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Infrared diode laser spectroscopy of the PCl radical

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The vibration-rotation spectrum of the PCl radical has been observed by infrared diode laser spectroscopy. The radical was generated by an ac discharge in a PCl_3 and H_2 mixture. The observed lines have been assigned to the $v = 1$–0 and $v = 2$–1 bands of $P^{35}Cl$ and to the $v = 1$–0 band of $P^{37}Cl$. All the observed lines were included in a least-squares analysis, where ground-state parameters were fixed to microwave values and isotopic relations were assumed to hold for molecular constants of the two isotopic species. The equilibrium values for vibrational changes of the rotational, the spin–spin interaction, and the spin-rotation interaction constants have thus been determined very accurately. It was found that the sign of the α^λ constant of PCl is the same as that of NCl, but is opposite to those of O_2, SO, S_2, and SeO.

I. INTRODUCTION

There are a number of diatomic molecules which have $^3\Sigma^-$ ground electronic states; examples are O_2,[1] SO,[2] S_2,[3] SeO,[4,5] NH,[6] NF,[7] NCl,[8] PH,[9,10] and PF.[11,12] High-resolution spectroscopic studies carried out on these molecules have yielded molecular constants with high accuracy, and it is interesting to compare such molecular constants with each other or with those calculated by *ab initio* molecular orbital methods.[13,14] It may be worth mentioning that the vibrational change of the spin–spin interaction constant $\alpha^\lambda = \lambda_{v=1} - \lambda_{v=0}$ is positive for O_2,[15] SO,[2] S_2,[16] and SeO,[17] but is negative for NCl.[18]

The PCl radical also has a $^3\Sigma^-$ ground electronic state, and its precise molecular parameters will be of some use for a systematic understanding of the structures of $^3\Sigma$ molecules. The PCl radical has previously been detected by a flash photolysis of PCl_3,[19] and an analysis of the observed vibronic bands gave the following vibrational constants: $\omega_e = 577$ cm^{-1} and $\omega_e x_e = 3.5$ cm^{-1} for the ground state and $\omega_e = 786$ cm^{-1} and $\omega_e x_e = 27$ cm^{-1} for the excited state and the term of the excited state of $T_e = 41\,234$ cm^{-1}. No further spectroscopic studies have been reported. Minowa *et al.*[20] have recently observed the microwave spectrum of PCl and have determined ground-state molecular constants.

II. EXPERIMENTAL

The PCl radical was produced in an infrared multiple reflection absorption cell 70 mm in diameter and 1 m in length, by an ac discharge in a PCl_3 and H_2 mixture with the partial pressures of 300 and 50 mTorr, respectively. The addition of hydrogen did not affect the efficiency of PCl production much, but stabilized the discharge in PCl_3.

The diode laser spectrometer employed in the present study has been described in detail previously.[21] The region of 560 to 575 cm^{-1} was scanned and about one hundred lines were observed, which appeared as triplets. Source-frequency modulation was employed throughout the present study, because the observed transitions were all of high-J and exhibit-

ed Zeeman effects too small to be modulated by an ac field of 500 G peak-to-peak superimposed with a dc field of 500 G.

The wave number of each line was determined by using N_2O lines[22] as standards and a vacuum-spaced etalon with the free spectral range of 0.009 93 cm^{-1} as an interpolation device. The data acquisition and the wave number determination were performed by a minicomputer. A curve fitting of the observed discrete data reproduced the wave number reading within 0.0001 cm^{-1}, and thus the uncertainty in the observed wave number was primarily due to that in the reference standard.

III. RESULTS AND DISCUSSION

The ground-state constants of $P^{35}Cl$ determined by microwave spectroscopy[20] were fed in a computer graphics program to predict rotational/fine structure transitions. Upper-state constants were adjusted in a trial-and-error fashion until a reasonable agreement was obtained between the calculated and observed spectra. For the $P^{37}Cl$ species, isotopic relations were employed in predicting the spectrum, after the assignment was made for $P^{35}Cl$. The observed spectrum includes (1) the fundamental band $v = 1$–0 of $P^{35}Cl$ for J'' from 10 to 70, (2) the hot band $v = 2$–1 of $P^{35}Cl$ for J'' from 20 to 57, and (3) the fundamental band $v = 1$–0 of $P^{37}Cl$ for J'' from 26 to 61, as listed in Tables I and II. The observed lines all correspond to R branch transitions; the scanned region does not cover the band origin. When the N numbering was displaced by ± 1, the standard deviation of the fit was increased by a factor of more than 5. Figure 1 shows a part of the observed spectrum. It is to be noted that the F_2 and F_3 components of the two $P^{37}Cl$ $v = 1$–0 transitions shown in Fig. 1 are not resolved; these two components cross each other around $N = 27$, not only for this band, but also for the two bands of $P^{35}Cl$. The fact that the transition has been observed for J as large as 70 suggests the rotational temperature to be much higher than the room temperature. The intensities of two closely spaced lines belonging to the two different isotopes were compared to estimate the effective rotational temperature to be 500 ± 100 K. A similar comparison of the fundamental and hot band transition in-

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TABLE I. Observed transitions of the $P^{35}Cl$ radical (cm^{-1}).

$N',J' \leftarrow N'',J''$	ν_{obs}	o − c	W	$N',J' \leftarrow N'',J''$	ν_{obs}	o − c	W
$v = 1 \leftarrow 0$							
12,12 11,11	552.7328	− 0.0002	1.00	44,45 43,44	566.0725	− 0.0014	1.00
12,13 11,12	552.8281	0.0000	1.00	44,43 43,42	566.0573	− 0.0006	1.00
12,11 11,10	552.6565	− 0.0002	1.00	63,63 62,62	572.3900	0.0000	1.00
13,13 12,12	553.2003	0.0026	0.01	63,64 62,63	572.4160	0.0008	1.00
13,12 12,11	553,1330	− 0.0002	1.00	63,62 62,61	572.4060	− 0.0002	1.00
28,28 27,27	559.7946	0.0008	1.00	64,64 63,63	572.6910	0.0001	1.00
28,29 27,28	559.8326	0.0006	1.00	64,65 63,64	572.7160	0.0007	1.00
28,27 27,26	559.7946	0.0006	1.00	64,63 63,62	572.7070	− 0.0001	1.00
31,31 30,30	561.0290	0.0007	1.00	65,65 64,64	572.9890	0.0006	1.00
31,32 30,31	561.0644	0.0009	1.00	65,66 64,65	573.0130	− 0.0004	1.00
31,30 30,29	561.0330	0.0008	1.00	65,64 64,63	573.0040	− 0.0007	1.00
32,32 31,31	561.4337	0.0002	1.00	66,66 65,65	573.2830	0.0005	1.00
32,33 31,32	561.4686	0.0008	1.00	66,67 65,66	573.3074	− 0.0001	1.00
32,31 31,30	561.4392	0.0009	1.00	66,65 65,64	573.2988	− 0.0002	1.00
38,38 37,37	563.7971	− 0.0002	1.00	67,67 66,66	573.5739	0.0006	1.00
38,39 37,38	563.8274	− 0.0005	1.00	67,68 66,67	573.5989	0.0007	1.00
38,37 37,36	563.8067	− 0.0001	1.00	67,66 66,65	573.5904	0.0006	1.00
39,39 38,38	564.1799	− 0.0002	1.00	68,68 67,67	573.8606	− 0.0001	1.00
39,40 38,39	564.2099	− 0.0003	1.00	68,69 67,68	573.8856	0.0000	1.00
39,38 38,37	564.1901	0.0000	1.00	68,67 67,66	573.8773	0.0000	1.00
42,42 41,41	565.3085	− 0.0006	1.00	69,69 68,68	574.1450	0.0002	1.00
42,43 41,42	565.3375	− 0.0005	1.00	69,70 68,69	574.1698	0.0002	1.00
42,41 41,40	565.3202	− 0.0003	1.00	69,68 68,67	574.1616	0.0001	1.00
43,43 42,42	565.6776	− 0.0014	1.00	70,70 69,69	574.4251	− 0.0004	1.00
43,44 42,43	565.7062	− 0.0014	1.00	70,71 69,70	574.4500	− 0.0003	1.00
43,42 42,41	565.6898	− 0.0010	1.00	70,69 69,68	574.4425	0.0002	1.00
44,44 43,43	566.0444	− 0.0012	1.00				
$v = 2 \leftarrow 1$							
22,23 21,22	552.7708	− 0.0001	1.00	51,52 50,51	563.9502	− 0.0000	1.00
22,22 21,21	552.7229	− 0.0002	1.00	51,51 50,50	563.9239	0.0003	1.00
22,21 21,20	552.7107	− 0.0002	1.00	51,50 50,49	563.9381	0.0003	1.00
23,24 22,23	553.2000	0.0005	0.01	52,53 51,52	564.2879	− 0.0000	1.00
23,23 22,22	553.1536	− 0.0001	1.00	52,52 51,51	564.2619	0.0004	1.00
23,22 22,21	553.1437	− 0.0006	1.00	52,51 51.50	564.2765	0.0006	1.00
40,41 39,40	560.0222	0.0002	1.00	55,56 54,55	565,2814	− 0.0001	1.00
40,40 39,39	559.9924	0.0002	1.00	55,55 54,54	565,2560	0.0006	0.01
40,39 39,38	560.0033	0.0006	1.00	55,54 54,53	565.2710	0.0005	0.01
43,44 42,43	561.1323	0.0004	1.00	56,57 55,56	565.6055	− 0.0006	1.00
43,43 42,42	561.1040	0.0007	1.00	56,56 55,55	565.5799	− 0.0002	1.00
43,42 42,41	561.1150	− 0.0001	1.00	56,55 55,54	565.5950	− 0.0003	0.01
50,51 49,50	563.6092	− 0.0001	1.00	57,58 56,57	565.9275	0.0001	1.00
50,50 49,49	563.5820	− 0.0004	1.00	57,57 56,56	565.9016	− 0.0000	1.00
50,49 49,48	563.5964	0.0000	1.00	57,56 56,55	565.9160	− 0.0009	1.00

TABLE II. Observed transitions of the $P^{37}Cl$ radical (cm^{-1}).

| $N',J' \leftarrow N'',J''$	ν_{obs}	O–C	W	$N',J' \leftarrow N'',J''$	ν_{obs}	O–C	W
$v = 1 \leftarrow 0$							
28, 29 27, 28	552.5943	0.0002	1.00	48, 47 47, 46	560.0912	0.0006	1.00
28, 28 27, 27	552.5558	0.0001	1.00	59, 60 58, 59	563.7070	− 0.0009	0.01
28, 27 27, 26	552.5558	0.0008	1.00	59, 59 58, 58	563.6820	− 0.0005	0.01
29, 30 28, 29	552.9982	− 0.0001	1.00	59, 58 58, 57	563.6985	0.0007	0.01
29, 29 28, 28	552.9611	0.0001	1.00	60, 61 59, 60	564.0169	0.0004	1.00
29, 28 28, 27	552.9611	− 0.0006	1.00	60, 60 59, 59	563.9912	0.0000	1.00
47, 48 46, 47	559.7590	0.0006	1.00	60, 59 59, 58	564.0066	0.0000	1.00
47, 47 46, 46	559.7314	0.0004	1.00	61, 62 60, 61	564.3211	− 0.0008	1.00
47, 46 46, 45	559.7444	0.0007	1.00	61, 61 60, 60	564.2963	− 0.0004	1.00
48, 49 47, 48	560.1050	0.0002	1.00	61, 60 60, 59	564.3117	− 0.0005	1.00
48, 48 47, 47	560.0775	− 0.0001	1.00				
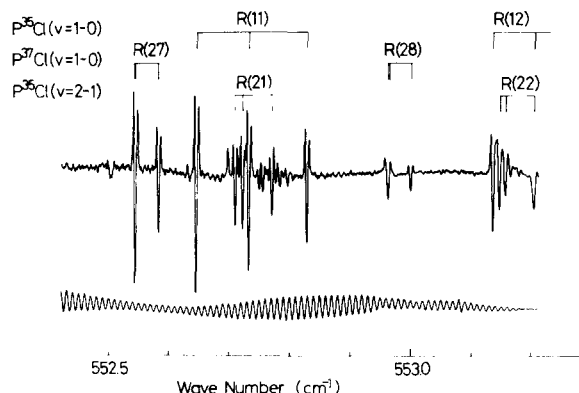
FIG. 1. A part of the observed vibration-rotation spectrum of the PCl radical in the $X\,^3\Sigma^-$ state. The lower trace shows etalon fringes.
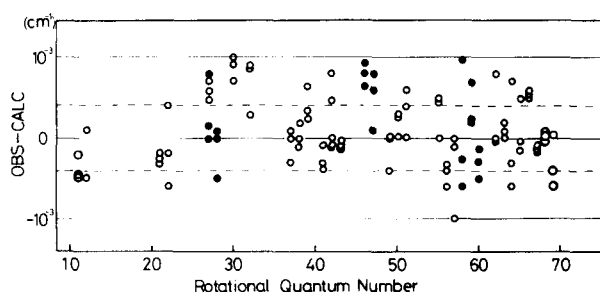

FIG. 2. Observed minus calculated wave numbers plotted against the rotational quantum number N'' of the transition. The open circles represent the deviations for the $P^{35}Cl$ spectral lines, whereas the closed circles denote the values for $P^{37}Cl$. The calculated wave numbers for the latter species were obtained using molecular parameters of $P^{35}Cl$ after converted by isotope mass relationships.

tensities led to the vibrational temperature of 500 ± 100 K, where the rotational temperature was assumed to be 500 ± 100 K, as obtained above.

The effective Hamiltonian employed in the present analysis is given by[23]

$$H = H_{vib} + H_{rot} + H_{ss} + H_{sr}$$
$$= T_{vib} + B_v N^2 - D_v N^4 + (2/3)\lambda_v(3S_z - S^2)$$
$$+ (1/3)\lambda_D\,[N^2,(3S_z - S^2)]_+ + \gamma_v N \cdot S,$$

where the vibrational dependence of each constant is given by

$$B_v = B_e - \alpha^B(v + 1/2) + \gamma^B(v + 1/2)^2,$$
$$\lambda_v = \lambda_e + \alpha^\lambda(v + 1/2),$$

and

$$\gamma_v = \gamma_e + \alpha^\gamma(v + 1/2).$$

A least-squares analysis was performed to determine upper-state parameters and the band origin, while ground-state parameters of $P^{35}Cl$ were constrained to the microwave results.[20] The data on the $P^{35}Cl$ and $P^{37}Cl$ species were simultaneously analyzed by assuming the isotope relations for the molecular constants listed in Table III. In contrast

TABLE III. Molecular constants of the PCl radical in the $X\,^3\Sigma^-$ state (cm^{-1}).[a]

Constant	Value	Reduced mass dependence[b]
ω_e	551.384 50(87)	$-1/2$
$\omega_e x_e$	2.225 94(35)	-1
B_e	0.252 874 80(25)	-1
α^B	0.001 511 88(34)	$-3/2$
γ^B	0.000 001 57(14)	-2
D_e	$0.212\ 40(19) \times 10^{-6}$	-2
λ_e	4.264 44(18)	0
α^λ	$-0.020\ 21(28)$	$-1/2$
λ_D	$0.455\ 2(23) \times 10^{-6}$	-1
γ_e	$-0.307\ 31(32) \times 10^{-2}$	-1
α^γ	$0.447(34) \times 10^{-4}$	$-3/2$

[a] Values in parentheses denote 2.5 standard deviations and apply to the last digits of the constants.
[b] Exponent n in μ^n, μ denoting the reduced mass.

with the results on NCl,[18] no inconsistencies have been observed between the spectral data of the two isotopic species, as shown in Fig. 2, where the observed minus calculated wave numbers are plotted against the rotational quantum number. The open circles represent the results on $P^{35}Cl$, whereas the closed circles indicate the differences between the observed wave numbers of $P^{37}Cl$ and those calculated for $P^{37}Cl$ from the results on $P^{35}Cl$ assuming isotope relations; two groups of circles are scattered in a similar range, i.e., within $\pm 10^{-3}$ cm^{-1}. The breakdown of the isotopic relations observed for NCl is probably accounted for by the smaller weight of this molecule than that of PCl. The molecular constants of $P^{35}Cl$ thus derived are listed in Table III. The standard error of the fit is 0.0005 cm^{-1}, which is close to the uncertainty 0.0004 cm^{-1} of the reference spectra.

Although the scanned region does not extend to the band origin and the P branch region, the molecular parameters are determined with high accuracy, because the ground-state parameters were fixed by the microwave results. When the B_e and ω_e values obtained in the present study are substituted in the formula $D_e = 4B_e^3/\omega_e^2$, the centrifugal distortion constant is calculated to be $2.127\ 492(14) \times 10^{-7}$ cm^{-1}, which agrees well with the observed value $2.1243(24) \times 10^{-7}$ cm^{-1}. The equilibrium bond length r_e is calculated from B_e to be 2.014 609(49) Å, where the error given in parentheses is entirely due to the uncertainty of Planck's constant. It is interesting that this length is larger than the values for Cl_2(1.9879 Å) and P_2(1.8934 Å).[1] This may be understood in the following way. The bond in the Cl_2 molecule is essentially a single bond, as indicated by the single bond covalent radius sum $0.99 \times 2 = 1.98$ Å, whereas the P_2 bond is close to a pure triple bond, since twice the triple bond covalent radius is $0.93 \times 2 = 1.86$ Å. The PCl bond length obtained in the present study is located between the single bond and double bond covalent radius sums, $1.10 + 0.99 = 2.09$ and $1.00 + 0.89 = 1.89$ Å, respectively. In fact, the microwave result[20] shows that the unpaired electron orbital (i.e., the highest occupied π orbital, 4π) may be approximately expressed by an LCAO MO: $(4\pi) = \sqrt{0.87}\,3p_\pi(P) - \sqrt{0.14}\,3p_\pi(Cl)$ and the next highest occupied π orbital by $(3\pi) = \sqrt{0.14}\,3p_\pi(P) + \sqrt{0.87}\,3p_\pi(Cl)$. Because the (4π) orbital is essentially antibonding, it cancels

nearly half of the bonding character of the (3π) orbital, leaving only about 28% of the bonding character in the 3π bond, in qualitative agreement with the expectation from the covalent radii. Table III shows that the spin–spin interaction constant of PCl decreases when the vibration is excited, i.e., α^λ is negative, in conformity with the results on NCl.

ACKNOWLEDGMENT

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