A } ^2\Sigma^+ \leftarrow \text{X } ^2\Pi_{3/2}$ -Übergänge

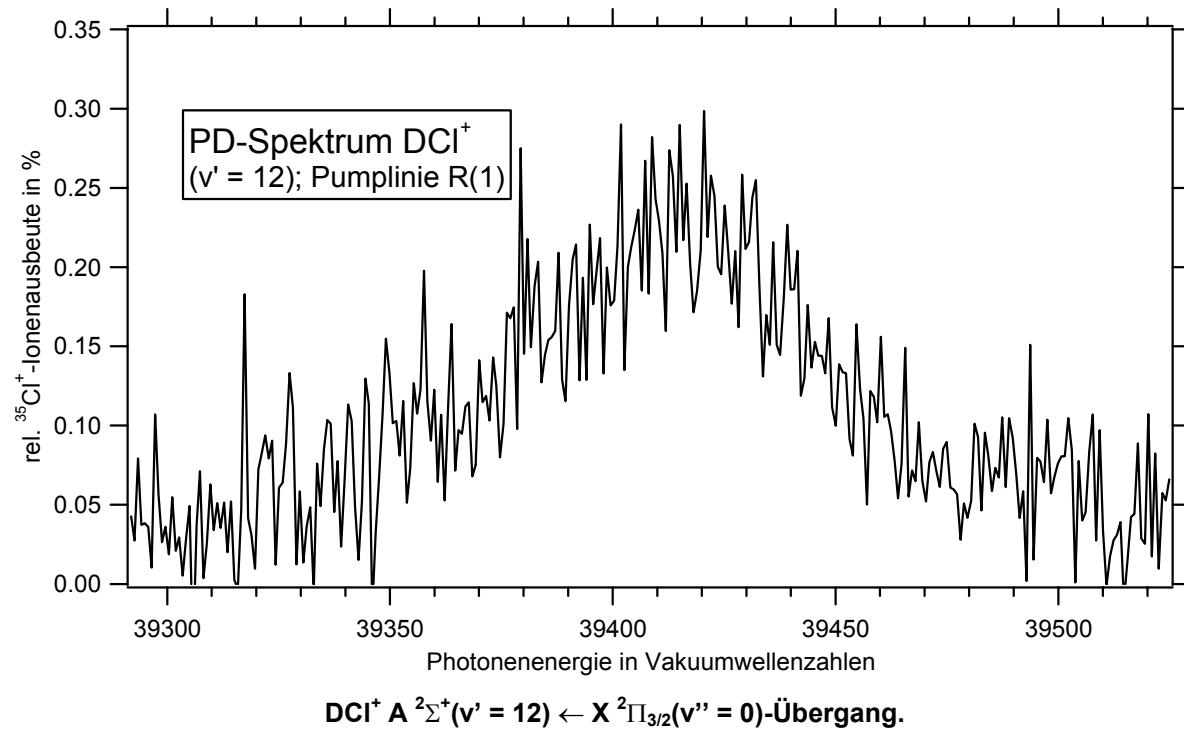
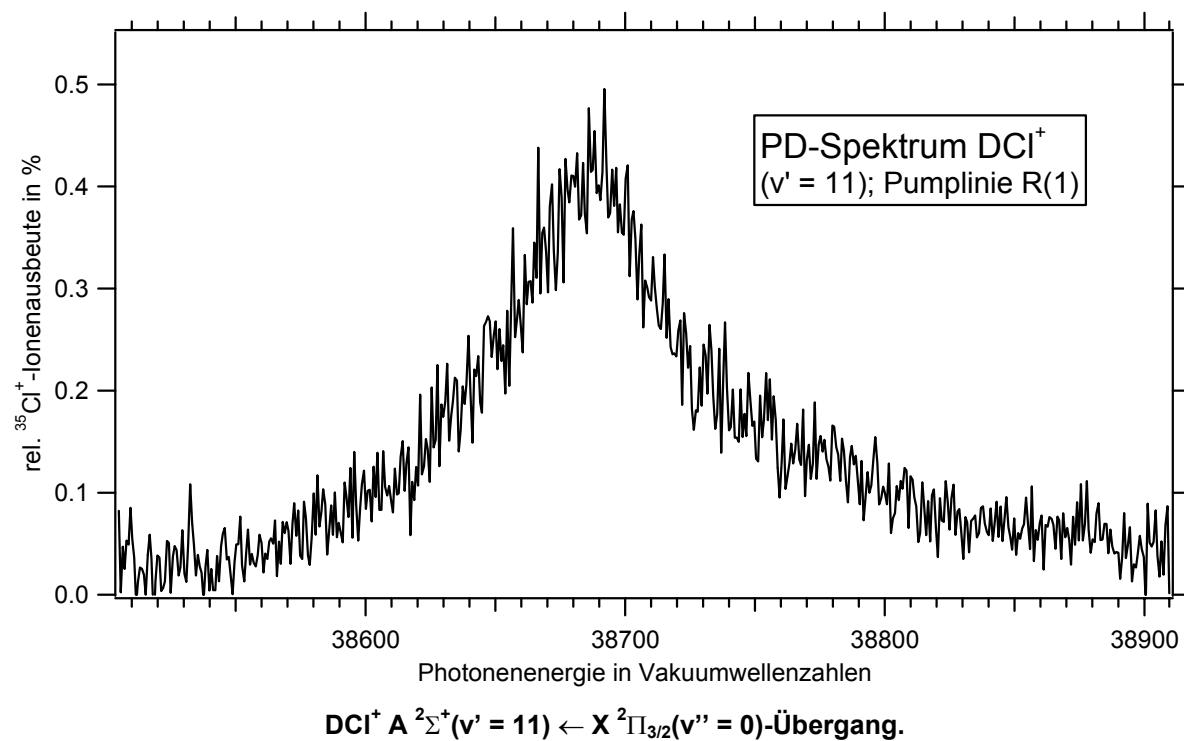












7.3 Übergangsintensitäten und Franck-Condon Faktoren

Nachfolgend sind die Übergangsintensitäten $S(J'', J')$ sowie die Franck-Condon Faktoren, die für die Berechnung der theoretischen $\text{HCl}^+ \text{A } ^2\Sigma^+(v' = 7-10)$ - bzw. $\text{DCI}^+ \text{A } ^2\Sigma^+(v' = 10-12)$ -Spektren herangezogen wurden, aufgelistet.

Übergangsintensitäten für $\text{HCl}^+ \text{A } ^2\Sigma^+ \leftarrow \text{HCl}^+ \text{X } ^2\Pi$ -Übergänge:

Zweig	P_1	Q_{21}	R_1	P_{21}	Q_1	R_{21}
$J'' = 1.5$	0.514	0.377	0.109	0.485	0.424	0.091
$J'' = 2.5$	0.635	0.626	0.24	0.564	0.746	0.19
$J'' = 3.5$	0.776	0.841	0.383	0.651	1.064	0.285
$J'' = 4.5$	0.929	1.036	0.535	0.735	1.388	0.377
$J'' = 5.5$	1.090	1.214	0.695	0.815	1.723	0.462
$J'' = 6.5$	1.260	1.377	0.863	0.889	2.070	0.541
$J'' = 7.5$	1.436	1.525	1.038	0.957	2.428	0.615
$J'' = 8.5$	1.620	1.661	1.220	1.019	2.799	0.683

Übergangsintensitäten für $\text{DCI}^+ \text{A } ^2\Sigma^+ \leftarrow \text{DCI}^+ \text{X } ^2\Pi$ -Übergänge:

Zweig	P_1	Q_{21}	R_1	P_{21}	Q_1	R_{21}
$J'' = 1.5$	0.508	0.388	0.105	0.492	0.412	0.095
$J'' = 2.5$	0.618	0.654	0.228	0.581	0.717	0.201
$J'' = 3.5$	0.747	0.894	0.359	0.681	1.011	0.308
$J'' = 4.5$	0.884	1.119	0.497	0.782	1.305	0.413
$J'' = 5.5$	1.027	1.334	0.639	0.881	1.604	0.516
$J'' = 6.5$	1.175	1.539	0.786	0.977	1.908	0.615
$J'' = 7.5$	1.327	1.735	0.938	1.071	2.218	0.711
$J'' = 8.5$	1.484	1.924	1.093	1.161	2.535	0.804
$J'' = 9.5$	1.644	2.104	1.252	1.248	2.859	0.894
$J'' = 10.5$	1.808	2.277	1.415	1.331	3.189	0.980
$J'' = 11.5$	1.976	2.443	1.582	1.411	3.526	1.062
$J'' = 12.5$	2.147	2.602	1.752	1.488	3.870	1.142
$J'' = 13.5$	2.322	2.753	1.926	1.562	4.221	1.218
$J'' = 14.5$	2.500	2.898	2.103	1.632	4.518	1.291

Franck-Condon Faktoren für $\text{HCl}^+ \text{A}^2\Sigma^+ \leftarrow \text{HCl}^+ \text{X}^2\Pi_{3/2}$ -Übergänge:

$\text{HCl}^+ \text{A}^2\Sigma^+ (\nu' = 7, N') \leftarrow \text{HCl}^+ \text{X}^2\Pi_{3/2} (\nu'' = 0, N'')$									
N'	$N'' = 0$	N'	$N'' = 1$	N'	$N'' = 2$	N'	$N'' = 3$	N'	$N'' = 4$
0	$0.89727 \cdot 10^{-4}$	1	$0.89109 \cdot 10^{-4}$	2	$0.88827 \cdot 10^{-4}$	3	$0.88881 \cdot 10^{-4}$	4	$0.89283 \cdot 10^{-4}$
1	$0.90701 \cdot 10^{-4}$	2	$0.91056 \cdot 10^{-4}$	3	$0.91756 \cdot 10^{-4}$	4	$0.92812 \cdot 10^{-4}$	5	$0.94237 \cdot 10^{-4}$
2	$0.92672 \cdot 10^{-4}$	3	$0.94035 \cdot 10^{-4}$	4	$0.95771 \cdot 10^{-4}$	5	$0.97898 \cdot 10^{-4}$	6	$0.10044 \cdot 10^{-3}$
3	$0.95687 \cdot 10^{-4}$	4	$0.98117 \cdot 10^{-4}$	5	$0.10097 \cdot 10^{-3}$	6	$0.10426 \cdot 10^{-3}$	7	$0.10805 \cdot 10^{-3}$
N'	$N'' = 5$	N'	$N'' = 6$						
5	$0.90035 \cdot 10^{-4}$	6	$0.91153 \cdot 10^{-4}$						
6	$0.96050 \cdot 10^{-4}$	7	$0.98277 \cdot 10^{-4}$						
7	$0.10343 \cdot 10^{-3}$	8	$0.10690 \cdot 10^{-3}$						
8	$0.11235 \cdot 10^{-3}$	9	$0.11723 \cdot 10^{-3}$						

$\text{HCl}^+ \text{A}^2\Sigma^+ (\nu' = 8, N') \leftarrow \text{HCl}^+ \text{X}^2\Pi_{3/2} (\nu'' = 0, N'')$									
N'	$N'' = 0$	N'	$N'' = 1$	N'	$N'' = 2$	N'	$N'' = 3$	N'	$N'' = 4$
0	$0.37884 \cdot 10^{-4}$	1	$0.37551 \cdot 10^{-4}$	2	$0.37368 \cdot 10^{-4}$	3	$0.37334 \cdot 10^{-4}$	4	$0.37452 \cdot 10^{-4}$
1	$0.38354 \cdot 10^{-4}$	2	$0.38492 \cdot 10^{-4}$	3	$0.38782 \cdot 10^{-4}$	4	$0.39233 \cdot 10^{-4}$	5	$0.39851 \cdot 10^{-4}$
2	$0.39309 \cdot 10^{-4}$	3	$0.39937 \cdot 10^{-4}$	4	$0.40735 \cdot 10^{-4}$	5	$0.41714 \cdot 10^{-4}$	6	$0.42889 \cdot 10^{-4}$
3	$0.40777 \cdot 10^{-4}$	4	$0.41932 \cdot 10^{-4}$	5	$0.43285 \cdot 10^{-4}$	6	$0.44854 \cdot 10^{-4}$	7	$0.46662 \cdot 10^{-4}$
N'	$N'' = 5$								
5	$0.37727 \cdot 10^{-4}$								
6	$0.40648 \cdot 10^{-4}$								
7	$0.44278 \cdot 10^{-4}$								
8	$0.48735 \cdot 10^{-4}$								

$\text{HCl}^+ \text{A}^2\Sigma^+ (\nu' = 9, N') \leftarrow \text{HCl}^+ \text{X}^2\Pi_{3/2} (\nu'' = 0, N'')$									
N'	$N'' = 0$	N'	$N'' = 1$	N'	$N'' = 2$	N'	$N'' = 3$	N'	$N'' = 4$
0	$0.17096 \cdot 10^{-4}$	1	$0.16915 \cdot 10^{-4}$	2	$0.16796 \cdot 10^{-4}$	3	$0.16742 \cdot 10^{-4}$	4	$0.16751 \cdot 10^{-4}$
1	$0.17324 \cdot 10^{-4}$	2	$0.17370 \cdot 10^{-4}$	3	$0.17481 \cdot 10^{-4}$	4	$0.17660 \cdot 10^{-4}$	5	$0.17912 \cdot 10^{-4}$
2	$0.17788 \cdot 10^{-4}$	3	$0.18072 \cdot 10^{-4}$	4	$0.18431 \cdot 10^{-4}$	5	$0.18869 \cdot 10^{-4}$	6	$0.19395 \cdot 10^{-4}$
3	$0.18504 \cdot 10^{-4}$	4	$0.19047 \cdot 10^{-4}$	5	$0.19680 \cdot 10^{-4}$	6	$0.20413 \cdot 10^{-4}$	7	$0.21257 \cdot 10^{-4}$
N'	$N'' = 5$								
5	$0.16828 \cdot 10^{-4}$								
6	$0.18242 \cdot 10^{-4}$								
7	$0.20018 \cdot 10^{-4}$								
8	$0.22227 \cdot 10^{-4}$								

$\text{HCl}^+ \text{A}^2\Sigma^+ (\nu' = 10, N') \leftarrow \text{HCl}^+ \text{X}^2\Pi_{3/2} (\nu'' = 0, N'')$									
N'	$N'' = 0$	N'	$N'' = 1$	N'	$N'' = 2$	N'	$N'' = 3$	N'	$N'' = 4$
0	$0.84832 \cdot 10^{-5}$	1	$0.83801 \cdot 10^{-5}$	2	$0.83035 \cdot 10^{-5}$	3	$0.82530 \cdot 10^{-5}$	4	$0.82286 \cdot 10^{-5}$
1	$0.85966 \cdot 10^{-5}$	2	$0.86062 \cdot 10^{-5}$	3	$0.86429 \cdot 10^{-5}$	4	$0.87077 \cdot 10^{-5}$	5	$0.88019 \cdot 10^{-5}$
2	$0.88276 \cdot 10^{-5}$	3	$0.89559 \cdot 10^{-5}$	4	$0.91154 \cdot 10^{-5}$	5	$0.93085 \cdot 10^{-5}$	6	$0.95382 \cdot 10^{-5}$
3	$0.91848 \cdot 10^{-5}$	4	$0.94427 \cdot 10^{-5}$	5	$0.97395 \cdot 10^{-5}$	6	$0.10080 \cdot 10^{-4}$	7	$0.10468 \cdot 10^{-4}$
N'	$N'' = 5$								
5	$0.82308 \cdot 10^{-5}$								
6	$0.89276 \cdot 10^{-5}$								
7	$0.98087 \cdot 10^{-5}$								
8	$0.10912 \cdot 10^{-4}$								

Franck-Condon Faktoren für $\text{DCI}^+ \text{A} \ ^2\Sigma^+ \leftarrow \text{DCI}^+ \text{X} \ ^2\Pi_{3/2}$ -Übergänge:

$\text{DCI}^+ \text{A} \ ^2\Sigma^+ (\nu' = 10, N') \leftarrow \text{DCI}^+ \text{X} \ ^2\Pi_{3/2} (\nu'' = 0, N'')$									
N'	$N'' = 0$	N'	$N'' = 1$	N'	$N'' = 2$	N'	$N'' = 3$	N'	$N'' = 4$
0	$0.1880 \ 10^{-4}$	1	$0.1870 \ 10^{-4}$	2	$0.1862 \ 10^{-4}$	3	$0.1857 \ 10^{-4}$	4	$0.1855 \ 10^{-4}$
1	$0.1893 \ 10^{-4}$	2	$0.1894 \ 10^{-4}$	3	$0.1899 \ 10^{-4}$	4	$0.1906 \ 10^{-4}$	5	$0.1916 \ 10^{-4}$
2	$0.1917 \ 10^{-4}$	3	$0.1931 \ 10^{-4}$	4	$0.1948 \ 10^{-4}$	5	$0.1969 \ 10^{-4}$	6	$0.1992 \ 10^{-4}$
3	$0.1955 \ 10^{-4}$	4	$0.1982 \ 10^{-4}$	5	$0.2012 \ 10^{-4}$	6	$0.2046 \ 10^{-4}$	7	$0.2084 \ 10^{-4}$

$\text{DCI}^+ \text{A} \ ^2\Sigma^+ (\nu' = 11, N') \leftarrow \text{DCI}^+ \text{X} \ ^2\Pi_{3/2} (\nu'' = 0, N'')$									
N'	$N'' = 0$	N'	$N'' = 1$	N'	$N'' = 2$	N'	$N'' = 3$	N'	$N'' = 4$
0	$0.1011 \ 10^{-4}$	1	$0.1006 \ 10^{-4}$	2	$0.1002 \ 10^{-4}$	3	$0.1000 \ 10^{-4}$	4	$0.9997 \ 10^{-5}$
1	$0.1018 \ 10^{-4}$	2	$0.1019 \ 10^{-4}$	3	$0.1022 \ 10^{-4}$	4	$0.1027 \ 10^{-4}$	5	$0.1033 \ 10^{-4}$
2	$0.1032 \ 10^{-4}$	3	$0.1040 \ 10^{-4}$	4	$0.1049 \ 10^{-4}$	5	$0.1061 \ 10^{-4}$	6	$0.1074 \ 10^{-4}$
3	$0.1052 \ 10^{-4}$	4	$0.1067 \ 10^{-4}$	5	$0.1084 \ 10^{-4}$	6	$0.1103 \ 10^{-4}$	7	$0.1125 \ 10^{-4}$

$\text{DCI}^+ \text{A} \ ^2\Sigma^+ (\nu' = 12, N') \leftarrow \text{DCI}^+ \text{X} \ ^2\Pi_{3/2} (\nu'' = 0, N'')$									
N'	$N'' = 0$	N'	$N'' = 1$	N'	$N'' = 2$	N'	$N'' = 3$	N'	$N'' = 4$
0	$0.5635 \ 10^{-5}$	1	$0.5610 \ 10^{-5}$	2	$0.5598 \ 10^{-5}$	3	$0.5601 \ 10^{-5}$	4	$0.5616 \ 10^{-5}$
1	$0.5675 \ 10^{-5}$	2	$0.5690 \ 10^{-5}$	3	$0.5719 \ 10^{-5}$	4	$0.5762 \ 10^{-5}$	5	$0.5817 \ 10^{-5}$
2	$0.5757 \ 10^{-5}$	3	$0.5813 \ 10^{-5}$	4	$0.5883 \ 10^{-5}$	5	$0.5968 \ 10^{-5}$	6	$0.6066 \ 10^{-5}$
3	$0.5881 \ 10^{-5}$	4	$0.5980 \ 10^{-5}$	5	$0.6094 \ 10^{-5}$	6	$0.6223 \ 10^{-5}$	7	$0.6367 \ 10^{-5}$

7.4 Abkürzungsverzeichnis

In der folgenden Tabelle sind die wichtigsten Abkürzungen und Symbole aufgeführt, die in dieser Arbeit verwendet werden:

Symbol	Langschrift/Erklärung
A	Spin-Bahn-Kopplungskonstante
AD	Spin-Bahn-Kopplungskonstante, höherer Term
AE	Auftrittsenergie
ASE	amplified spontaneous emission
B	Rotationskonstante
BBO	β -Bariumborat (β -BaB ₂ O ₄)
c	Lichtgeschwindigkeit
D	Zentrifugalaufweitungskonstante, quadratischer Term
D ₀	Dissoziationsenergie
e	Elementarladung
eV	Elektronenvolt
E	Energie
F(J)	Termenergie
FWHM	full width at half maximum
h	Plancksches Wirkungsquantum
H	Zentrifugalaufweitungskonstante, kubischer Term
$\Delta_f H^\circ$	Bildungswärme
IE	Ionisierungsenergie
I	Trägheitsmoment
I	Intensität
J	Gesamtdrehimpulsquantenzahl
n	Hauptquantenzahl
N	Rotationsquantenzahl
k	Kraftkonstante
k	Geschwindigkeitskonstante
KDP	Kaliumdihydrogenphosphat
I, L	Bahndrehimpulsquantenzahl
m	Masse
M	Multiplizität
MCP	micro channel plate
MPI	multiphoton ionization
Nd:YAG	Yttrium-Aluminium-Granat
P	Parität
PES	Photoelektronenspektroskopie
Q	Bahn-Rotations-Kopplungskonstante
QD	Bahn-Rotations-Kopplungskonstante, höherer Term
r	Kern-Kern-Abstand
R	Rydbergkonstante
Symbol	Langschrift/Erklärung

R	Übergangsmoment
REMPI	resonance enhanced multiphoton ionization
RLSF	rotational line strength factor
s	Flugstrecke
s, S	Spindrehimpulsquantenzahl
S _(J,J)	Übergangsintensität
SHG	second harmonic generation
t	Flugzeit
T	Temperatur
THG	third harmonic generation
TOF	time of flight
U	Spannung
UV	ultraviolett
v	Geschwindigkeit
v	Schwingungsquantenzahl
δ	Quantendefekt
γ	Spin-Rotations-Kopplungskonstante
λγ	Wellenlänge
μ	elektrisches Dipolmoment
μ	reduzierte Masse
v	Frequenz
˜v	Wellenzahl
ω	Winkelgeschwindigkeit
τ	Lebensdauer
ψ	Wellenfunktion

7.5 Lebenslauf

Persönliche Daten	Michael Michel geb. Schumacher Hornstraße 19 10963 Berlin geb. am 27.02.1966 in Berlin geschieden, zwei Kinder
Schulausbildung	1972 - 1974 Besuch der Elbe - Grundschule 1974 - 1976 Besuch der Adolf - Glaßbrenner - Grundschule 1976 - 1978 Besuch der Bürgermeister - Herz - Grundschule 1978 - 1984 Besuch des Leibniz - Gymnasiums, Dez. 1984 Abitur
Hochschulausbildung	1985-1989 FU Berlin Studiengang Politologie 01.10.1989 FU Berlin Studiengang Chemie 24.05.1993 Vordiplom im Fach Chemie 17.12.1998 Diplom im Fach Chemie 01.01.1999 FU Berlin Promotionsstudium am ITPC
Erziehungsurlaub	Dez. 1993 – Dez. 1995