Infrared Absorption Spectrum of CD_4 at 4500 cm^{-1}*†

K. Fox,‡ K. T. Hecht, R. E. Meredith, and C. W. Peters
The Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan

(Received February 9, 1962)

A high-resolution infrared absorption spectrum is presented for the region of the first overtone of the triply degenerate vibrational fundamental ν_3 of CD_4. The measured lines between 4430 and 4550 cm^{-1} are reproduced and tabulated. Comparisons are made between the tetrahedral splittings in this spectrum and those in the spectra ν_3 and $\nu_1+\nu_4$ of CH_4.

RECENT experimental and theoretical interest in the high-resolution infrared absorption spectra of CH_4[1-3] motivated an investigation of the first overtone of the triply degenerate vibrational fundamental ν_3 of CD_4. The spectrum was obtained with a 3-m focal length double-passed Ebert spectrometer, with

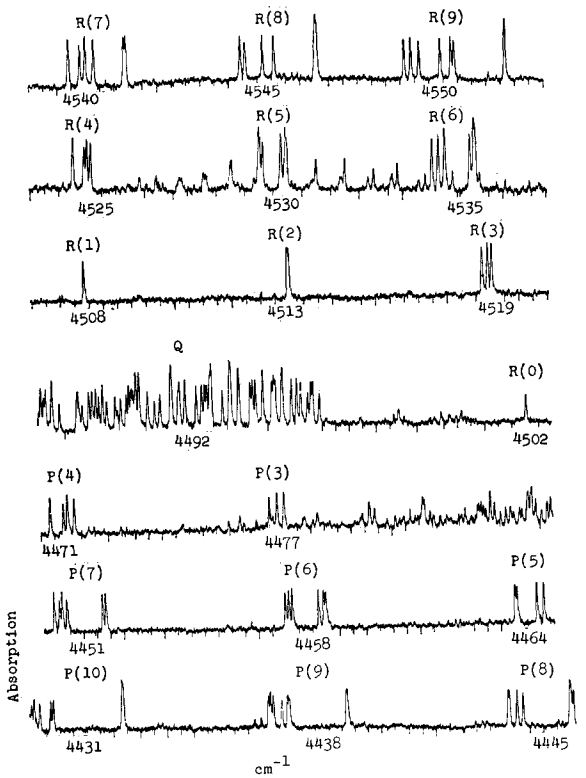

FIG. 1. Infrared absorption spectrum of CD_4 at 4500 cm^{-1}.

TABLE I. Wave numbers of measured lines in 4500 cm^{-1} region of CD_4.

P	*Q*		*R*
4476.12 cm^{-1}	4494.35 cm^{-1}	4486.68 cm^{-1}	4500.47 cm^{-1}
4475.92	.17	.46	
.69	.11	.28	4506.35
	.02	.22	
4469.96	4493.81	.09	4512.08
.76	.69	.07	.12
.64	.54	4485.93	
.25	.27	.77	4517.59
	.06	.61	.74
4463.55	.01	.30	.85
.35	4492.95	.16	
4462.76	.68	.06	4523.05
.69	.47	4484.91	.37
	.38	.83	.45
4457.15	.32	.70	.56
.08	4491.98	.64	
4456.95	.73	.50	4528.35
.17	.50	4483.97	.45
.07	.17	.88	.97
4455.96	.13	.71	4529.11
	.04	.53	
4450.73	4490.98	.40	4533.38
.63	.89	.29	.44
4449.61	.72	.12	.63
.47	.39	.05	4534.33
.39	.22	4482.86	.47
.23	4489.98	.77	
	.65	.64	4538.47
4444.31	.50	.48	.80
.22	.29	.31	.95
.21	.04	.18	4539.18
4442.83	4488.94	.05	4540.06
.65	.86	4481.98	.10
.43	.81	.91	
.40	.74	.84	4543.39
	.66	.80	.53
4437.74	.49	.43	4544.03
.71	.41	4480.23	.36
4436.04	.34	.18	4545.57
.00	.09	4479.82	
4435.83	4487.95	4478.78	4548.10
.58	.84	.62	.29
.50	.76		.52
.44	.65		4549.13
	.55		.44
4431.23	.36		.53
4429.23	.23		4550.99
.16			
4428.83			
.67			
.59			
.51			

* A preliminary discussion of this work was given at the Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio (1961).

† Research supported in part by the U.S. Air Force Cambridge Research Laboratories.

‡ NSF Predoctoral Fellow (1960-61); University of Michigan IST Postdoctoral Fellow (1961-62).

[1] E. K. Plyler, E. D. Tidwell, and L. R. Blaine, J. Research Natl. Bur. Standards **64A**, 201 (1960).

[2] D. H. Rank, D. P. Eastman, G. Skorinko, and T. A. Wiggins, J. Mol. Spectroscopy **5**, 78 (1960).

[3] K. T. Hecht, J. Mol. Spectroscopy **5**, 355 and 390 (1960).

TABLE II. Tetrahedral fine structure patterns.[a]

	Theory		Experiment			
			ν_3 of CH_4[b]	$\nu_1+\nu_4$ of CH_4[c]	$2\nu_3$ of CD_4	
J	(Dominant approx.)		$P(J)$	$P(J)$	$P(J)$	$R(J)$
3	A_1	6.0	(6.0)	(6.0)	(6.0)	(6.0)
	F_1	1.0	0.5	1.0	1.1	0.8
	F_2	−3.0	−3.4	−3.0	−3.1	−2.9
			×.0262	×.112	×.0475	×.0299 cm^{-1}
4	F_2	13	13.3	13.0	12.5	14.7
	E	−2	−2.3	−1.8	−1.9	−3.3
	F_1	−7	−7.0	−7.1	−6.5	−7.8
	A_1	−14	(−14)	(−14)	(−14)	(−14)
			×.0138	×.0615	×.0268	×.0178 cm^{-1}
5	$F_2^{(2)}$	27.5	27.2	30.1	24.9	28.0
	E	21	(21)	(21)	(21)	(21)
	F_1	−14	−13.8	−13.6	−13.6	−16.2
	$F_2^{(1)}$	−27.5	−27.3	−30.1	−25.3	−26.0
			×.00838	×.0352	×.0170	×.0140 cm^{-1}
6	A_1	63	(63)	(63)	(63)	(63)
	F_1	48	45	48	52	56
	$F_2^{(1)}$	31	26	30	41	35
	A_2	−33	−27	−19	−42	−44
	$F_2^{(2)}$	−51	−50	−38	−57	−59
	E	−57	−50	−44	−64	−59
			×.00554	×.0302	×.00934	×.00894 cm^{-1}
7	$F_2^{(2)}$	29	29	36	24	32
	E	19	19	25	18	19
	$F_1^{(2)}$	13	12	17	15	14
	A_1	2.8	−1.4	1.4	10	4.4
	$F_1^{(1)}$	−25	−25	−25	−26	−31
	$F_2^{(1)}$	−29	(−29)	(−29)	(−29)	(−29)
			×.0139	×.0621	×.0286	×.0261 cm^{-1}
8	$F_2^{(2)}$	45	49	50	36	51
	$E^{(2)}$	40	44	43	34	45
	$F_1^{(1)}$	23	24	24	24	21
	$F_2^{(1)}$	4.0	−4.3	−4.0	16	4.8
	$E^{(1)}$	−48	−48	−47	−48	−53
	$F_1^{(2)}$	−50	−48	−49	−49	−53
	A_1	−53	(−53)	(−53)	(−53)	(−53)
			×.00999	×.0514	×.0214	×.0209 cm^{-1}
9	A_1	75	(75)	(75)	(75)	(75)
	$F_1^{(2)}$	67	66	66	70	65
	$F_2^{(2)}$	57	55	53	63	53
	A_2	32	33	32	42	21
	$F_2^{(3)}$	6	−5	−5	27	4
	E	0	−9	−13	24	0
	$F_1^{(1)}$	−81	−71	−69	−123	−77
	$F_2^{(1)}$	−85	−75	−73	−120	−77
			×.00843	×.0454	×.0116	×.0191 cm^{-1}

[a] Numbers in this table are relative splittings from "center of gravity," with A, E, F types weighted by 1, 2, 3, respectively. The observed absolute splittings are equal to the relative splitting numbers multiplied by the indicated factors in cm^{-1}.

[b] Reference 1.

[c] D. E. Brown, thesis, University of Michigan (1957); published as a report entitled "High Resolution Infrared Spectroscopy with Special Reference to Methane," ORA, University of Michigan, Ann Arbor, Michigan (1961).

spectral resolution of about 0.03 cm^{-1}. The absorption cell was of the White type, giving a path of 3.5 m. The CD_4 pressure was 3 cm of Hg. Absolute line positions were determined with an estimated error of 0.02 cm^{-1}.

The observed spectrum of CD_4 between 4430 and 4550 cm^{-1} is reproduced in Fig. 1. It consists of single P, Q, and R branches with sizable tetrahedral fine structure splittings. This spectrum bears a striking resemblance to $2\nu_3$ of CH_4,[2] except that in the latter case the tetrahedral splittings are extremely small. In contrast, the large number of lines of the much richer spectrum $2\nu_4$ of CH_4[1] cannot be accounted for by the tetrahedral fine structure lines of *single* P, Q, and R branches. In Table I are listed the measured lines of $2\nu_3$ of CD_4.

A detailed theoretical investigation of this spectrum has been made.[4] Single infrared-active P, Q, and R branches are in fact predicted in the limit in which the separation between the E and F_2 vibrational substates of $2\nu_3$ is large compared with the Coriolis splittings arising from the $2B\zeta_3(\mathbf{P}\cdot\mathbf{l}_3)$ term. It is interesting to compare the observed fine structure patterns with the universal relative splittings predicted by theory in dominant approximation[3] which holds for all states having the rotational angular momentum as a good quantum number. This comparison is given in Table II, along with the relative splittings for some other vibrational states. In the theoretical account of $2\nu_3$ of CD_4 it is shown that the agreement with dominant approximation is to be expected even though the rotational angular momentum is *not* a good quantum number.

There is a set of comparatively weak lines with somewhat regular spacing, which are in the region of 4525 to 4535 cm^{-1}. These are broader than the other lines of the spectrum, and have irregular shapes. No contaminant has been found to which these lines can be ascribed,[5] and their origin remains a troublesome point.

[4] K. Fox, thesis, University of Michigan (1961). A detailed account will be published.

[5] A spectrum of the same region (E. D. Palik, private communication, 1960), with the CD_4 produced by a different chemical reaction, also shows these lines.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 36, NUMBER 12 JUNE 15, 1962

Spectroscopy in Liquid-Rare-Gas Solvents. Infrared Spectra of CH_4 in Argon and of HCl in Xenon*

JOEL KWOK AND G. WILSE ROBINSON†

Gates and Crellin Laboratories of Chemistry,‡ California Institute of Technology, Pasadena California

(Received November 24, 1961)

A low-temperature cell employing barium fluoride windows and indium metal gaskets has been built and is being used for the study of rotational, vibrational, and electronic motions of molecules in liquid rare gases. The ν_3 fundamental of CH_4 in liquid argon shows a single, relatively sharp Q branch. The P and R branches are probably present but apparently are lost in the wings of the Q branch. The infrared spectrum near 3.5 μ of HCl in liquid xenon shows well-resolved P, Q, and R branches, but the individual rotational lines are not resolved. The O branch is not resolved from the tail of the P branch, but there is some indication of the S branch on the high-frequency side of the spectrum. The Q branch is shifted 36 cm^{-1} to the low-frequency side of its gas-phase position. The appearance of O, Q, and S branches is expected because of the presence of an induced dipole moment through the polarizability of the solvent. The agreement between the observed spectrum and that anticipated on the basis of nearly free rotation gives good evidence for the existence of quantized rotational motions of HCl in liquid xenon.

I. INTRODUCTION

THE primary objective of this work is to obtain information concerning "local environments" in simple, dense fluids, such as argon, krypton, and xenon, through the study of rotational, vibrational, and electronic motions of dissolved solutes. If diffusional processes, i.e., large amplitude or random displacements, are very slow compared with the spectroscopic frequency, then the spectrum of the dissolved molecule is determined by the instantaneous configuration of its local environment. The observed spectrum is, of course, a superposition over the different local environments of all the solute molecules. On the other hand, if the measuring process is slow compared with random fluctuations, then the spectrum will be determined by the time average of the environmental perturbations. Recent neutron diffraction experiments[1] apparently

* Supported in part by the National Science Foundation and the U. S. Army Research Office.

† Alfred P. Sloan Fellow.

‡ Contribution No. 2781.

[1] C. T. Chudley and R. J. Elliott, Proc. Phys. Soc. (London) 77, 353 (1961).