

The High-Resolution Infrared Spectrum of Iodine Monochloride

HARTMUT G. HEDDERICH AND PETER F. BERNATH^{1,2}

*Centre for Molecular Beams and Laser Chemistry, Department of Chemistry, University of Waterloo,
Waterloo, Ontario, Canada N2L 3G1*

AND

GLENN A. MCRAE

Physical Chemistry Branch, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada K0J 1J0

The high-resolution infrared spectrum of iodine monochloride has been observed in absorption by Fourier transform spectroscopy. About 750 rovibrational transitions for the two isotopomers $I^{35}\text{Cl}$ and $I^{37}\text{Cl}$ have been assigned. The new infrared data were combined with millimeter-wave transition frequencies from the literature to yield precise Dunham coefficients, Y_{ij} , for the $X^1\Sigma^+$ electronic ground state of ICl. In addition, mass-reduced Dunham constants, U_{ij} , have been derived. © 1992 Academic Press, Inc.

INTRODUCTION

Iodine monochloride has been the subject of numerous spectroscopic studies over the last 6 decades. The molecule shows several unusual properties such as predissociation, curve crossings, avoided crossings, and the existence of diffuse and continuous spectra and, therefore, has been of considerable interest to spectroscopists. The spectroscopic properties of ICl have been studied by a number of techniques such as visible absorption spectroscopy (1–14), emission spectroscopy (15–18), laser-induced fluorescence spectroscopy (19–27), vacuum ultraviolet spectroscopy (28–31), laser-induced photochemistry (32) and microwave and millimeter-wave spectroscopy (33–37), as well as microwave–optical double-resonance spectroscopy (38–42). Information about potential energy curves and curve crossings in ICl was obtained in a photofragmentation experiment (43). Molecular beam experiments (44–46) were carried out to obtain information about rotational temperatures, rotational–translational relaxation, and dissociation of ICl. Brand *et al.* used two-photon polarization spectroscopy (47–52) and three-photon resonance spectroscopy (53, 54) to gain information about perturbed electronic states. In addition there are several excellent *ab initio* calculations of the molecular properties of the ground and excited states of ICl (55–57).

However, there is only one publication about the vibration–rotation spectrum of

¹ Also Department of Chemistry, University of Arizona, Tucson, AZ 85721.

² Camille and Henry Dreyfus Teacher–Scholar.

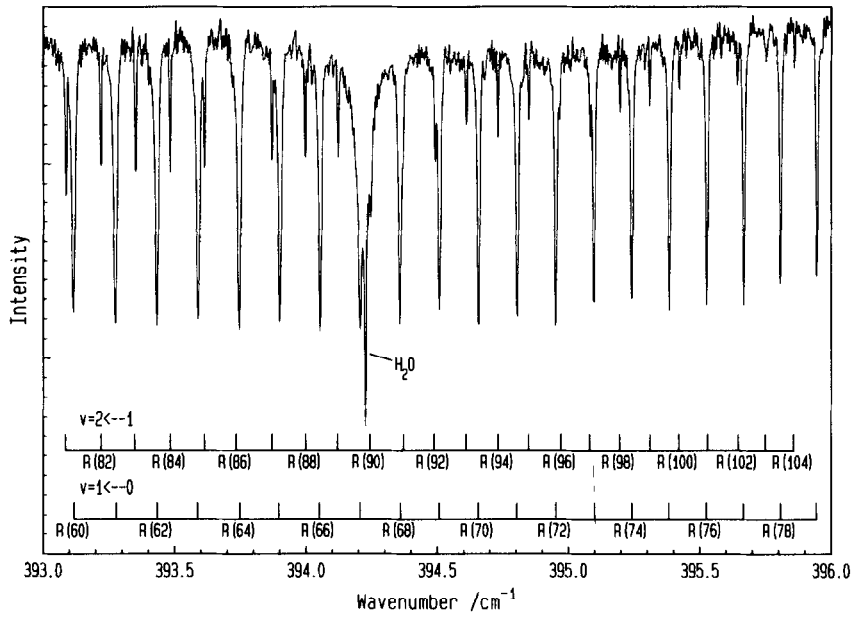


FIG. 1. Portion of the infrared spectrum of $I^{35}Cl$ close to the *R*-branch bandheads. H_2O lines were used as absolute wavenumber standards.

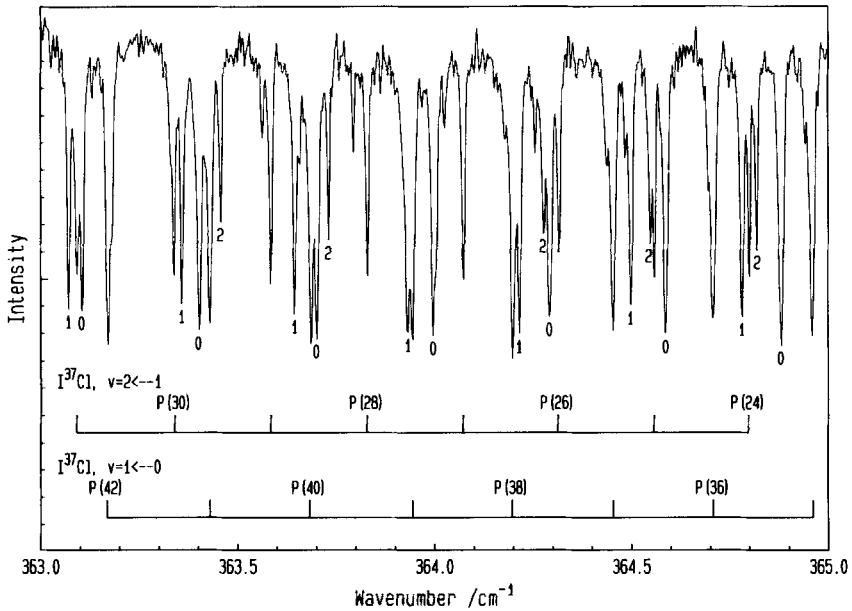


FIG. 2. Portion of the high-resolution infrared spectrum of ICl between 363 and 365 cm^{-1} . The bands of $I^{35}Cl$ are indicated as follows: (0) $v=1 \leftarrow 0$; (1) $v=2 \leftarrow 1$; and (2) $v=3 \leftarrow 2$.

TABLE I
 Observed Line Positions of ICl in cm^{-1}

J''	observed	o.-c.^a / 10^{-3}	J''	observed	o.-c. / 10^{-3}	J''	observed	o.-c. / 10^{-3}	J''	observed	o.-c. / 10^{-3}
$\text{I}^{35}\text{Cl}, v=1-0$			$\text{I}^{35}\text{Cl}, v=1-0$			$\text{I}^{35}\text{Cl}, v=1-0$			$\text{I}^{35}\text{Cl}, v=1-0$		
P(106)	351.34562	-46	P(53)	367.75630	133	P(4)	380.35847	-402	R(44)	390.40687	22
P(105)	351.68250	74	P(52)	368.03726	7	P(3)	380.59159	-189	R(45)	390.58441	31
P(102)	352.68203	-81	P(51)	368.31912	73	P(2)	380.81994	-346	R(46)	390.76047	3
P(100)	353.34638	114	P(50)	368.59792	-64	R(1)	381.73279	40	R(47)	390.93561	-4
P(99)	353.67462	-34	P(49)	368.87567	-203	R(2)	381.95873	178	R(48)	391.10939	-35
P(98)	354.00326	-41	P(48)	369.15621	39	R(3)	382.18183	138	R(49)	391.28285	15
P(97)	354.33191	52	P(47)	369.43386	96	R(4)	382.40197	-90	R(50)	391.45471	17
P(96)	354.65579	-232	P(46)	369.70948	52	R(5)	382.62400	-21	R(51)	391.62554	29
P(95)	354.98332	-51	P(44)	370.25830	32	R(6)	382.84358	-90	R(52)	391.79480	-3
P(94)	355.30793	-62	P(43)	370.53191	97	R(7)	383.06265	-102	R(53)	391.96341	12
P(93)	355.63234	6	P(42)	370.80322	36	R(8)	383.28077	-101	R(54)	392.13098	37
P(92)	355.95518	18	P(41)	371.07386	10	R(9)	383.49855	-26	R(55)	392.29646	-34
P(91)	356.27695	22	P(40)	371.34474	113	R(10)	383.71377	-100	R(56)	392.46215	29
P(90)	356.59690	-55	P(39)	371.61285	41	R(11)	383.92857	-107	R(57)	392.62648	70
P(89)	356.91662	-55	P(38)	371.88018	-4	R(12)	384.14363	21	R(58)	392.78830	-27
P(88)	357.23452	-137	P(37)	372.14760	63	R(13)	384.35510	-103	R(59)	392.95040	18
P(87)	357.55383	22	P(36)	372.41333	64	R(14)	384.56920	145	R(60)	393.11021	-52
P(86)	357.87026	-6	P(35)	372.67792	56	R(15)	384.77873	45	R(61)	393.26958	-53
P(85)	358.18660	57	P(34)	372.94101	2	R(16)	384.98812	39	R(62)	393.42863	29
P(84)	358.50011	-63	P(33)	373.20432	73	R(17)	385.19551	-58	R(63)	393.58459	-81
P(83)	358.81431	-13	P(32)	373.46446	-68	R(18)	385.40386	50	R(64)	393.74220	82
P(82)	359.12726	13	P(31)	373.72564	-1	R(19)	385.60933	-21	R(65)	393.89635	17
P(80)	359.74963	13	P(30)	373.98485	-27	R(20)	385.81444	-19	R(66)	394.05063	79
P(78)	360.36792	8	P(29)	374.24403	49	R(21)	386.01894	31	R(67)	394.20223	-11
P(77)	360.67542	-8	P(27)	374.75735	9	R(22)	386.22115	-39	R(68)	394.35371	1
P(76)	360.98254	39	P(26)	375.01314	59	R(23)	386.42361	26	R(69)	394.50413	22
P(75)	361.28831	52	P(25)	375.26602	-77	R(24)	386.62423	16	R(70)	394.65300	3
P(74)	361.59107	-135	P(24)	375.51904	-94	R(25)	386.82342	-27	R(71)	394.80044	-44
P(72)	362.19855	-9	P(23)	375.77222	9	R(26)	387.02251	30	R(72)	394.94738	-25
P(70)	362.80112	31	P(22)	376.02225	-97	R(27)	387.21952	-11	R(73)	395.09313	-9
P(69)	363.09995	-42	P(21)	376.27311	-16	R(28)	387.41569	-26	R(74)	395.23762	-4
P(68)	363.39838	-54	P(20)	376.52204	-22	R(29)	387.61096	-22	R(75)	395.38060	-34
P(67)	363.69587	-59	P(19)	376.76845	-176	R(30)	387.80560	30	R(76)	395.52310	4
P(66)	363.99472	174	P(18)	377.01746	36	R(31)	387.99807	-25	R(77)	395.66394	-8
P(65)	364.28878	30	P(17)	377.26325	32	R(32)	388.19038	15	R(78)	395.80388	6
P(64)	364.58344	48	P(16)	377.50812	41	R(33)	388.38114	10	R(79)	395.94228	-17
P(63)	364.87685	42	P(15)	377.75123	-21	R(34)	388.57076	2	R(80)	396.07979	-13
P(62)	365.16876	-12	P(14)	377.99265	-146	R(35)	388.75968	34	R(81)	396.21603	-19
P(61)	365.46013	-18	P(13)	378.23583	11	R(36)	388.94709	27	R(82)	396.35147	12
P(60)	365.75155	83	P(12)	378.47658	31	R(37)	389.13308	-12	R(83)	396.48515	-16
P(59)	366.04019	8	P(11)	378.71527	-50	R(38)	389.31831	-15	R(84)	396.61795	-15
P(58)	366.32943	96	P(10)	378.95418	-2	R(39)	389.50240	-21	R(85)	396.74983	11
P(57)	366.61598	16	P(9)	379.19153	-4	R(40)	389.68592	27	R(86)	396.88035	18
P(56)	366.90248	34	P(7)	379.66260	-53	R(41)	389.86823	65	R(87)	397.00956	12
P(55)	367.18745	1	P(6)	379.89569	-163	R(42)	390.04832	-7	R(88)	397.13760	7
P(54)	367.47276	104	P(5)	380.12907	-137	R(43)	390.22871	63	R(89)	397.26434	-10

^a observed minus calculated line positions using the mass-reduced Dunham constants of Table IV.

ICl in the infrared region (58). The origin of the fundamental band of ICl in the electronic ground state lies at 384 cm^{-1} , a region which is not easily accessible with traditional infrared spectrometers. In this work we present the infrared absorption spectrum of ICl, which closes the spectral gap for ICl between the millimeter-wave measurements and the electronic spectra in the near-infrared, visible, and ultraviolet regions.

EXPERIMENTAL DETAILS

The high-resolution infrared spectrum of ICl was observed with the Bruker IFS 120 HR Fourier transform spectrometer at the University of Waterloo. The resolution was 0.003 cm^{-1} with liquid-helium-cooled Si:B detectors and a $3.5\text{-}\mu\text{m}$ Mylar beamsplitter.

TABLE I—Continued

J''	observed	$\frac{o.-c.}{/10^{-5}}$	J''	observed	$\frac{o.-c.}{/10^{-5}}$	J''	observed	$\frac{o.-c.}{/10^{-5}}$	J''	observed	$\frac{o.-c.}{/10^{-5}}$
$I^{35}Cl, v = 1 - 0$			$I^{35}Cl, v = 2 - 1$			$I^{35}Cl, v = 2 - 1$			$I^{35}Cl, v = 2 - 1$		
R(90)	397.39011	-7	P(73)	358.93252	-42	P(11)	375.69776	-162	R(46)	387.67574	-55
R(91)	397.51486	13	P(72)	359.23577	93	P(9)	376.17274	-40	R(47)	387.84983	-34
R(92)	397.63840	30	P(70)	359.83630	72	P(8)	376.40837	-6	R(48)	388.02200	-93
R(93)	397.76096	68	P(69)	360.13542	100	P(7)	376.64186	-78	R(49)	388.36632	127
R(94)	397.88182	54	P(68)	360.43352	128	P(6)	376.87491	-87	R(51)	388.53456	14
R(95)	398.00109	-1	P(67)	360.72980	76	P(5)	377.10797	11	R(52)	388.70199	-66
R(96)	398.12001	29	P(66)	361.02536	54	P(3)	377.56782	-98	R(53)	388.86958	-16
R(97)	398.23726	11	P(64)	361.61390	58	R(2)	378.92707	124	R(54)	389.03545	-25
R(98)	398.35368	28	P(62)	362.19855	82	R(3)	379.14753	-70	R(55)	389.19968	-84
R(99)	398.46835	-9	P(60)	362.77880	76	R(4)	379.36875	-81	R(56)	389.36420	0
R(100)	398.58210	-20	P(59)	363.06687	22	R(5)	379.58862	-118	R(57)	389.52662	-13
R(101)	398.69496	1	P(58)	363.35477	53	R(6)	379.81043	147	R(58)	389.68557	-258
R(102)	398.80650	9	P(57)	363.64110	29	R(7)	380.02592	-112	R(59)	389.84772	-69
R(103)	398.91531	-136	P(55)	364.21070	-15	R(8)	380.24349	-54	R(60)	390.00732	-21
R(104)	399.02496	-77	P(54)	364.49523	90	R(9)	380.45896	-98	R(61)	390.16543	-7
R(105)	399.13331	-27	P(53)	364.77710	32	R(10)	380.67423	-54	R(62)	390.32222	-10
R(106)	399.24036	13	P(52)	365.05855	36	R(12)	381.10031	-84	R(63)	390.47765	-35
R(107)	399.34591	23	P(50)	365.61824	31	R(13)	381.31232	-39	R(64)	390.63229	-24
R(108)	399.45011	20	P(48)	366.17412	58	R(14)	381.52026	-292	R(65)	390.78558	-32
R(109)	399.55275	-19	P(46)	366.72543	41	R(15)	381.73279	23	R(66)	390.93562	-251
R(110)	399.65441	-35	P(45)	366.99967	47	R(16)	381.94110	25	R(67)	391.08834	-86
R(111)	399.75437	-99	P(44)	367.27257	23	R(17)	382.14712	-93	R(68)	391.23886	-26
R(112)	399.85654	178	P(43)	367.54492	47	R(18)	382.35367	-48	R(69)	391.38814	26
R(113)	399.95373	80	P(42)	367.81563	11	R(19)	382.55793	-123	R(70)	391.53540	-9
R(115)	400.14587	24	P(41)	368.08628	72	R(20)	382.76200	-106	R(71)	391.68194	0
R(116)	400.24035	-20	P(40)	368.35442	-13	R(23)	383.36777	-44	R(72)	391.82733	11
R(117)	400.33258	-86	P(35)	369.68332	-57	R(24)	383.56671	-101	R(74)	392.11374	-57
$I^{35}Cl, v = 2 - 1$			P(34)	369.94702	40	R(25)	383.76493	-120	R(75)	392.25593	-18
P(106)	348.40213	-158	P(33)	370.20886	55	R(26)	383.96275	-69	R(76)	392.39692	17
P(103)	349.40612	3	P(32)	370.46918	22	R(27)	384.16065	100	R(77)	392.53603	-19
P(96)	351.70902	-98	P(31)	370.72988	132	R(28)	384.35464	-11	R(78)	392.67425	-26
P(94)	352.35669	-255	P(30)	370.98668	-43	R(29)	384.54963	89	R(79)	392.81099	-65
P(93)	352.68203	-33	P(29)	371.24524	63	R(30)	384.74247	84	R(81)	393.08256	17
P(91)	353.32559	1	P(28)	371.50103	-4	R(32)	385.12337	-71	R(82)	393.21557	-43
P(90)	353.64581	13	P(27)	371.75631	-16	R(33)	385.31261	-102	R(83)	393.34810	-34
P(89)	353.96536	59	P(26)	372.01005	-77	R(34)	385.50020	-188	R(84)	393.47975	5
P(88)	354.28246	-40	P(25)	372.26230	-182	R(35)	385.68856	-85	R(85)	393.60939	-39
P(86)	354.91610	9	P(24)	372.51682	45	R(36)	385.87464	-99	R(87)	393.86710	69
P(82)	356.17035	14	P(23)	372.76733	-23	R(37)	386.05722	-352	R(88)	393.99348	53
P(81)	356.48117	-6	P(22)	373.01594	-176	R(38)	386.24509	37	R(89)	394.11892	92
P(80)	356.79145	21	P(21)	373.26670	-8	R(40)	386.61086	151	R(90)	394.24345	68
P(79)	357.10059	35	P(20)	373.51474	-7	R(41)	386.78973	-25	R(93)	394.60691	-94
P(78)	357.40760	-63	P(19)	373.76178	0	R(42)	386.96870	-79	R(94)	394.72694	-33
P(77)	357.71549	29	P(14)	374.97958	-116	R(43)	387.14719	-68	R(95)	394.84406	-143
P(76)	358.02177	61	P(13)	375.22120	-15	R(44)	387.32456	-58	R(98)	395.19283	-14
P(75)	358.32796	186	P(12)	375.46047	-43	R(45)	387.50173	45	R(99)	395.30611	-29

The spectral bandpass was limited to 325–760 cm^{-1} by a cold filter for the upper limit and by the detector response for the lower limit.

A 1-m long alumina tube equipped with polyethylene windows (1-mm thick) was used for all experiments. All spectra were taken at room temperature. First, the cell was filled with 700 mTorr of ICl and 50 scans were coadded. The spectrum showed only rovibrational transitions of the fundamental band of $I^{35}Cl$. In a second experiment the alumina tube was filled with 5 Torr of ICl and 75 scans were coadded. Now a much denser and more intense spectrum was observed (Figs. 1 and 2).

RESULTS

The spectrum observed at low pressure was used to obtain the line positions for the fundamental band of $I^{35}Cl$. These lines were saturated in the second spectrum taken at a pressure of 5 Torr. However, the high-pressure spectrum was useful for the observation of hot band transitions of $I^{35}Cl$ as well as the fundamental and hot band transitions of $I^{37}Cl$.

TABLE I—Continued

J''	observed	o.-c. / 10^{-5}	J''	observed	o.-c. / 10^{-5}	J''	observed	o.-c. / 10^{-5}	J''	observed	o.-c. / 10^{-5}
$I^{35}\text{Cl}, v = 2 \leftarrow 1$			$I^{35}\text{Cl}, v = 3 \leftarrow 2$			$I^{35}\text{Cl}, v = 3 \leftarrow 2$			$I^{37}\text{Cl}, v = 1 \leftarrow 0$		
R(100)	395.41912	48	P(16)	371.47216	187	R(60)	386.89025	101	P(57)	359.17232	24
R(102)	395.63965	16	P(15)	371.71218	15	R(61)	387.04595	15	P(54)	359.98811	-17
R(103)	395.74843	32	P(14)	371.95307	38	R(62)	387.20135	14	P(53)	360.25866	24
R(104)	395.85587	34	P(13)	372.19198	-31	R(63)	387.35460	-87	P(52)	360.52807	46
R(107)	396.16900	-151	P(10)	372.90523	55	R(68)	388.10906	-36	P(51)	360.79589	6
R(108)	396.27022	-286	P(9)	373.14036	36	R(69)	388.25524	-149	P(47)	361.85972	65
R(112)	396.66746	-373	R(7)	376.97563	2	R(74)	388.97630	48	P(46)	362.12264	17
$I^{35}\text{Cl}, v = 3 \leftarrow 2$			$I^{35}\text{Cl}, v = 3 \leftarrow 2$			$I^{35}\text{Cl}, v = 3 \leftarrow 2$			$I^{37}\text{Cl}, v = 1 \leftarrow 0$		
P(76)	355.04561	-20	R(8)	377.19165	17	R(76)	389.25544	17	P(45)	362.38486	-4
P(74)	355.65366	38	R(9)	377.40683	57	R(77)	389.39225	-99	P(44)	362.64657	20
P(73)	355.95518	-30	R(10)	377.61912	-83	R(80)	389.79836	-175	P(43)	362.90526	-160
P(72)	356.25692	26	R(11)	377.83124	-131	R(81)	389.93171	-167	P(41)	363.42531	36
P(71)	356.55658	-24	R(12)	378.04348	-57	R(83)	390.19771	134	P(40)	363.68152	-101
P(69)	357.15371	-36	R(13)	378.25529	82	R(87)	390.70732	-84	P(38)	364.19509	30
P(68)	357.45128	12	R(15)	378.67160	-40	$I^{37}\text{Cl}, v = 1 \leftarrow 0$			P(37)	364.45014	67
P(67)	357.74601	-121	R(16)	378.87796	-117	P(95)	348.09382	185	P(36)	364.70353	36
P(66)	358.04158	-68	R(17)	379.08624	109	P(94)	348.40213	111	P(35)	364.95566	-23
P(62)	359.21019	-195	R(18)	379.28948	-60	P(92)	349.01576	-54	P(34)	365.20718	-46
P(61)	359.50269	65	R(20)	379.69440	-223	P(91)	349.32352	99	P(33)	365.45902	60
P(59)	360.07836	-39	R(21)	379.89569	-256	P(89)	349.93269	51	P(32)	365.70846	24
P(57)	360.65159	26	R(22)	380.09815	-61	P(88)	350.23612	52	P(31)	365.95751	47
P(56)	360.93713	106	R(23)	380.29690	-128	P(87)	350.53901	94	P(30)	366.20547	58
P(55)	361.21997	19	R(25)	380.69364	-4	P(86)	350.83978	18	P(29)	366.45253	78
P(54)	361.50333	87	R(26)	380.89114	137	P(85)	351.14053	33	P(28)	366.69603	-161
P(53)	361.78531	121	R(28)	381.27712	-151	P(84)	351.44131	147	P(27)	366.94195	-60
P(52)	362.06507	36	R(29)	381.46918	-221	P(82)	352.03752	121	P(25)	367.42950	8
P(50)	362.62208	-73	R(30)	381.66261	-43	P(81)	352.33238	-75	P(24)	367.67170	32
P(47)	363.45252	34	R(31)	381.85233	-124	P(80)	352.62936	35	P(23)	367.91175	-62
P(46)	363.72692	37	R(32)	382.04113	-186	P(79)	352.92397	3	P(22)	368.15228	-8
P(44)	364.27177	-41	R(33)	382.23046	-83	P(78)	353.21836	44	P(21)	368.39136	-1
P(42)	364.81435	71	R(34)	382.41843	-5	P(77)	353.51132	36	P(20)	368.62650	-290
P(41)	365.08361	80	R(35)	382.60346	-109	P(76)	353.80376	71	P(18)	369.10261	11
P(39)	365.61824	23	R(36)	382.78929	-20	P(75)	354.09408	-11	P(17)	369.33755	-1
P(37)	366.14958	56	R(39)	383.33884	123	P(73)	354.67243	-120	P(16)	369.57158	-6
P(36)	366.41371	76	R(40)	383.51881	74	P(72)	354.96213	20	P(15)	369.80455	-18
P(35)	366.67563	-20	R(41)	383.69621	-119	P(71)	355.24963	35	P(14)	370.03719	37
P(31)	367.71782	95	R(42)	383.87506	-54	P(69)	355.82144	32	P(12)	370.49569	-236
P(30)	367.97484	34	R(43)	384.05266	-2	P(68)	356.10544	-18	P(10)	370.95517	-13
P(29)	368.23177	69	R(44)	384.22703	-160	P(67)	356.39009	93	P(9)	371.18246	3
P(28)	368.48707	47	R(49)	385.09110	-29	P(66)	356.67252	77	P(8)	371.40832	-25
P(27)	368.74130	24	R(50)	385.25957	-97	P(65)	356.95408	69	P(7)	371.63446	75
P(26)	368.99521	74	R(51)	385.42846	-9	P(64)	357.23452	45	P(6)	371.85707	-79
P(25)	369.24715	32	R(53)	385.75837	-279	P(63)	357.51391	11	P(5)	372.08114	13
P(24)	369.49768	-44	R(54)	385.92607	32	P(62)	357.79264	7	P(4)	372.30246	-69
P(23)	369.74818	-18	R(55)	386.08920	1	P(61)	358.07035	-4	R(1)	373.61584	81
P(21)	371.22685	-64	R(58)	386.57291	25	P(60)	358.34741	16	R(3)	374.04427	-2
			R(59)	386.73109	-44	P(58)	358.89843	34	R(5)	374.46879	-73

The spectral analysis program PC-DECOMP, developed by J. W. Brault, was used for data analysis. The line profiles were fit to Voigt lineshape functions. The signal-to-noise ratio for the strongest unsaturated lines in the spectrum taken at 5 Torr was about 50. The precision of the line positions is better than 0.0005 cm^{-1} , but many of the weaker lines were determined only to about $\pm 0.001 \text{ cm}^{-1}$. The absolute calibration was accomplished with some impurity H_2O lines (59) in the cell.

Bands with $v = 1 \leftarrow 0$ to $v = 3 \leftarrow 2$ for $I^{35}\text{Cl}$ and $v = 1 \leftarrow 0$ to $v = 2 \leftarrow 1$ for $I^{37}\text{Cl}$ were picked out using an interactive color Loomis-Wood program. Data reduction was made by using the well-known Dunham equation (60) for the energy levels,

$$T(v, J) = \sum_{ij} Y_{ij} \left(v + \frac{1}{2} \right)^i [J(J+1)]^j, \quad (1)$$

TABLE I—Continued

J''	observed	$\frac{o-c}{10^{-5}}$	J''	observed	$\frac{o-c}{10^{-5}}$	J''	observed	$\frac{o-c}{10^{-5}}$	J''	observed	$\frac{o-c}{10^{-5}}$
$I^{37}Cl, v = 1 \leftarrow 0$			$I^{37}Cl, v = 1 \leftarrow 0$			$I^{37}Cl, v = 2 \leftarrow 1$			$I^{37}Cl, v = 2 \leftarrow 1$		
R(6)	374.68017	-46	R(66)	385.46276	-116	P(55)	356.86535	-85	R(11)	372.81214	274
R(7)	374.89023	-49	R(68)	385.75837	20	P(54)	357.13688	33	R(14)	373.41816	-8
R(8)	375.09976	-5	R(69)	385.90295	-74	P(52)	357.67397	-39	R(16)	373.82020	117
R(9)	375.30674	-114	R(71)	386.19118	-31	P(51)	357.94215	33	R(18)	374.21642	69
R(11)	375.72094	-5	R(72)	386.33320	-57	P(50)	358.20768	-62	R(19)	374.41263	9
R(16)	376.73469	-131	R(73)	386.47416	-81	P(49)	358.47619	237	R(20)	374.60797	-35
R(17)	376.93518	-77	R(75)	386.75368	-44	P(48)	358.73893	56	R(21)	374.80218	-90
R(18)	377.13392	-96	R(76)	386.89025	-182	P(47)	359.00203	8	R(24)	375.38131	15
R(19)	377.33318	39	R(78)	387.16578	107	P(46)	359.26488	32	R(25)	375.57121	-59
R(20)	377.52847	-121	R(79)	387.29855	-84	P(44)	359.78845	158	R(27)	375.95105	108
R(21)	377.72408	-146	R(81)	387.56527	-23	P(42)	360.30626	98	R(31)	376.69331	-57
R(22)	377.91895	-143	R(82)	387.69565	-126	P(41)	360.56353	50	R(32)	376.87491	-236
R(23)	378.11314	-106	R(84)	387.95796	150	P(40)	360.81970	-10	R(33)	377.05910	-51
R(24)	378.30580	-119	R(85)	388.08439	-20	P(36)	361.83766	54	R(34)	377.24137	46
R(25)	378.49723	-152	R(87)	388.33762	7	P(35)	362.08975	74	R(35)	377.42127	9
R(26)	378.68882	-67	R(88)	388.46165	-74	P(34)	362.34120	128	R(36)	377.59972	-67
R(27)	378.87796	-123	R(91)	388.83159	132	P(33)	362.59090	106	R(37)	377.77691	-166
R(28)	379.06693	-94	R(93)	389.06967	-33	P(32)	362.83905	26	R(38)	377.95543	-27
R(29)	379.25421	-131	R(96)	389.42122	-6	P(31)	363.08772	96	R(39)	378.13271	93
R(31)	379.62652	-119	R(98)	389.64731	-260	P(30)	363.33282	-92	R(40)	378.30580	-101
R(32)	379.81043	-183	R(102)	390.09398	22	P(29)	363.57998	24	R(42)	378.65286	-88
R(33)	379.99523	-54	R(106)	390.51941	-28	P(28)	363.82515	40	R(43)	378.82484	-78
R(34)	380.17735	-90	R(109)	390.82992	262	P(27)	364.06926	47	R(44)	378.99534	-112
R(35)	380.35847	-122	$I^{37}Cl, v = 2 \leftarrow 1$			P(26)	364.31237	54	R(45)	379.16609	-15
R(36)	380.53877	-132	P(86)	348.00789	-183	P(24)	364.79513	16	R(46)	379.33451	-46
R(37)	380.71841	-104	P(82)	349.20589	195	P(23)	365.03528	23	R(49)	379.83425	-57
R(39)	381.07435	-70	P(81)	349.50139	126	P(22)	365.27468	53	R(51)	380.16129	-147
R(40)	381.24992	-137	P(79)	350.09189	223	P(21)	365.51247	21	R(52)	380.32405	-109
R(41)	381.42622	-26	P(78)	350.38469	169	P(20)	365.75039	101	R(54)	380.64631	-40
R(42)	381.60004	-59	P(77)	350.67491	-48	P(19)	365.98617	67	R(55)	380.80657	67
R(43)	381.77235	-138	P(76)	350.96902	219	P(18)	366.22105	41	R(56)	380.96327	-76
R(45)	382.11517	-163	P(75)	351.25564	-167	P(14)	367.15116	-9	R(60)	381.58352	-233
R(46)	382.28592	-84	P(74)	351.54770	86	P(13)	367.38122	-20	R(62)	381.89024	-10
R(47)	382.45448	-119	P(73)	351.83548	6	P(12)	367.61142	84	R(63)	382.04113	15
R(49)	382.78929	-104	P(72)	352.12309	4	P(11)	367.83825	-51	R(65)	382.33726	-176
R(51)	383.11976	-102	P(71)	352.40961	-11	P(10)	368.06645	52	R(66)	382.48593	-50
R(53)	383.44546	-155	P(70)	352.69616	72	P(9)	368.29226	16	R(69)	382.92151	-66
R(54)	383.60690	-164	P(69)	352.98112	92	P(8)	368.51635	-93	R(71)	383.20639	-87
R(56)	383.92848	7	P(68)	353.26380	-21	P(7)	368.74130	-15	R(74)	383.62714	39
R(57)	384.08577	-99	P(67)	353.54871	185	P(6)	368.96542	80	R(75)	383.76493	52
R(58)	384.24291	-113	P(66)	353.82895	20	R(2)	370.92943	149	R(79)	384.30385	-27
R(59)	384.40061	35	P(62)	354.94619	-54	R(3)	371.14154	50	R(80)	384.43446	-185
R(61)	384.70785	-166	P(60)	355.50080	84	R(5)	371.56345	-77			
R(62)	384.86171	-82	P(59)	355.77596	83	R(7)	371.98344	10			
R(63)	385.01307	-141	P(58)	356.04999	65	R(8)	372.19198	60			
R(64)	385.16460	-76	P(57)	356.32289	30	R(10)	372.60445	4			

where v and J are the vibrational and rotational quantum numbers. The Dunham coefficients are isotope-dependent and vary approximately with powers of the reduced mass ratio μ/μ^* ,

$$Y_{ij}^* = Y_{ij} \left(\frac{\mu}{\mu^*} \right)^{(i/2+j)}, \quad (2)$$

where the asterisk designates an isotopically substituted species. Table III gives the Dunham constants calculated in least-squares fits from our infrared data (Table I) and the millimeter-wave data of Willis and Clark (36, 37) (Table II) for $I^{35}Cl$ and $I^{37}Cl$, respectively. The millimeter-wave data, corrected for the effect of hyperfine

TABLE II
Pure Rotational Transitions of ICl (37) in cm^{-1}

$^{127}\text{I}^{35}\text{Cl}$					$^{127}\text{I}^{37}\text{Cl}$				
v''	$J' \leftarrow J''$	observed	o.-c. ^a / 10^{-8}	unc. / 10^{-8}	v''	$J' \leftarrow J''$	observed	o.-c. / 10^{-8}	unc. / 10^{-8}
0	18 ← 17	4.099 134 48	-4	100	0	18 ← 17	3.925 760 20	77	100
0	22 ← 21	5.009 484 93	22	100	0	27 ← 26	5.887 021 35	226	200
0	26 ← 25	5.919 492 81	-72	100	0	28 ← 27	6.104 828 70	9	100
0	27 ← 26	6.146 936 83	173	100	1	28 ← 27	6.076 724 59	-93	100
0	30 ← 29	6.829 096 08	-263	200					
0	31 ← 30	7.056 427 68	-196	200					
0	35 ← 34	7.965 445 22	265	300					
0	39 ← 38	8.873 911 03	-36	100					
0	44 ← 43	10.008 637 38	58	100					
1	13 ← 12	2.946 893 01	31	100					
1	22 ← 21	4.985 925 30	10	100					
1	26 ← 25	5.891 642 21	-412	300					
1	27 ← 26	6.118 015 15	-52	100					
1	31 ← 30	7.023 219 38	-49	100					
2	22 ← 21	4.962 249 25	-196	200					
2	27 ← 26	6.088 957 72	199	200					
2	31 ← 30	6.989 849 96	118	100					
3	27 ← 26	6.059 755 18	-10	100					
3	31 ← 30	6.956 316 09	-28	100					

^a observed minus calculated line positions using the mass-reduced Dunham constants of Table IV.

structure, are listed in the Ph.D. thesis of R. E. Willis (37). The uncertainties of the millimeter-wave lines in our fits are listed in Table II.

Finally, all the infrared and millimeter-wave lines were combined and fitted to the mass-reduced Dunham expression including Watson's correction due to the breakdown of the Born-Oppenheimer approximation (61, 62),

$$Y_{ij} = \mu^{-(i+2j)/2} U_{ij} \left[1 + \left(\frac{m_e}{m_{\text{Cl}}} \right) \Delta_{ij}^{\text{Cl}} \right], \quad (3)$$

where μ is the reduced mass, U_{ij} are the mass-independent parameters, m_{Cl} is the atomic mass of chlorine, m_e is the electron mass, and Δ_{ij} are the mass scaling

TABLE III
Dunham Coefficients for I^{35}Cl and I^{37}Cl in cm^{-1}

Coefficient	I^{35}Cl	I^{37}Cl
Y_{10}	384 . 294 16(15) ^a	376 . 066 83(13)
Y_{20}	-1 . 503 091(91)	-1 . 439 020(45)
$10^3 Y_{30}$	-2 . 426(15)	-2 . 274 ^b
Y_{01}	0 . 114 157 656(15)	0 . 109 322 776(40)
$10^3 Y_{11}$	-0 . 532 643(14)	-0 . 499 081(39)
$10^6 Y_{21}$	-1 . 299 1(32)	-1 . 256(14)
$10^6 Y_{02}$	-0 . 040 260 5(61)	-0 . 036 943(30)
$10^9 Y_{12}$	-0 . 209 33(95)	-0 . 170 2(28)
$10^{12} Y_{03}$	-0 . 018 0(12)	-0 . 035 4(35)

^a Errors quoted in parentheses are one standard deviation.

^b Calculated using the isotope relationship (Eq.2) and fixed.

TABLE IV

Mass-Reduced Dunham Coefficients for ICl in cm^{-1}

Coefficient	value
U_{10}	2012.1287(39) ^a
U_{20}	-41.2007(21)
U_{30}	-0.3531(19)
U_{01}	3.1296285(49)
U_{11}	-0.0764555(18)
$10^3 U_{21}$	-0.9778(23)
$10^3 U_{02}$	-0.0302536(45)
$10^6 U_{12}$	-0.8171(36)
$10^9 U_{03}$	-0.422(24)
Δ_{10}^{Cl}	-0.131(122)
Δ_{01}^{Cl}	-0.695(103)

^a Errors quoted in parentheses are one standard deviation.

factors for the nuclei. The mass-independent Dunham constants are listed in Table IV.

ACKNOWLEDGMENTS

This work was supported by the Phillips Laboratory/Propulsion Directorate, Edwards Air Force Base, CA, and the Centre of Excellence in Molecular and Interfacial Dynamics (CEMAID). We thank M. Prisant for providing us with a copy of Ref. (37). Acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. H.G.H. thanks the Deutsche Forschungsgemeinschaft for a postdoctoral scholarship.

RECEIVED: April 7, 1992

REFERENCES

1. W. E. CURTIS AND J. PATKOWSKI, *Nature* **127**, 707 (1931).
2. W. E. CURTIS AND J. PATKOWSKI, *Philos. Trans. R. Soc. London* **232**, 395-430 (1931).
3. W. G. BROWN AND G. E. GIBSON, *Phys. Rev.* **40**, 529-543 (1932).
4. R. S. MULLIKEN, *Phys. Rev.* **46**, 549-571 (1934).
5. E. HULTHÉN, N. JOHANSSON, AND U. PILSÄTER, *Ark. Fys.* **14**, 31-48 (1958).
6. E. HULTHÉN, N. JÄRLSÄTER, AND L. KOFFMAN, *Ark. Fys.* **18**, 479-489 (1960).
7. F. E. CUMMINGS AND W. KLEMPERER, *J. Chem. Phys.* **60**, 2035-2039 (1974).
8. M. A. A. CLYNE AND I. S. MCDERMID, *J. Chem. Soc. Faraday Trans. 2*, **72**, 2252-2268 (1976).
9. C. D. OLSON AND K. K. INNES, *J. Chem. Phys.* **64**, 2405-2411 (1976).
10. G. W. KING AND R. G. MCFADDEN, *Chem. Phys. Lett.* **58**, 119-121 (1978).
11. R. D. GORDON AND K. K. INNES, *J. Mol. Spectrosc.* **78**, 350-352 (1979).
12. G. W. KING, I. M. LITTLEWOOD, R. G. MCFADDEN, AND J. R. ROBINS, *Chem. Phys.* **41**, 379-386 (1979).
13. J. A. COXON, R. M. GORDON, AND M. A. WICKRAMAARATCHI, *J. Mol. Spectrosc.* **79**, 363-379 (1980).
14. M. SIESE, F. BÄSSMANN, AND E. TIEMANN, *Chem. Phys.* **99**, 467-477 (1985).
15. J. A. COXON AND M. A. WICKRAMAARATCHI, *J. Mol. Spectrosc.* **79**, 380-395 (1980).
16. J. D. SPIVEY, J. G. ASHMORE, AND J. TELLINGHUISEN, *Chem. Phys. Lett.* **109**, 456-461 (1984).
17. M. A. STEPP, M. A. KREMER, P. C. TELLINGHUISEN, AND J. TELLINGHUISEN, *J. Mol. Spectrosc.* **146**, 169-180 (1991).
18. J. B. HUDSON, L. J. SAULS, P. C. TELLINGHUISEN, AND J. TELLINGHUISEN, *J. Mol. Spectrosc.* **148**, 50-58 (1991).

19. G. W. HOLLEMAN AND J. I. STEINFELD, *Chem. Phys. Lett.* **12**, 431-433 (1971).
20. R. H. BARNES, C. E. MOELLER, J. F. KIRCHER, AND C. M. VERBER, *Appl. Phys. Lett.* **24**, 610-612 (1974).
21. M. D. HAVEY AND J. J. WRIGHT, *J. Chem. Phys.* **68**, 4754-4756 (1978).
22. S. J. HARRIS, W. C. NATZLE, AND C. B. MOORE, *J. Chem. Phys.* **70**, 4215-4219 (1979).
23. M. DIEGELMANN, K. HOHLA, F. REBENTROST, AND K. L. KOMPA, *J. Chem. Phys.* **76**, 1233-1247 (1982).
24. T. SUZUKI AND T. KASUYA, *J. Chem. Phys.* **81**, 4818-4825 (1984).
25. M. KITAMURA, T. KONDOW, K. KUCHITSU, T. MUNAKATA, AND T. KASUYA, *J. Chem. Phys.* **82**, 4986-4990 (1985).
26. M. KITAMURA, T. KONDOW, K. KUCHITSU, T. MUNAKATA, AND T. KASUYA, *Chem. Phys. Lett.* **118**, 130-133 (1985).
27. M. H. M. JANSSEN, R. M. BOWMAN, AND A. H. ZEWAIL, *Chem. Phys. Lett.* **172**, 99-108 (1990).
28. P. VENKATESWARLU, *Can. J. Phys.* **53**, 812-824 (1975).
29. E. KERR, M. MACDONALD, R. J. DONOVAN, J. P. T. WILKINSON, D. SHAW, AND I. MUNRO, *J. Photochem.* **31**, 149 (1985).
30. R. H. LIPSON AND A. R. HOY, *J. Chem. Phys.* **90**, 6821-6826 (1989).
31. K. P. LAWLEY, E. A. KERR, R. J. DONOVAN, A. HOPKIRK, D. SHAW, AND A. J. YENCHA, *J. Phys. Chem.* **94**, 6201-6208 (1990).
32. A. I. CHICHIN, S. A. CHASOVNIKOV, AND L. N. KRASNOPEROV, *Chem. Phys. Lett.* **138**, 371-376 (1987).
33. R. T. WEIDNER, *Phys. Rev.* **72**, 1268-1269 (1947).
34. C. H. TOWNES, B. D. WRIGHT, AND F. R. MERRITT, *Phys. Rev.* **73**, 1249 (1948).
35. E. HERBST AND W. STEINMETZ, *J. Chem. Phys.* **56**, 5342-5346 (1972).
36. R. E. WILLIS, JR., AND W. W. CLARK III, *J. Chem. Phys.* **72**, 4946-4950 (1980).
37. R. E. WILLIS, Ph.D. Thesis, Department of Physics, Duke University, U.S.A., 1979.
38. H. KNÖCKEL AND E. TIEMANN, *Chem. Phys. Lett.* **64**, 593-595 (1979).
39. H. KNÖCKEL AND E. TIEMANN, *Chem. Phys.* **70**, 345-351 (1982).
40. S. G. HANSEN AND B. J. HOWARD, *Chem. Phys. Lett.* **85**, 249-252 (1982).
41. S. G. HANSEN, J. D. THOMPSON, C. M. WESTERN, AND B. J. HOWARD, *Mol. Phys.* **49**, 1217-1229 (1983).
42. J. R. JOHNSON, T. J. SLOTTERBACK, D. W. PRATT, K. C. JANDA, AND C. M. WESTERN, *J. Phys. Chem.* **94**, 5661-5664 (1990).
43. M. S. DE VRIES, N. J. A. VAN VEEN, M. HUTCHINSON, AND A. E. DE VRIES, *Chem. Phys.* **51**, 159-168 (1980).
44. A. LÜBBERT, G. ROTZOLL, AND F. GÜNTHER, *J. Chem. Phys.* **69**, 5174-5179 (1978).
45. D. KEIL, A. LÜBBERT, AND K. SCHÜGERL, *J. Chem. Phys.* **79**, 3845-3850 (1983).
46. Y. LE COAT, J.-P. GUILLOTIN, AND L. BOUBY, *J. Phys. B* **24**, 3285-3294 (1991).
47. J. C. D. BRAND, U. D. DESHPANDE, A. R. HOY, AND S. M. JAYWANT, *J. Mol. Spectrosc.* **100**, 416-428 (1983).
48. J. C. D. BRAND, D. BUSSIÈRES, A. R. HOY, S. M. JAYWANT, AND D. B. MILLER, *Opt. Commun.* **48**, 195-199 (1983).
49. J. C. D. BRAND, D. BUSSIÈRES, A. R. HOY, AND S. M. JAYWANT, *Can. J. Phys.* **62**, 1947-1953 (1984).
50. J. C. D. BRAND, A. R. HOY, AND S. M. JAYWANT, *J. Mol. Spectrosc.* **106**, 388-394 (1984).
51. J. C. D. BRAND, D. BUSSIÈRES, AND A. R. HOY, *J. Mol. Spectrosc.* **113**, 388-398 (1985).
52. J. C. D. BRAND AND A. R. HOY, *J. Mol. Spectrosc.* **114**, 197-209 (1985).
53. J. C. D. BRAND, D. BUSSIÈRES, A. R. HOY, AND S. M. JAYWANT, *Chem. Phys. Lett.* **109**, 101-104 (1984).
54. J. C. D. BRAND, D. BUSSIÈRES, AND A. R. HOY, *Mol. Phys.* **53**, 525-529 (1984).
55. M. S. CHILD AND R. B. BERNSTEIN, *J. Chem. Phys.* **59**, 5916-5925 (1973).
56. K. BALASUBRAMANIAN, *Chem. Phys.* **95**, 225-234 (1985).
57. K. BALASUBRAMANIAN, *J. Mol. Spectrosc.* **110**, 339-346 (1985).
58. W. V. F. BROOKS AND B. CRAWFORD, JR., *J. Chem. Phys.* **23**, 363-365 (1955).
59. J. W. C. JOHNS, *J. Opt. Soc. Am. B* **2**, 1340-1354 (1985).
60. J. L. DUNHAM, *Phys. Rev.* **41**, 721-731 (1932).
61. J. K. G. WATSON, *J. Mol. Spectrosc.* **45**, 99-113 (1973).
62. J. K. G. WATSON, *J. Mol. Spectrosc.* **80**, 411-421 (1980).