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Citation: The Journal of Chemical Physics **100**, 3422 (1994); doi: 10.1063/1.467246 View online: http://dx.doi.org/10.1063/1.467246 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/100/5?ver=pdfcov Published by the AIP Publishing

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Detection and characterization of gas-phase InCl using resonance enhanced multiphoton ionization

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(Received 9 September 1993; accepted 9 November 1993)

We report resonance enhanced multiphoton ionization (REMPI) spectra of gas-phase indium monochloride (InCl) between 330 and 490 nm. The spectra originate from one-, two-, and three-photon resonances with electronic states that reside between 27 000 and 75 000 cm⁻¹. We assign 12 new Rydberg states. From these Rydberg origins we can extrapolate the adiabatic ionization potential IP_a=77 460±600 cm⁻¹ (9.60±0.08 eV). The Rydberg states exhibit vibrational frequencies ranging between 307 and 355 cm⁻¹.

I. INTRODUCTION

We report extensive new spectra for the short-lived indium monochloride molecule InCl that we obtained using resonance enhanced multiphoton ionization (REMPI) spectroscopy. The REMPI spectra arise though one-, two-, and three-photon resonances with excited states that reside between 27 000 and 75 000 cm⁻¹. Between laser wavelengths of 330 and 490 nm we identify 14 band systems. Twelve of these systems arise from previously unreported states.

This study is motivated by the practical importance of Group III B halides to the manufacturing of semiconductor devices. InCl is the volatile species used to transport indium metal to surfaces during the chemical vapor deposition (CVD) of indium containing films, e.g., InGaAsP and InP/InGaAsP.^{1,2} The present results allow use of REMPI spectroscopy as a sensitive detector of gas-phase InCl. In other studies we have used REMPI spectroscopy to characterize other Group III B species: BF,³ BCl,⁴ AIF,⁵ AlCl,⁶ and GaCl.⁷

This study greatly expands the known states of InCl. Previous workers have reported conventional UV spectra of only two other excited electronic states. The lowest triplet state, the ³II state, produces two band systems labeled $A^{3}\Pi_{0^{+}}(\nu=27\ 770\ \text{cm}^{-1})$ and $B^{3}\Pi_{1}(\nu=28\ 570\ \text{cm}^{-1})$. The lowest energy singlet state, the $C^{1}\Pi$ state, resides above $\nu_{00}=37\ 410\ \text{cm}^{-1.8-11}$ More recently, other spectroscopists have reported higher resolution UV absorption spectra of these states.¹²⁻¹⁷ The $X^{1}\Sigma^{+}$ ground state has been well characterized by microwave spectroscopy.¹⁸⁻²⁰

Because the higher electronic states of InCl are mostly ion-like Rydberg states, the properties of InCl⁺ are particularly relevant to the interpretation of REMPI spectra. Berkowitz and Dehmer observed the photoelectron spectra of InCl and determined an adiabatic ionization potential, $IP_a=9.51 \text{ eV}.^{21}$ More recently, Balfour and Chandrasekhar reported the emission spectrum of InCl⁺.²² In a subsequent paper these authors pointed out that the band system, assigned as the $A' {}^{1}\Sigma - X {}^{1}\Sigma$ of InCl,²² is actually the $B {}^{2}\Sigma - X {}^{2}\Sigma$ band system of InCl⁺.²³

II. EXPERIMENTAL METHODS

The apparatus and general procedures used in this work are described elsewhere.²⁴ The apparatus consisted of a dye laser, time-of-flight (TOF) mass spectrometer, and computer data acquisition system. The data for this work were collected simultaneously with the REMPI spectra of GaCl.⁷

GaCl and InCl are obtained when solid mixtures of $InCl_3$ and Ga metal are heated in a tantalum foil oven. During this study the solid reactants were intimately mixed with mortar and pestle and loaded into a tantalum boat. This boat was placed into the mouth of a resistively heated oven that resided within the vacuum system. The oven was heated gradually until signal was detected from GaCl⁺ or Ga⁺. This occurred at temperatures estimated to be 600–800 K. Temperatures were not characterized in detail, since the samples were heated inhomogeneously.

The resistively heated oven was located approximately 2 cm from the ionization region of the time-of-flight mass analyzer. Species generated in the oven effused into the mass spectrometer ionization region where they were ionized by the output of an excimer-pumped dye laser (10–35 mJ/pulse, 25 ns duration, 0.2 cm⁻¹ bandwidth) focused with a 150 mm focal length lens. The ions were mass resolved, and mass peaks of interest were recorded as a function of laser wavelength using a gated integrator. Up to three separate masses were monitored simultaneously.

REMPI spectra were obtained using the laser dyes (Exciton Chemical $Co.^{25}$) PTP (330–350 nm), DMQ (345–375 nm), QUI (375–405 nm), DPS (400–415 nm), Stilbene 420 (412–440 nm), Coumarin 440 (420–460 nm), Coumarin 460 (440–480 nm), and Coumarin 480 (460–500 nm). In the figures we have corrected the base line to eliminate discontinuities among the data sets taken with different laser dyes, but no compensation was made for the gradual variations in laser energy across the tuning range of each dye, or gradual changes in intensity due to sample degradation with time.

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0021-9606/94/100(5)/3422/7/\$6.00

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FIG. 1. The m/z 150 REMPI spectrum of ¹¹⁵In³⁵Cl between 320 and 400 nm. IP marks the wavelength at which the number of laser photons InCl molecules must absorb to ionize and form InCl⁺ changes from 3 to 4.

III. RESULTS

A. Proof of carrier

Figures 1-3 show the REMPI spectra carried by m/z 150 ions (¹¹⁵In³⁵Cl⁺) observed in the oven effluent when we heated Ga metal with InCl₃. Corresponding m/z 152 (¹¹⁵In³⁷Cl) REMPI spectra were also observed. At each wavelength the intensity ratio of the m/z 150 and 152 REMPI signals was 10:3, as expected for naturally occurring Cl isotopes. The REMPI spectra of ¹¹⁵In³⁵Cl and ¹¹⁵In³⁷Cl exhibit no distinguishable isotope shifts. Because the natural abundance of ¹¹³In is only 4.3%, the m/z 148 (¹¹³In³⁵Cl) signal was too weak to produce useful REMPI spectra. As discussed below, the spectra exhibit states assigned previously to InCl.

The REMPI data show no evidence that other species contributed to the m/z 150 REMPI spectra. REMPI signals from other species did appear at other masses. We observed signals from indium atoms (m/z 113 and 115), and GaCl (m/z 104, 106, and 108). An unresolved continuum was carried by m/z 139 that may have originated from Ga₂ and/or GaCl₂. We tentatively assigned m/z 181 signals to tantalum, most likely formed by the photodissociation of TaCl_x formed in the tantalum oven.

We have estimated an approximate detection sensitivity for InCl from our experimental conditions. By postulating that 100% of the InCl₃ within each sample volatilizes only through formation of InCl, we estimate that the concentration of InCl within the ionizer was 6×10^{10} molecules cm⁻³. This concentration is estimated using the pressure rise of the chamber as the sample is heated, the pumping speed of the chamber, and the weight and usable lifetime of the samples. Around $\lambda_{laser} = 365.14$ nm, m/z 150 spectra typically exhibit signal-to-noise ratios of S/N = 120:1. Thus, we estimate that REMPI detection achieves a single laser pulse sensitivity of at least 10⁹ molecules cm⁻³ (laser pulse)⁻¹. However, because not all InCl₃ forms InCl, this sensitivity estimate for InCl is very conservative.

B. Analyses of REMPI spectra and identification of Rydberg states

Table I lists the REMPI bands and their assignments between 500 and 320 nm. Each row of Table I lists the λ_{max} , laser wavelength of a REMPI band; the REMPI mechanism that produced the band; the energy of the upper electronic state; and the upper electronic state assignment combined with the upper and ground-state vibrational levels, respectively. All assigned transitions originate from the ground $X^{1}\Sigma^{+}$ state. The energy uncertainty associated with each REMPI band is a function of individual peak structure and width. Laser intensity and bandwidth



FIG. 2. The m/z 150 REMPI spectrum of ¹¹⁵In³⁵Cl between 435 and 500 nm.

had no influence upon this energy uncertainty. Generally, the energy uncertainty associated with each band maximum is about ± 20 cm⁻¹.

The REMPI mechanism n+m indicates that n photons are absorbed to reach the resonant state and m photons are absorbed to ionize from the resonant state. We observe 1+2, 1+1+1 (two resonant states), 2+1, and 3+1 REMPI processes. The energy of the resonant state, and therefore the number of photons absorbed to reach that state is determined from the vibrational intervals. The total photon order, either three or four photons, is assigned by the requirement that the sum of all laser photons exceeds the adiabatic ionization energy of InCl.

Between 330 and 355 nm the REMPI spectrum exhibits long vibrational progressions that match those of the $A {}^{3}\Pi_{0^{+}} \leftarrow X {}^{1}\Sigma^{+}$ and $B {}^{3}\Pi_{1} \leftarrow X {}^{1}\Sigma^{+}$ band systems reported previously.¹¹ The $A {}^{3}\Pi_{0^{+}}$ and $B {}^{3}\Pi_{1}$ components of the ${}^{3}\Pi$ state reside between 28 000–31 000 cm⁻¹ (see one-photon energy inset of Fig. 1). These states are reached by a onephoton absorption. To ionize from the ${}^{3}\Pi$ state, InCl must absorb two more laser photons. Thus, we deduce that the $A {}^{3}\Pi_{0^{+}}$ and $B {}^{3}\Pi_{1}$ components produce signal through a 1+2 REMPI process.

The REMPI spectra exhibit many previously unreported band systems. We posit that these higher excited states are Rydberg states. We assign the electronic origin of each new band system on the bases of the vibrational structure, and the position of its origin within a Rydberg series. Several band systems show one or two quanta of vibration of the upper electronic state, i.e., 1–0 and 2–0 bands. Most systems also exhibit one or two hot bands that originate from thermally populated vibrational levels of the ground state (i.e., 0-1 and 0-2 bands). Previously determined spectroscopic constants of InCl $(X^{1}\Sigma^{+})$ show that the v''=1-v''=0 interval is $\Delta G''_{1/2} = 315$ cm⁻¹ and that the v''=2-v''=0 interval is 629 cm^{-1.16} Hot bands of correctly assigned REMPI band systems must reproduce these intervals.

The vibrational analysis confirms the origins of the states designated by F, K, N, Q, and S. These band systems are comprised of both hot bands and excited-state bands, and the change in vibrational spacing identifies the origin band. The states I, L, M, show hot bands, but no excited-state bands, so the identification of the origins is less certain. In these states we assume the origin is the blue-most band. The state T exhibits hot bands and one excited vibrational band. However, the hot bands are blended and the excited-state band is broad.

For the T state and the G and H states the origins are supported by alignment in a Rydberg series. Rydberg states align into series that conform to the equation

$$v_{00} = \mathrm{IP}_a - \frac{R}{(n-\delta)^2},$$

where v_{00} is the origin, IP_a is the adiabatic ionization potential, *R* is the Rydberg constant of 109 737 cm⁻¹, **n** is the principal quantum number, and δ is quantum defect. The quantum defect is nearly constant and characterizes a given Rydberg series. Seven origins form three Rydberg



FIG. 3. The m/z 150 REMPI spectrum of ¹¹⁵In³⁵Cl between 400 and 435 nm.

series containing two or three members. Using the Rydberg formula, the combined least-squares fit for these series yields $IP_a = 77460 \pm 600 \text{ cm}^{-1} (9.60 \pm 0.08 \text{ eV})$ and δ (series α : states $K, S = 3.99 \pm 0.01$, δ (series β : states $F, L, T = 3.801 \pm 0.004$, and δ (series γ : states $H, N = 3.670 \pm 0.005$. The uncertainties are two standard deviations. Most of the uncertainty for IP_a originates from the use of short Rydberg series in the calculation.

The present IP_a, derived from the concurrent fit of several Rydberg series, lies slightly higher than the previously reported value, IP_a=9.51 eV.^{21(a)} The prior IP_a was assigned to coincide at the signal threshold of the photoelectron spectrum. However, a Franck–Condon analysis, using spectroscopic constants for the ground state and ion, predicts the 1–0 band to be ~10% more intense than the 0–0 band, and the 2–0 to be ~70% of the 0–0 band. This distribution of vibrational bands will displace the true IP_a above the photoionization signal threshold and suggests the increased value IP_a~9.7 eV.^{21(b)} Thus, the REMPI and photoionization spectra of InCl support a revision of the IP_a to slightly higher energy.

Since the Franck–Condon factors predicted for the photoionization spectrum of InCl approximately predict the intensity patterns of Rydberg spectra, we expect each Rydberg state in the REMPI spectrum to exhibit a 1.0:1.1:0.7 intensity ratio among the 0–0, 1–0, and 2–0 bands. In contrast, the Rydberg states exhibit strong 0–0 bands and attenuated or absent 1–0 and 2–0 bands. In a REMPI experiment predissociation depletes the population of Rydberg molecules waiting to absorb the ionizing photon. If the predissociation rate increases with vibrational energy, the intensity of vibrational bands will pro-

gressively diminish above the 0–0 band. Thus, for InCl the departure of the intensity patterns from those predicted by the Franck–Condon analysis is evidence that the Rydberg states of InCl suffer from rapid predissociation. We note that predissociation is reported to affect the spectra of the other Group III B chlorides AlCl, GaCl, and TlCl.^{6,7,26}

In congested spectral regions we locate new origins by extrapolating the Rydberg formulas that describe previously assigned Rydberg origins. A reasonable solution of the Rydberg formula for the M state origin at 66 966 cm⁻¹ is n=7 and $\delta=3.766$. Using this solution, the extrapolation of the Rydberg formula predicts that the n = 6 member of this Rydberg series resides at 55 465 cm⁻¹. The data exhibit a corresponding band at 360.40 nm that we assign as the G (54 757 cm⁻¹) state origin. The G origin is also supported by its location as the terminus of a progression. Similarly, a reasonable solution of the Rydberg formula for the N state origin is n=7 and $\delta=3.676$. Extrapolation of this Rydberg solution predicts the n=6 Rydberg origin 57 142 cm⁻¹. We observe a corresponding band at 349.11 nm that we assign as the H origin ($v_{00} = 57259 \text{ cm}^{-1}$). Hot bands also support the H origin assignment. Fits of the Rydberg formula to the G and M state origins (series ζ) yields $\delta = 3.766 \pm 0.004$ and fits of the H and N origins (series γ) yields $\delta = 3.670 \pm 0.005$.

Table II summarizes the spectroscopic information derived for each electronic state of InCl. This information includes the λ_{laser} of each origin; the REMPI mechanism that produces the band system; the name of the Rydberg series; the principal quantum number *n* and quantum defect δ found for each origin; $\Delta G_{1/2}$, the vibrational interval of the upper state; v_{00} (obs), the observed state energy;

TABLE I. REMPI bands of indium monochloride observed between 500 and 320 nm.

λ_{laser}	REMPI	State energy	
(nm)	mechanism	$(cm^{-1})^{-1}$	Assignment
400 75	2 1 1	61 407	T 0 2
488.20	3+1	61 427	10-3
403.17	3+1	62 052	I = 0 - 2
480.89	3+1 3+1	62 371	1 0-0
480.61	5+1	62 403	1 0-0
478.71		62 650	J 0-0
476.91		62 888	
475.70	3+1	63 047	I 20
473.91	3 + 1	63 286	J 2-0
472.64	3 + 1	63 456	I 3-0
471.11	3+1	63 662	I 4-0
468.76	3 + 1	63 981	I 5-0
461.34	3+1	65 010	K 0-1
459.14	3+1	65 321	K 0-0
458.64	3+1	65 393	** 1 0
456.80	3+1	65 656	K 10
453.78	3+1	66 220	
452.10	3+1	66 415	M2 0-2
451.50	3+1	66 588	L 0-1
450.40	3+1	66 593	N 0_3
430.37	3+1	66 655	M 0-1
449.47	3+1	66 726	
448.31	3+1	66 899	N 0-2
447.86	3 + 1	66 966	M 0-0
446.23	3 + 1	67 212	N 0-1
444.17	3 + 1	67 527	N 0-0
442.73	3 + 1	67 742	
442.02	3 + 1	67 852	N 1-0
439.84	3+1	68 188	N 20
437.83	3 + 1	68 500	N 3-0
436.40	3+1	68 726	
435.70	3+1	68 836	N 4-0
434.38		69 014	
434.18		60 244	
432.30	3 - 1	69 418	
431.18	3+1	69 557	
430.64	3+1	69 644	
430.21	3 + 1	69 713	
429.33	3 + 1	69 857	Q 0-2
429.26		69 868	
428.77		69 948	
428.50	3 + 1	69 992	<i>S</i> 0–2
427.38	3+1	70 181	Q = 0-1
426.60	3 + 1	70 305	S 0-1
426.57	3 + 1	70 309	
425.48	3+1	70 488	Q 0-0
424.71	3 + 1	/0 61 /	S 0-0
423.43	3+1	70 830	Q 1-0 S 10 T 0 1
422.07	3 + 1	70 938	5 1-0, 1 0-1
422.22	3+1	71 095	
421.44	3+1	71 165	0 2-0
420.78	3+1	71 277	T 0-0
419.56	3 + 1	71 483	
418.93	3+1	71 591	T 1-0
418.38	3+1	71 686	
417.94		71 760	
417.40		71 853	
406.37		73 804	
404.60		74 127	
395.04		50 614	
393.41		50 823	

λ_{laser} (nm)	REMPI mechanism	State energy (cm ⁻¹)	Assignment
391.63		51 054	
376.82		53 061	
375.55		53 240	
372.25		53 712	
371.24		53 858	
369.35	2+1	54 134	F 02
367.27	2+1	54 440	F 01
365.14	2+1	54 757	F 00
362.80	2+1	55 112	F 1-0
360.40	2+1,	55 478,	G 00
	1 + 1 + 1	27 739	F 2-0
358.25	2 + 1	55 811	G 1-0
357.14	2+1	55 986	H 0-4
356.23	2 + 1	56 128	G 2–0
355.25	1 + 2,	28 142,	A 10
	2 + 1	56 284	H 03
354.13	2+1	56 461	G 3–0
353.14	2 + 1	56 618	H 0–2
352.16	2 + 1	56 776	G 40
351.16	1+2	28 469	A 2-0
	2 + 1	56 938	<i>H</i> 0–1
349.11	2+1	57 259	H 00
347.38	1+2	28 779	A 3-0
346.98		57 623	
345.87	1+2	28 904	B 1-0
345.20	2 + 1	57 922	H 2–0
343.53	1+2	29 101	A 4-0
341.68	1+2	29 259	B 20
337.96	1+2	29 580	<i>B</i> 3–0
335.95	1+2	29 757	A 6-0
334.62	1+2	29 877	B 4-0

 v_{00} (calc), the origin energy obtained from the combined least-squares fit of the Rydberg origins; and Δ , the difference between v_{00} (obs) and v_{00} (calc). In the following sections we briefly describe the REMPI band systems displayed in Figs. 1-3.

1. The REMPI spectrum between 320 and 400 nm

Figure 1 displays the REMPI spectrum between 320 and 400 nm. In this region we observe five different progressions that are produced through 1+2, 2+1, and 1+1+1 REMPI processes. As discussed above, the $A^{3}\Pi_{0^{+}}$ and $B^{3}\Pi_{1}$ components of the $^{3}\Pi$ state produce bands between 330 and 355 nm through a 1+2 REMPI mechanism. Between 343 and 361 nm the *H*, *G*, and *F* states exhibit progressions that arise from a 2+1 mechanism. The *H* band system exhibits many hot bands and several vibrational bands in its excited state. The *H* band system exhibits 0-1, 0-2, 0-3, and 0-4 hot bands that establish the origin at 349.11 nm ($v_{00}=57\ 259\ cm^{-1}$). The excited vibrational levels of the *H* state are not resolved. Presumably, these bands coincide with members of the *A* and *B* state progressions.

Between 352 and 361 nm the G band system shows a progression of five weak bands. The red-most member of this progression lies at 360.40 nm. When we assign the G state to reside at the two-photon energy, the origin (v_{00})

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TABLE II. Summary of the spectroscopic information known for the electronic states of InCl. A numeric quantum defect, δ , denotes an assigned Rydberg state and a "V" denotes a state that is predominately valence in nature. The quantum defect of the Rydberg state is calculated using IP_a=77 460 cm⁻¹.

State	λ _{origin} (nm)	REMPI mechanism	Series name	Principal quantum number	Quantum defect	$\frac{\Delta G_{1/2}}{(\mathrm{cm}^{-1})}$	$v_{00}(obs)$ (cm ⁻¹)	v ₀₀ (calc) (cm ⁻¹)	Δ (cm ⁻¹)
$\overline{X^{1}\Sigma^{+}}$					V	319	0		
$A^{3}\Pi_{0^{+}}$	(347.38)*	1+2			V		27 770		
$B^{3}\Pi_{1}$	(345.87) ^b	1+2			V		28 570		
C'II		•••			V		37 410		
F	365.14	2+1	β	6	3.801	355	54 757°	54 761	4
G	360.40	2+1	5	6	3.766	333	55 478	55 477	1
H	349.11	2 + 1	Ŷ	6	3.669	332	57 259°	57 245	14
Ι	480.89	3 + 1		6	3.303	338	62 371	62 367	4
J	478.71	3+1		6	3.278	318	62 650	62 657	-7
K	459.14	3 + 1	α	7	3.993	335	65 321°	65 319	2
L	449.47	3 + 1	β	7	3.802		66 726°	66 733	-7
М	447.86	3 + 1	5	7	3.766	•••	66 966	66 968	2
N	444.17	3+1	Ŷ	7	3.676	325	67 527°	67 562	-35
Q	425.48	3 + 1	•	4	0.033	307	70 488		
S	424.71	3+1	α	8	3.995	341	70 617°	70 622	5
Т	420.78	3+1	β	8	3.786	314	71 277 ^c	71 233	44

*Wavelength of the 3-0 band. Origin is not observed.

^bWavelength of the 1-0 band. Origin is not observed.

°This value is used for the calculation of IP_a .

=55 478 cm⁻¹) combines with the M state to form the n=6,7 members of a Rydberg series with the quantum defect $\delta = 3.766 \pm 0.004$.

The F band system exhibits 0–1 and 0–2 hot bands at 367.27 and 369.35 nm, respectively. When assigned to lie at the energy of two laser photons, these bands reproduce the ground-state vibrational intervals which, with the increase in vibrational spacing for the excited-state bands, establishes that the intense band at 365.14 nm ($v_{00} = 54757 \text{ cm}^{-1}$) is the electronic origin.

The $G \leftarrow \leftarrow X$ 0–0 band and $F \leftarrow \leftarrow X$ 2–0 band coincide at 360.40 nm. Since the $A^{3}\Pi_{0^{+}}$ state resides at half the energy of the F and G states, a sequence of allowed onephoton transitions may enhance the intensity of the 360.40 nm band. This 1+1+1 REMPI mechanism would proceed through the transitions: $G(v=0) \leftarrow A(v=0) \leftarrow X(v$ =0) or $F(v=2) \leftarrow A(v=0) \leftarrow X(v=0)$.

In Fig. 1 the arrow labeled "IP" near 387 nm marks where the ion signal begins to increase as the laser wavelength scans to higher energy. This increased signal reflects the change in the number of photons required to ionize InCl. To the red of 390 nm, InCl must absorb four photons to ionize. To the blue of 385 nm, InCl needs to absorb only three photons to ionize. Thus, this increased InCl⁺ signal near 387 nm provides a crude estimate of the ionization potential. Three 387 nm photons correspond to an ionization energy of ~77 500 cm⁻¹ (9.6 eV). This value is identical to the IP_a obtained by this study from the combined fit of the Rydberg series.

2. The REMPI spectrum between 435 and 500 nm

Figure 2 displays the REMPI spectrum between 435 and 500 nm. All assigned bands arise from 3+1 REMPI mechanisms. The three distinct Rydberg series continue with $N(\text{series } \gamma)$ at 444.17 nm $(v_{00}=67527 \text{ cm}^{-1})$, $L(\text{series } \beta)$ at 449.47 nm $(v_{00}=66726 \text{ cm}^{-1})$, and $M(\text{series } \zeta)$ at 447.86 nm $(v_{00}=66966 \text{ cm}^{-1})$. Hot bands support these origin assignments (Table I).

The K state exhibits an origin at 459.14 nm ($v_{00} = 65\ 321\ \mathrm{cm}^{-1}$). The 0–1 hot band at 461.34 nm supports this origin assignment. The solution of the Rydberg equation for the K state is n=7 and $\delta=3.993$. From this solution we would predict that the n=6 Rydberg state origin will appear near 399.7 nm ($\sim 50\ 020\ \mathrm{cm}^{-1}$). However, the REMPI spectrum exhibits no appropriate bands. REMPI bands at this energy must arise through the higher order, 2+2 REMPI mechanism. Therefore, the absence of the n=6 Rydberg state may originate from a small ionization rate.

The *I* state produces an extensive band system between 488.25 and 468 nm. Hot bands from v'' = 0-3 levels confirm that the origin lies at 480.89 nm ($v_{00}=62$ 371 cm⁻¹). The Rydberg equation solution gives n=6 and $\delta=3.303$.

We have tentatively assigned the J state as a distinct Rydberg state. Presumably, its hot bands are obscured. However, the J state origin could be the perturbed v=1level of the I state.

3. The REMPI spectrum between 400 and 435 nm

Figure 3 displays the REMPI spectrum between 400 and 435 nm. In this region 3+1 REMPI mechanisms produce all assigned bands. The most intense band is the *T* state origin at 420.78 nm ($v_{00}=71\ 277\ \text{cm}^{-1}$). This origin assignment is supported by the 0–1 hot band at 422.67 nm and the alignment of the origin within Rydberg series β . Starting at 420 nm and extending to shorter wavelengths, the REMPI signal intensity falls off and bands become indistinct. The progression of bands between 430 and 420 nm is a blend of several coincident progressions. The S state contributes to part of this progression. Extrapolation of Rydberg series α predicts that the S state origin band resides at 424.7 nm, coincident with the T 0-2 band.

Other REMPI bands also reside between 420–435 nm. The most apparent belong to the Q band system comprised of an origin at 425.48 nm, two hot bands, and two bands of the excited state. We tentatively assign the Q band system to arise from nf Rydberg states analogous to those observed in the REMPI spectrum of GaCl.⁷ Alternatively, the Q bands could be the next member of a Rydberg series containing the I state.

IV. DISCUSSION

Initially, we expected to find correspondences between the REMPI spectra of InCl and GaCl that would resolve state assignments.⁷ Our analysis of the GaCl REMPI spectrum yielded assignments of *ns*, $np\pi$, $np\sigma$, and two *nf* Rydberg series. But assignments by analogy with GaCl are of limited value because they can be ambiguous. For example, the prominent Rydberg series β of InCl has the proper relative intensity to support its assignment as the $np\pi$ Rydberg series by analogy with GaCl. But when we attempt to assign the less intense $np\sigma$ states by analogy with GaCl, we find that both series γ or series ζ of InCl are suitable candidates. Similar ambiguities arise for the other Rydberg series of InCl.

Comparisons with the electronic spectra of TlCl may be more relevant. Using an elegant two-color absorption/ fluorescence scheme Linder and Tiemann collected spectra of TlCl between 55 000 and 60 000 $\text{cm}^{-1.26}$ They observed a strong state designated $E_1 0^+$ and three weaker states designated $E_2 0^+$, $E_3 0^+$, and $F_1 1$. The origins were placed at 55 491, 56 444, 57 298, and 57 885 cm^{-1} . The ionization potential of 9.70 eV for TlCl²⁷ yields the term values 22 735, 21 782, 20 928, and 20 341 cm⁻¹. Using IP_a =77460 cm⁻¹ for InCl, we predict corresponding states of InCl at 54 726, 55 679, 56 533, and 57 120 cm^{-1} . These agree well with the F, G, and H states observed for InCl at 54 757, 55 478, and 57 259 cm^{-1} . Lindner and Tiemann also found the $E_1 0^+$ state to be predissociated for $v \ge 3$. We have proposed that predissociation accounts for the short or absent vibrational progressions observed in most excited states of InCl.

In summary we have reported the first observation of any Rydberg state of InCl and greatly expanded the number of known electronic states. Through extrapolation of Rydberg series we have determined an adiabatic ionization potential that can support improved thermochemical calculations for InCl and InCl⁺. REMPI spectroscopy offers a new way to detect InCl sensitively. A convenient scheme involves excitation of the $F(v'=0) \leftarrow \leftarrow X^1 \Sigma^+(v''=0)$ two-photon transition at 365.14 nm. At this wavelength we have conservatively estimated a sensitivity of REMPI detection for InCl of 10⁹ molecules cm⁻³ (laser pulse)⁻¹.

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