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Methylene Chloride: The Mid-Infrared Spectrum of an Almost Vibrationally Unperturbed Molecule

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The infrared gas phase spectra of $^{12}CH_2Cl_2$, $^{13}CH_2Cl_2$, and $^{12}CD_2Cl_2$ have been studied in the region below 6200 cm^{-1} under conditions of high resolution. Some 30 vibrational levels can be identified for each isotopic species and assigned unequivocally in terms of the band contours displayed. Direct observation has been made of the very weak ν_2 fundamentals in all species, and of the "inactive" torsion fundamental of CD_2Cl_2. Rotational analyses have been performed on the observed Q-branch features of over 30 bands. For each isotopic species, it is found, with one exception, that all vibration levels fit accurately the simple second-order perturbation expression involving ν's and x's. The sole exception in each species is the overtone region of the $CH_2(CD_2)$ stretching vibrations. Here anharmonicity effects bring vibrationally interacting levels into close enough proximity for resonance effects to become just slightly more than of second-order importance. Full analyses including Fermi resonance are made. The effects of the Darling–Dennison resonance between the overtones of the CH stretching fundamentals are observed and corrected for in terms of a simple assumption. Most of the resulting anharmonicity constants bear isotopic relationships similar to those established for H_2O and D_2O. It is concluded that, with the exception of the CH(CD) stretching overtone region, methylene chloride isotopomers behave as vibrationally unperturbed molecular systems in the mid-infrared region.

1. INTRODUCTION

Methylene chloride, being a readily available compound and the simplest dichloroalkane, has received a considerable amount of spectroscopic attention over the years. The first concerted study of the infrared and Raman spectra of CH_2Cl_2, $CHDCl_2$, and CD_2Cl_2 species in gaseous and liquid phases by Palma *et al.* (*1*) was reported in 1964. Subsequent thorough studies have been made in the infrared of crystal and solid solution spectra by Marzocchi and Manzelli (*2*) and of liquid phase spectra by Saëki and Tanabe (*3*). The first and second overtone regions of the CH stretching fundamentals have been observed in liquid phase spectra and approximately analyzed in terms of anharmonicity constants and effective resonance parameters by Avanessoff *et al.* (*4*). Local mode behavior in multiple overtones of the CH stretching vibrations has been considered by Henry and co-workers (*5*) from liquid phase spectra. A thorough study of intensities in the Raman gas phase spectra of CH_2Cl_2, $CHDCl_2$, and CD_2Cl_2 has been made by Escribano *et al.* (*6*), who have improved the precision with which

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the fundamental frequencies are known. A number of studies in the microwave region have established the molecular geometry with fair precision, the most recent being that of Davis *et al.* (*7*). Numerous force constant calculations have been attempted, of which Refs. (*6*) and (*7*) are the most recent; all suffer from insufficient data of the requisite precision to determine a complete set of physically realistic parameters.

As part of an in-depth study of this molecule, we have investigated the region 6200–500 cm^{-1} in the infrared gas phase spectra of $^{12}CH_2Cl_2$, $^{13}CH_2Cl_2$, and $^{12}CD_2Cl_2$ species at a resolution of ~0.1 cm^{-1}, or better where required. This allows the contours of all bands to be clearly defined, and normally permits K structure in individual bands to be assigned and analyzed, if strong perturbations are not present. The results of this study are presented here. Most unusually for a polyatomic molecule, they require that all three isotopomers behave as vibrationally unperturbed molecules throughout almost the entire region, due either to strongly interacting vibrational levels remaining sufficiently far apart, or to fortuitously small resonance parameters in cases where vibrational levels are in close proximity.

2. EXPERIMENTAL DETAILS

Samples of $^{13}CH_2Cl_2$ and $^{12}CD_2Cl_2$ were purchased from Merck, Sharp, and Dohme. After drying, all samples were found to have comparatively high purity, small amounts (~1%) of $^{12}CH_2Cl_2$ and $^{12}CHDCl_2$, being present in the $^{13}CH_2Cl_2$ and $^{12}CD_2Cl_2$ samples, respectively, as expected. A possible impurity in the CD_2Cl_2 is suspected (see Sect. 3) but remains unidentified. All samples contained natural isotopic abundances of ^{35}Cl and ^{37}Cl. This meant that in favorable cases, spectra of $^{35}Cl_2$ and $^{35}Cl^{37}Cl$ species could both be assigned. In a very few cases structure due to the $^{37}Cl_2$ species could also be observed.

Spectra were recorded on the Nicolet FTIR spectrometer at Aberdeen and on the Bruker FTIR spectrometer at Bologna at resolutions of between 0.12 and 0.04 cm^{-1}. The former is sufficient to enable K structure in B- and C-type bands (and some A-type bands) to be clearly resolved. The latter is necessary for more extended analyses involving J structure, the spacing of which is less than 0.2 cm^{-1}. Sample pressures ranged from 0.5 to 15 Torr in multiple reflection gas cells with path lengths of 0.5 up to 13 m.

Spectra were calibrated with respect to the instrumental He–Ne laser, and measurements from the two instruments agreed to better than 0.01 cm^{-1} on spectra recorded under comparable conditions. The uncertainties in the data reported in this paper arise almost entirely from the quality of the analysis that could be performed, or not, as the case may be. Values quoted should be considered accurate to ±1 in the last digit.

3. SPECTRAL DATA AND ASSIGNMENTS

A. Fundamentals

General survey spectra of $^{12}CH_2Cl_2$ and $^{12}CD_2Cl_2$ in the regions of interest, recorded at 1 cm^{-1} resolution, are shown in Figs. 1 and 2. Assignments are given below the relevant bands, on the basis that vibrations of A_1, B_1, and B_2 symmetry of the C_{2v} point group give rise to B-, C-, and A-type bands, using the conventional numbering

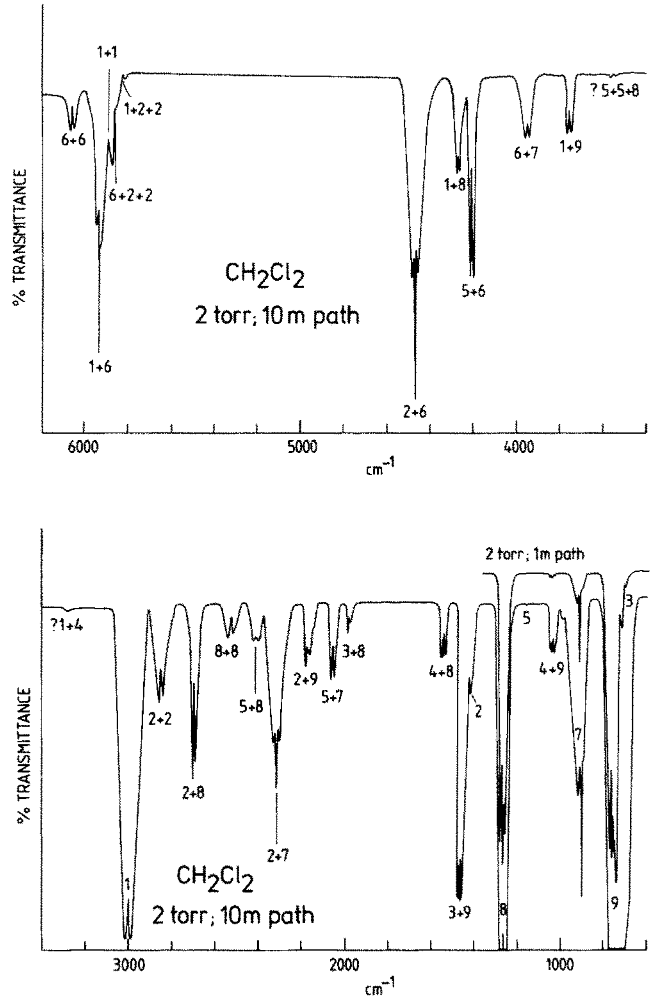

FIG. 1. The gas phase infrared spectrum of $^{12}CH_2Cl_2$ in the region 6200–600 cm^{-1} at a resolution of ca. 1 cm^{-1}. No change of scale at 2000 cm^{-1}.

of fundamentals. It will be observed that the spectra provide a rich source of information on overtone and combination levels, as well as on the fundamentals themselves. In CH_2Cl_2, we find ourselves quite unable to observe the antisymmetric CH_2 stretching fundamental, ν_6, observed in the Raman (*6*), although it may be found as a weak *C*-type band in CD_2Cl_2. In all cases, the extremely weak ν_2 and ν_3 fundamentals can be observed, the former on the low-frequency side of the much more intense $\nu_3 + \nu_9$ band in CH_2Cl_2 species, but clear of obstruction in CD_2Cl_2, the latter always on the low-frequency side of the extremely intense ν_9 fundamental. In CD_2Cl_2, the ν_7 CD_2 rocking fundamental *C*-type band cannot be found, although clearly visible in CH_2Cl_2 species. Its position in CD_2Cl_2 can be estimated from observed perturbations to the *K* structure in the *Q* branch of the overlapping ν_9 fundamental, caused by Coriolis resonance between the two. The estimated position of ν_7 is within 1 cm^{-1} of the quoted Raman

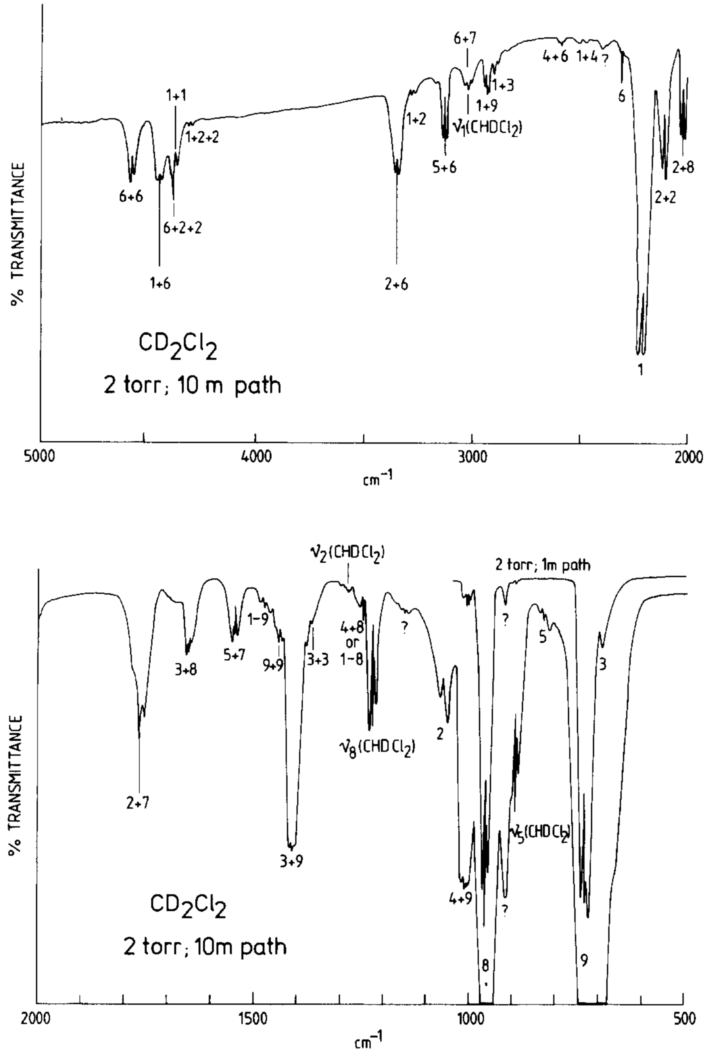

FIG. 2. The gas phase infrared spectrum of $^{12}CD_2Cl_2$ in the region 5000–600 cm^{-1} at a resolution of ca. 1 cm^{-1}. Note the change of scale at 2000 cm^{-1}.

value, which we accept as being the more reliable. In Fig. 2, the "inactive" ν_5 torsion fundamental of CD_2Cl_2 can be seen clearly between the very intense ν_8 and ν_9 *A*-type fundamentals, from which it steals intensity through Coriolis resonance and appears as a very weak *A*-type feature within 1 cm^{-1} of the quoted Raman frequency. In CH_2Cl_2 species, the vibration can just be seen in the correct region, but no accurate measure of the band origin can be made, so the Raman frequency is accepted.

Table I gives the fundamental vibration frequencies determine for the species $^{12}CH_2{}^{35}Cl_2$, $^{13}CH_2{}^{35}Cl_2$, $^{12}CD_2{}^{35}Cl_2$, and $^{12}CHD^{35}Cl_2$, with the Cl isotopic frequency shifts, where observed. For CH_2Cl_2 species, the data for ν_1, ν_2, ν_3, ν_7, ν_8, ν_9 derive

TABLE I

Fundamental Vibration Frequencies (in cm^{-1}) for Isotopic Methylene Chlorides

		$^{12}CH_2{}^{35}Cl_2$	$^{13}CH_2{}^{35}Cl_2$	$^{12}CD_2{}^{35}Cl_2$	$^{12}CHD^{35}Cl_2$
A_1	ν_1	2997.66	2991.26	2205.65	2251^a
	ν_2	1435.0	1431.1	1060.81	1282^a
	ν_3	712.9	695.5	687.6	692^a
	ν_4	281.5^a	-	279^a	280^a
A_2	ν_5	1153^a	1153	825	890.4
B_1	ν_6	3055^a	-	2303.72	3024^a
	ν_7	898.66	889.75	713^a	785^a
B_2	ν_8	1268.86	1264.66	961.04	1223.7
	ν_9	759.82	738.66	730.26	739.3^a
		$^{12}CH_2{}^{35}Cl^{37}Cl$	$^{13}CH_2{}^{35}Cl^{37}Cl$	$^{12}CD_2{}^{35}Cl^{37}Cl$	
	$\Delta\nu_7$	0.29	-	-	
	$\Delta\nu_8$	0.15	0.16	-	
	$\Delta\nu_9$	2.17	2.23	2.42	
		$^{12}CH_2{}^{37}Cl_2$			
	$\Delta\nu_9$	4.66			

[a] Gas-phase Raman results quoted by Escribano et al. (6).

from high-resolution rotational analyses, discussed in Section 4. For CD_2Cl_2 species, this applies to ν_1, ν_2, ν_3, ν_6, ν_8, ν_9. For other fundamentals that were not observed, the Raman data of Escribano *et al.* (*6*) have been accepted.

Two particularly intense *A*-type fundamentals of $CHDCl_2$ could be measured accurately in the spectrum of CD_2Cl_2, and the values are included in Table I. In each case, the values are just over 1 cm^{-1} higher than the Raman estimates, possibly due to the degradation of the *Q* branches to lower wavenumbers. Two other $CHDCl_2$ fundamentals could be identified, but their weakness and irregular *B*-/*C*-type hybrid contours precluded accurate estimation of the band origins.

In our CD_2Cl_2 spectra, an unaccounted for absorption occurs centered at 912 cm^{-1}, as can be seen clearly in Fig. 2. It lies between ν_8 of CD_2Cl_2 and ν_5 of $CHDCl_2$, present as isotopic impurity. The feature appears to have nothing to do with either fundamental band, but occurs in all our spectra, regardless of gas cell used, and remains unexplained. The only other unassigned features are extremely weak absorptions at ~2390 cm^{-1}, which could be a ternary combination, and an apparent *A*-type band at 1150 cm^{-1}, which is difficult to reconcile with a difference band—the only possibility in this region.

Unassigned features, or uncertain assignments are identified with a question mark in Figs. 1 and 2.

B. Overtones and Combinations

Figures 1 and 2 identify the overtone and combination absorptions that we could observe, and the vibration frequencies are collected in Table II. In many cases, rotational analyses of the *K* structure have been made, sometimes over the entire band, sometimes over only limited regions due to overlap or perturbations. In the case of weaker or apparently severely perturbed bands, estimates of the vibration frequencies have been made which are considered to be reliable to better than 1 cm^{-1}. In a number of cases, Cl isotopic shifts could be determined accurately, and these data are also included in Table II. It will be seen that in most cases the same overtone and combination bands could be observed in the spectra of CH_2Cl_2 and CD_2Cl_2 species.

During the accumulation of the data in Table II, it became apparent to us that the heavy isotopic frequency shifts (^{12}C-^{13}C and ^{35}Cl-^{37}Cl) on the overtone and combination levels are in all cases very close to the sum of the shifts observed on the corresponding fundamentals. This is indicative of a situation where Fermi resonance perturbations are very small throughout the entire region studied—a most unusual situation in a polyatomic molecule. Such resonances cause a mixing of the vibrational levels concerned, and consequently mixing of the small isotopic frequency shifts on heavy isotopic substitution. Unless the latter are fortuitously very similar for the two levels concerned, the shift on an overtone or combination level is observed to be significantly different to that expected from the sum of the shifts on its constituent fundamentals, which it should equal in the absence of anharmonicity. Anharmonicity effects can be estimated to contribute about 2% to an observed isotopic shift, or a discrepancy of about 0.2 cm^{-1} on a 10-cm^{-1} frequency shift. Misfits significantly larger than 2% are normally indicative of Fermi resonance effects on either the overtone or combination level concerned or on one, other, or both of the constituent fundamentals.

The observed ^{13}C and ^{37}Cl frequency shifts and those predicted from observations on the fundamentals of $^{12}CH_2{}^{35}Cl_2$ are collected in Table III. In all cases the agreement is remarkably close, the poorest agreement being for $2\nu_8$ where a misfit of 0.44 cm^{-1} is found. The data in Table III enable estimates to be made of the ^{13}C frequency shifts on ν_4, which lies below the range of our spectra, and on ν_6, which cannot be observed. Two estimates of the former are identical at 1.3 cm^{-1}, while six estimates of the latter all fall in the range 11.2–12.1 cm^{-1}.

Accepting that the collected data of Tables I–III are representative of essentially unperturbed vibrational levels for the isotopic species concerned, we may calculate a large number of heavy isotopic frequency shifts on the fundamentals themselves. These, and the directly observed shifts, are listed in Table IV. They constitute a rich source of apparently accurate isotopic information with which to improve the precision of determination of the potential function.

4. ROTATIONAL ANALYSES

At the resolutions employed in recording spectra in this study, a large number of bands exhibited rotational structure which could be assigned readily and analyzed.

TABLE II

Overtone and Combination Vibration Frequencies (in cm^{-1}) for Isotopic Methylene Chlorides

	$^{12}CH_2{}^{35}Cl_2$	$^{13}CH_2{}^{35}Cl_2$	$^{12}CD_2{}^{35}Cl_2$
$\nu_4+\nu_9$(A)	1040.5 vw	1018 vw	1010.4 m
$2\nu_3$(B)	-	-	1365 vw
$\nu_3+\nu_9$(A)	1470.6 m	1431.7 m	1415.5 m
$2\nu_9$(B)	-	-	1440 vw
$\nu_4+\nu_8$(A)	1550.0 vw	1544.5 vw	1242 vw
$\nu_3+\nu_8$(A)	1984.7 vw	1963.0 vw	1650.0 w
$\nu_5+\nu_7$(A)	2060.57 w	2051.8 w	1543 w
$\nu_2+\nu_9$(A)	2189 w	2164 w	-
$\nu_2+\nu_7$(C)	2319.7 m	2307.2 m	1764.0 m
$\nu_5+\nu_8$(C)	2416.16 w	2411.87 w	-
$2\nu_8$(B)	2527.43 vw	2519.5 vw	-
$\nu_2+\nu_8$(A)	2700.9 m	2692.4 m	2019.3 m
$2\nu_2$(B)	2853.57 w	2845.4 w	2110.2 m
$\nu_1+\nu_4$(B)	-	-	2493 vw
$\nu_1+\nu_3$(B)	-	-	2892 vw
$\nu_1+\nu_9$(A)	3755 w	3727 w	2937 vw
$\nu_6+\nu_7$(B)	3947 vw	3926 vw	3015 vw
$\nu_5+\nu_6$(A)	4203.1 m	4191.1 w	3126.77 w
$\nu_1+\nu_8$(A)	4266 w	4255.1 w	-
$\nu_1+\nu_2$(B)	-	-	3266 vw
$\nu_2+\nu_6$(C)	4466.89 m	4451.82 m	3351.99 m
$\nu_1+2\nu_2$(B)	5827 vw	5813 vw	4312 vw
$2\nu_1$(B)	5910 w	5897 w	4379.0 w
$\nu_6+2\nu_2$(C)	5860.5 vw	5841.5 vw	4386.6 vw
$\nu_1+\nu_6$(C)	5935.5 m	5917.0 m	4449.71 m
$2\nu_6$(B)	6071 w	6048 w	4574.4 w

	$^{12}CH_2{}^{35}Cl{}^{37}Cl$	$^{13}CH_2{}^{35}Cl{}^{37}Cl$	$^{12}CD_2{}^{35}Cl{}^{37}Cl$
$\Delta(\nu_4+\nu_9)$	5.6	5.5	5.50
$\Delta(\nu_3+\nu_9)$	5.1	4.9	5.5
$\Delta(\nu_3+\nu_8)$	3.0	-	-
$\Delta(\nu_5+\nu_7)$	0.44	0.45	-
$\Delta(\nu_5+\nu_8)$	0.39	0.32	-
$\Delta(2\nu_8)$	0.32	0.34	-

	$^{12}CH_2{}^{37}Cl_2$		$^{12}CD_2{}^{37}Cl_2$
$\Delta(\nu_4+\nu_9)$	-		11.5
$\Delta(\nu_5+\nu_8)$	0.68		-

TABLE III

Observed and Predicted ^{13}C Isotopic Frequency Shifts (in cm^{-1}) on Overtone and Combination Levels of CH_2Cl_2

	Δν obsd.	Δν pred.
$\nu_4+\nu_9$	22.5[a]	-
$\nu_3+\nu_9$	38.9	38.55
$\nu_4+\nu_8$	5.5[a]	-
$\nu_3+\nu_8$	21.7	21.60
$\nu_5+\nu_7$	8.77	8.91
$\nu_2-\nu_9$	25	25.07
$\nu_2+\nu_7$	12.5	12.81
$\nu_5+\nu_8$	4.29	4.20
$2\nu_8$	8.0	8.40
$\nu_2+\nu_8$	8.5	8.10
$2\nu_2$	8.1	7.8
$\nu_1+\nu_9$	28	27.57
$\nu_6+\nu_7$	21[b]	-
$\nu_5+\nu_6$	12.0[b]	-
$\nu_1+\nu_8$	10.9	10.60
$\nu_2+\nu_6$	15.07[b]	-
$\nu_1+2\nu_2$	14	14.2
$2\nu_1$	13	12.80
$\nu_6+2\nu_2$	19.0[b]	-
$\nu_1+\nu_6$	18.5[b]	-
$2\nu_6$	23[b]	-

[a] These observations enable a ^{13}C shift on ν_4 of 1.3 ± 0.1 cm^{-1} to be predicted, using the observed shifts on ν_8 and ν_9.

[b] These observations enable a ^{13}C shift on ν_6 of 11.7 ± 0.4 cm^{-1} to be predicted, using the observed shifts on ν_1, ν_2, ν_5 and ν_7.

With the exception of ν_7 (*C*-type) and ν_8 (*A*-type) of $^{12}CH_2Cl_2$, which are currently the subjects of full asymmetric rotor analyses, only *K* structure, i.e., *Q*-branch structure, has been analyzed. Many *B*-type and *C*-type bands exhibited clearly defined and sharp *Q*-branch features which could be measured accurately. Assignment and analysis of *K* structure in the central *Q* branch of *A*-type bands was also possible in a number of cases, notably for the ν_8 and ν_9 fundamentals in all species. Analyses were performed by a least-squares fitting procedure in terms of expressions either quadratic or cubic in *K* for *B*-/*C*-type bands, and linear in K^2 for *A*-type bands. In almost all cases, *K* numbering was straightforward, but in cases where numbering different by one seemed possible, or where only one branch of a band could be observed (as in ν_2 of CH_2Cl_2 species and ν_3 in all cases), the numbering which gave the $A_0 - \bar{B}_0$ value closest to the microwave value was accepted.

TABLE IV

Isotopic Frequency Shifts (in cm^{-1}) on Fundamentals of Methylene Chloride, Observed Directly and Deduced from Overtone and Combination Data

	From $^{12}CH_2{}^{35}Cl_2$				From $^{12}CD_2{}^{35}Cl_2$
	$\Delta\nu(^{35}Cl^{37}Cl)$	$\Delta\nu(^{37}Cl_2)$	$\Delta\nu(^{13}C)$	$\Delta\nu(^{13}C^{35}Cl^{37}Cl)$	$\Delta\nu(^{35}Cl^{37}Cl)$
$\Delta\nu_1$	0.00[a]	0.00[a]	6.40	6.40[a]	0.00[a]
$\Delta\nu_2$	0.0[a]	0.0[a]	3.9	3.9[a]	0.00[a]
$\Delta\nu_3$	2.9[a]	-	17.4	20.1[a]	3.08[a]
$\Delta\nu_4$	3.4[a]	-	1.3[a]	4.6[a]	3.08[a]
$\Delta\nu_5$	0.20[a]	-	0.00	0.17[a]	-
$\Delta\nu_6$	0.00[a]	0.00[a]	11.7	11.7[a]	0.00
$\Delta\nu_7$	0.29[b]	-	8.91	9.19[a]	0.39[a,c]
$\Delta\nu_8$	0.15	-	4.20	4.36	-
$\Delta\nu_9$	2.17	4.66	21.17	23.40	2.42

[a] Values calculated from overtone and combination data. Values of zero are derived from bands in which no isotopic splittings can be observed.

[b] From high resolution analysis of ν_7.

[c] From $\nu_2 + \nu_7$.

Table V gives the results obtained for 21 *B*-type and *C*-type bands. In each case the number of data (*Q*-branch frequencies) employed and the derived ground state $(A_0 - \bar{B}_0)$ rotational constant is given. For each isotopic species comparison of the average value found for $(A_0 - \bar{B}_0)$ is made with the much more precisely determined microwave value (*7*). Table VI lists the results obtained for 13 *A*-type bands. Again, the number of data employed in each analysis is given.

Since the bands analyzed are in general unexceptional in appearance, it seems unnecessary to show representative samples in detail here. However, in the case of the very weak CH_2 deformation fundamental, ν_2, it would appear that this is the first report of any observed structure in the gas phase. Figure 3 shows the structure observed in our spectra on the low-frequency side of the very much more intense $\nu_3 + \nu_9$ combination band for both $^{12}CH_2Cl_2$ and $^{13}CH_2Cl_2$. Because of the very large ^{13}C isotope shift on $\nu_3 + \nu_9$ (the combination tone of the two CCl_2 stretching fundamentals), the overlapping in $^{13}CH_2Cl_2$ is much more severe, and the *Q*-branch structures of $\nu_3 + \nu_9$ can be seen clearly in the lower trace. In $^{12}CH_2Cl_2$ they lie nearly 40 cm^{-1} higher. For both bands, only *Q* branches in the *P* wing can be assigned, the numbering shown being that consistent with values of $(A_0 - \bar{B}_0)$ derived from the analyses which are closest to the microwave values.

TABLE V

Rotational Analyses of *B*-Type and *C*-Type Bands of Isotopic Methylene Chlorides (all data are in cm^{-1} units)

	ν	$(A'-\bar{B}')$	$(\alpha^A-\alpha^{\bar{B}})$	$10^6\Delta'_K$	No. of data	$(A_o-\bar{B}_o)$
			$^{12}CH_2{}^{35}Cl_2$			
$\nu_1{}^a$	2997.66	0.95401	0.00327	7.5	27	0.95737
$\nu_2{}^b$	1435.0	0.9468	0.0085	-	8	0.9553
$\nu_7{}^c$	898.66	0.96475	-0.00377	16.8	-	0.96098
$2\nu_2$	2853.57	0.95455	0.00607	13	32	0.96062
$2\nu_8$	2527.43	0.95128	0.00966	13	19	0.96194
$\nu_5+\nu_8$	2416.16	0.94805	0.01272	13	30	0.96077
$\nu_2+\nu_6$	4466.89	0.95971	0.00478	-	15	0.96449
	Microwave $(A_o-\bar{B}_o)$ = 0.96098 cm^{-1}.				Average:	0.96021
			$^{12}CH_2{}^{35}Cl{}^{37}Cl$			
$\nu_5+\nu_8$	2415.77	0.94750	0.01258	12	30	0.96008
			$^{13}CH_2{}^{35}Cl_2$			
$\nu_1{}^a$	2991.26	0.91298	0.00382	4.8	23	0.91680
$\nu_2{}^b$	1431.1	0.9051	0.0086	-	8	0.9137
$2\nu_2{}^d$	2845.4	0.9179	0.0092	-	11	0.9271
$2\nu_8$	2519.47	0.90880	0.00980	8.1	19	0.91860
$\nu_5+\nu_8$	2411.87	0.90605	0.01260	11	21	0.91865
$\nu_2+\nu_6$	4451.82	0.91180	0.00480	-	15	0.91660
	Microwave $(A_o-\bar{B}_o)$ = 0.91928 cm^{-1}.				Average:	0.91858

[a] More realistic mathematical analyses of the Q branch structures in ν_1 of $^{12}CH_2Cl_2$ and $^{13}CH_2Cl_2$ would result if the numbering were changed by one unit, lowering the vibration frequencies by $2(A'-\bar{B}')$ and raising the values of $(A_o-\bar{B}_o)$ to the microwave values. However, the band centers seem so obvious visually in both cases that we assume the analyses are slightly inaccurate due to irregularities in the Q branch structures and lack of use of Q branch origins.

[b] Approximate analysis, based on ^PQ_K structure only.

[c] Preliminary results from full asymmetric rotor high resolution analysis.

[d] Approximate analysis, based on limited Q branch data.

5. ANHARMONICITY CONSTANTS

Since the vibrational data of Tables I–III show no evidence of significant Fermi resonance perturbations, they may be analyzed in terms of fundamental frequencies and anharmonicity constants, x_{ij}. The particular relationships which apply here are few in number, and are as follows:

TABLE V—*Continued*

	ν	$(A'-\bar{B}')$	$(\alpha^A-\alpha^{\bar{B}})$	$10^6\Delta'_K$	No. of data	$(A_0-\bar{B}_0)$
			$^{12}CD_2{}^{35}Cl_2$			
ν_1	2205.65	0.68087	0.00326	4.6	42	0.68413
ν_2	1060.81	0.68431	0.00048	16	27	0.68479
$\nu_3{}^d$	687.6	0.6763	0.0104	-	11	0.6867
ν_6	2303.72	0.68213	0.00157	0.0	19	0.68370
$2\nu_2$	2110.20	0.68206	0.00205	4.6	18	0.68411
$\nu_2+\nu_6$	3351.99	0.68137	0.00306	4.5	23	0.68443
$\nu_1+\nu_6$	4449.71	0.67514	0.00840	-	14	0.68354
	Microwave $(A_0-\bar{B}_0)$ = 0.68503 cm^{-1}.				Average:	0.68448

$$(2\nu_i) = 2(\nu_i) + 2x_{ii},$$

$$(\nu_i + \nu_j) = (\nu_i) + (\nu_j) + x_{ij},$$

$$(\nu_i + 2\nu_j) = (\nu_i) + 2(\nu_j) + 2x_{jj} + 2x_{ij}$$

$$= (\nu_i) + (2\nu_j) + 2x_{ij}.$$

Using these relations yields the anharmonicity constants of Table VII for $^{12}CH_2{}^{35}Cl_2$, $^{13}CH_2{}^{35}Cl_2$, and $^{12}CD_2{}^{35}Cl_2$. The values in this table are those consistent with a model in which all vibrational perturbations are of second-order importance. Two interesting comments can be made.

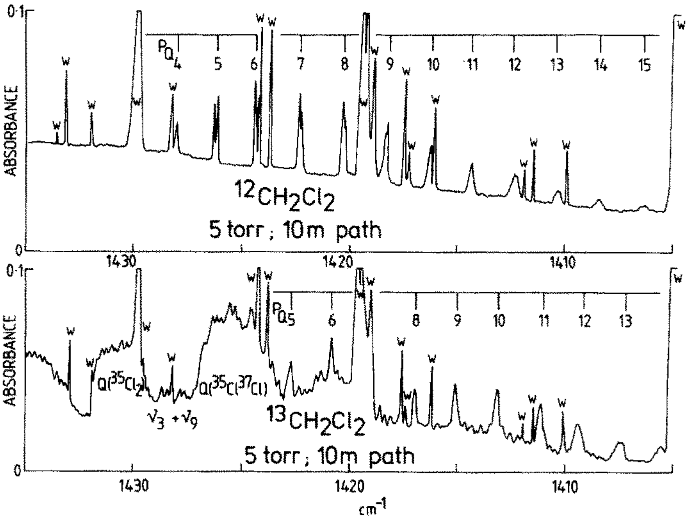

FIG. 3. Rotational structure in the ν_2 fundamentals of $^{12}CH_2Cl_2$ and $^{13}CH_2Cl_2$ at a resolution of ca. 0.1 cm^{-1}. Peaks due to water vapor are identified by *w*.

TABLE VI

Rotational Analyses of *A*-Type Bands of Isotopic Methylene Chlorides (all data are in cm^{-1} units)

	ν	$\bar{B}'+\bar{B}''$	$10^5\alpha^{\bar{B}}$	$(\alpha^A-\alpha^{\bar{B}})$	No. of data
			$^{12}CH_2{}^{35}Cl_2$		
ν_8[a]	1268.859	0.212910	8.7	0.004893	-
ν_9	759.825	-	-	0.01008	12
$\nu_5+\nu_7$	2060.575	-	-	0.00468	19
			$^{12}CH_2{}^{35}Cl^{37}Cl$		
ν_9	757.653	-	-	0.00995	13
$\nu_5+\nu_7$	2060.135	-	-	0.00463	13
			$^{12}CH_2{}^{37}Cl_2$		
ν_9	755.16	-	-	0.00985	7
			$^{13}CH_2{}^{35}Cl_2$		
ν_8	1264.68	-	-	0.0050	6
ν_9	738.656	-	-	0.00934	8
			$^{13}CH_2{}^{35}Cl^{37}Cl$		
ν_9	736.430	-	-	0.00895	8
			$^{12}CD_2{}^{35}Cl_2$		
ν_8[b]	961.04	0.21027	39	-	14
ν_9	730.26	-	-	0.00570	14
$\nu_5+\nu_6$	3126.77	-	-	0.00467	13
			$^{12}CD_2{}^{35}Cl^{37}Cl$		
ν_9	727.84	-	-	0.00565	17

[a] Preliminary results from full asymmetric rotor high resolution analysis.

[b] Analysis of limited range of J structure.

First, the numerical values seem very consistent across the isotopic species. For each constant, the values for $^{12}CH_2{}^{35}Cl_2$ and $^{13}CH_2{}^{35}Cl_2$ are closely similar and almost invariably numerically larger than for $^{12}CD_2{}^{35}Cl_2$. The signs of the constants are also very regular, the most significant positive value, x_{57}, for CH_2Cl_2 species being slightly less positive for CD_2Cl_2. In cases where a change of sign occurs between CH_2Cl_2 and CD_2Cl_2, the values are always close to zero. A number of close resonance possibilities exist. In $^{12}CH_2Cl_2$, $2\nu_3$ lies very close to ν_2. We cannot observe $2\nu_3$, but the ^{37}Cl shift on it of $\sim 6\ \mathrm{cm}^{-1}$ would undoubtedly cause a displacement of ν_2 to lower frequencies in $^{12}CH_2{}^{35}Cl^{37}Cl$, the unperturbed ^{37}Cl shift on which should be zero. Although splitting of some of the Q branches is observed in ν_2, notably $^PQ_5$, $^PQ_6$, $^PQ_7$ (see Fig. 3), it does not seem to be consistent with structure from $^{12}CH_2{}^{35}Cl^{37}Cl$. Even if it is, the downward displacement is small ($<0.2\ \mathrm{cm}^{-1}$) which implies a very small resonance parameter. In CD_2Cl_2, $\nu_4+\nu_9$ lies very close to ν_8 and is much more intense than in CH_2Cl_2

species. Intensity borrowing through a resonance is suspected, but even here the vibrational effect is small, the value of x_{49} changing from -0.8 cm^{-1} in $^{12}CH_2Cl_2$ (where the levels are well separated), to only $+1.3$ cm^{-1} in $^{12}CD_2Cl_2$. Effects of the major resonance expected between the symmetric CH$_2$ stretch, ν_1, and the overtone of the CH$_2$ deformation, $2\nu_2$, are small though probably present, since $2\nu_2$ is considerably more intense than ν_2. The reason for this derives from the separation of the two levels by ~ 140 cm^{-1} rather than from a very small resonance parameter, as will be shown in the following section.

Second, the effects of Fermi resonance on the CH and CD overtone regions can be tested directly from the data of Tables I and II. In CH_2Cl_2 species, ν_6, ν_2, $\nu_2 + \nu_6$, and $2\nu_2 + \nu_6$ are known accurately, but only the last can be in Fermi resonance with $\nu_1 + \nu_6$. If resonance is truly of second-order importance, the values of ν_6, ν_2, x_{22} derived from $2\nu_2$, and x_{26} derived from $\nu_2 + \nu_6$ should yield $2\nu_2 + \nu_6$. A discrepancy of 2 cm^{-1} is observed. The situation in CD_2Cl_2 is even better. Here, both $\nu_1 + \nu_6$, $2\nu_2 + \nu_6$ and $2\nu_1$, $\nu_1 + 2\nu_2$ are known accurately. Similar calculations reveal discrepancies of 2 and 3 cm^{-1}, respectively. These resonances are treated explicitly in the following section, but the small magnitude of these misfits show how nearly these methylene chloride species behave as vibrationally unperturbed molecules in the region below 6200 cm^{-1}.

6. VIBRATIONAL RESONANCES IN THE CH$_2$ AND CD$_2$ OVERTONE REGIONS

Figure 4 shows the regions in question for all three isotopic species. All five bands expected can be observed in each case, but particularly clearly in the CD_2Cl_2 spectrum.

The resonating levels available for analysis in CH_2Cl_2 species are the ν_1, $2\nu_2$ diad and the pentad $2\nu_6$, $\nu_1 + \nu_6$, $2\nu_2 + \nu_6$, $2\nu_1$, $\nu_1 + 2\nu_2$. For CD_2Cl_2, to these can be added the diad $\nu_1 + \nu_2$, $3\nu_2$, of which the former is observed. Along with the fundamentals ν_2 and ν_6 and the combination level $\nu_2 + \nu_6$, the data for each isotopic species should be analyzable in terms of the parameters ν_1, ν_2, ν_6, x_{11}, x_{22}, x_{66}, x_{12}, x_{16}, x_{26}, and k_{122}, according to the scheme:

$$[\nu_6]$$

$$[\nu_2]$$

$$[\nu_2 + \nu_6 + x_{26}]$$

$$\begin{bmatrix} \nu_1 & k_{122}/2 \\ k_{122}/2 & 2\nu_2 + 2x_{22} \end{bmatrix}$$

$$\begin{bmatrix} \nu_1 + \nu_6 + x_{16} & k_{122}/2 \\ k_{122}/2 & \nu_6 + 2\nu_2 + 2x_{22} + 2x_{26} \end{bmatrix}$$

$$\begin{bmatrix} 2\nu_6 + 2x_{66} & 0 & 0 & 0 \\ 0 & 2\nu_1 + 2x_{11} & k_{122}/(2)^{1/2} & 0 \\ 0 & k_{122}/(2)^{1/2} & \nu_1 + 2\nu_2 + 2x_{22} + 2x_{12} & (3/2)^{1/2}k_{122} \\ 0 & 0 & (3/2)^{1/2}k_{122} & 4\nu_2 + 12x_{22} \end{bmatrix}.$$

TABLE VII

Vibrational Anharmonicity (x_{ij}) Constants (in cm^{-1}) for Isotopic Methylene Chlorides

i	j	$^{12}CH_2{}^{35}Cl_2$	$^{13}CH_2{}^{35}Cl_2$	$^{12}CD_2{}^{35}Cl_2$
1	1	-42.7	-42.8	-16.1
1	2	-	-	-0.5
1	3	-	-	-1.2
1	4	-	-	-8.2
1	6	-117.2	-117.6	-59.7
1	8	-0.5	-0.8	-
1	9	-2.5	-2.9	+1.1
2	2	-8.2	-8.4	-5.7
2	6	-23.1	-22.6	-12.6
2	7	-14.0	-13.6	-9.8
2	8	-3.0	-3.4	-2.5
2	9	-5.8	-5.8	-
3	3	-	-	-6.4
3	8	+2.9	+2.8	+1.4
3	9	-2.1	-2.5	-2.3
4	8	-0.4	-0.5	+2.0
4	9	-0.8	-1.0	+1.3
5	6	-4.9	-5.2	-1.0
5	7	+8.9	+9.1	+5
5	8	-5.7	-5.8	-
6	6	-19.5	-19.3	-16.5
6	7	-6.7	-6.7	-1.7
8	8	-5.1	-4.9	-
9	9	-	-	-10.3

In the case of CD_2Cl_2, the diad

$$\begin{bmatrix} \nu_1 + \nu_2 + x_{12} & 3^{1/2}k_{122}/2 \\ 3^{1/2}k_{122}/2 & 3\nu_2 + 6x_{22} \end{bmatrix}$$

can also be included. The results of diagonalizing these matrices are given in Table VIIIB, where they can be compared with the results in the absence of explicit treatment of the k_{122} resonance, shown in Table VIIIA. Small changes to the relevant anharmonicity constants occur, resonance parameters of $|k_{122}| = 32.5$, 34.0, and 22.7 cm^{-1} for $^{12}CH_2{}^{35}Cl_2$, $^{13}CH_2{}^{35}Cl_2$, $^{12}CD_2{}^{35}Cl_2$ are determined, and enable almost perfect reproduction of all observed data. The resonance parameters are considered reliable to within about 10%.

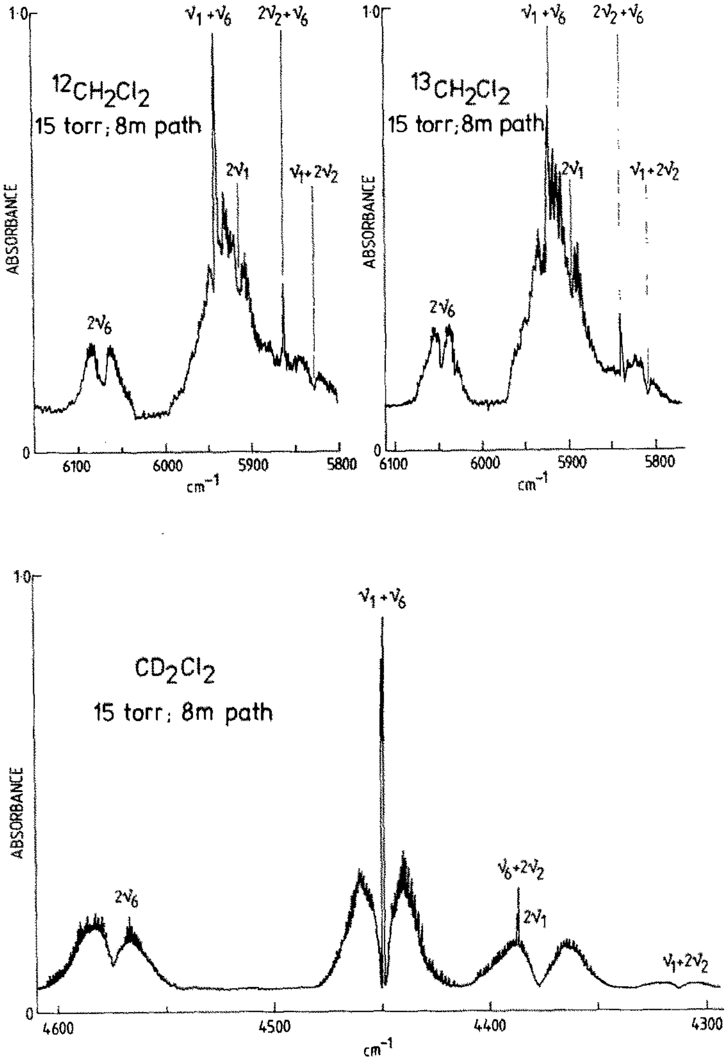

FIG. 4. The CH and CD overtone regions of $^{12}CH_2Cl_2$, $^{13}CH_2Cl_2$, and $^{12}CD_2Cl_2$ at a resolution of ca. 0.1 cm^{-1}.

A careful study of the anharmonicity constants for the CH stretching modes, x_{11} and x_{66}, in either of Table VII or VIII reveals the almost certain presence of Darling–Dennison resonance between the CH_2 stretching overtones, $2\nu_1$ and $2\nu_6$, through the quartic parameter k_{1166}. Whereas the values of x_{11} and x_{66} for CD_2Cl_2 remain approximately equal in both sets of constants, they are very unequal for CH_2Cl_2 species, x_{11} apparently being more than twice the magnitude of x_{66}. This seems quite unreasonable, and can be qualitatively ascribed to the effect of the resonance between $2\nu_6$ and $2\nu_1$, pushing $2\nu_6$ to higher and $2\nu_1$ to lower frequencies, the effect in CD_2Cl_2 being

TABLE VIII

CH_2 and CD_2 Stretching and Deformation Vibration Frequencies and Anharmonicity Constants (in cm^{-1}) for Methylene Chloride: (A) with no Fermi Resonance, and (B) with Fermi Resonance (k_{122}) Included[a] (Values in Parentheses are Those with Darling–Dennison Resonance (k_{1166}) Also Included)[b]

		$^{12}CH_2{}^{35}Cl_2$	$^{13}CH_2{}^{35}Cl_2$	$^{12}CD_2{}^{35}Cl_2$
A	ν_1	2997.66	2991.26	2205.65
	ν_2	1435.0	1431.1	1060.81
	ν_6	3055.0	3043.3	2303.72
	x_{11}	-42.7 (-30.0)	-42.8 (-28.8)	-16.1 (-13.8)
	x_{12}	-12.1	-11.8	-0.5
	x_{16}	-117.2	-117.6	-59.7
	x_{22}	-8.2	-8.4	-5.7
	x_{26}	-23.1	-22.6	-12.6
	x_{66}	-19.5 (-32.2)	-19.3 (-33.3)	-16.5 (-18.8)
	k_{1166}	-117.2	-117.6	-59.7
B	$\nu_1{}^*$	2995.80	2989.25	2204.27
	ν_2	1435.0	1431.1	1061.00
	ν_6	3055.0	3043.3	2303.83
	$x_{11}{}^*$	-43.0 (-29.7)	-44.4 (-29.9)	-16.8 (-14.4)
	$x_{12}{}^*$	-13.3 (-13.7)	-13.0 (-13.5)	-2.7 (-2.7)
	$x_{16}{}^*$	-119.0	-119.6	-60.5
	$x_{22}{}^*$	-7.3	-7.4	-5.3
	x_{26}	-23.1	-22.6	-13.1
	x_{66}	-19.5 (-32.4)	-19.3 (-33.4)	-16.6 (-19.0)
	k_{122}	32.5 (32.5)	34.0 (34.0)	22.7 (22.8)
	k_{1166}	-119.0	-119.6	-60.5

[a] Asterisked parameters take effective values consistent with explicit treatment of the k_{122} Fermi resonance.

[b] $k_{1166} = x_{16}$ is assumed, as observed to be obeyed closely in XH_2 systems. See text.

less marked due to the smaller resonance parameter. No quantitative treatment can be attempted without some measure of the magnitude of the resonance parameter k_{1166}. Examination of data available for simple XH_2 molecules (*8*) reveals that k_{1166} is very similar to the anharmonicity constant x_{16} in absolute magnitude. For example, for H_2O the corresponding constants are $x_{13} = -165.8$, $k_{1133} = -155.0\ cm^{-1}$; for H_2S, $x_{13} = -94.7$, $k_{1133} = -91.4\ cm^{-1}$; for H_2Se, $x_{13} = -84.9$, $k_{1133} = -83.2\ cm^{-1}$. By constraining $k_{1166} = x_{16}$, and including the Darling-Dennison parameter $k_{1166}/2$ linking $2\nu_6$ and $2\nu_1$ in our refinements, we obtain the anharmonicity constants in parentheses in Table VIII, all other constants remaining unchanged. The effect in CH_2Cl_2 species

TABLE IX

Comparison of XH_2 and XD_2 Stretching and Deformation Anharmonicity Constants (in cm^{-1}) for Water and Methylene Chloride

	H_2O	D_2O		CH_2Cl_2	CD_2Cl_2
x_{11}	-42.6	-22.6	x_{11}	-30.0	-16.1
x_{12}	-15.9	-7.6	x_{12}	-12.1	-0.5
x_{13}	-165.8	-87.1	x_{16}	-117.2	-59.7
x_{22}	-16.8	-9.2	x_{22}	-8.2	-5.7
x_{23}	-20.3	-10.6	x_{26}	-23.1	-12.6
x_{33}	-47.6	-26.1	x_{66}	-32.2	-16.5
k_{1133}	-155.0	-	k_{1166}	-117.2[a]	-

[a] Constrained to equal x_{16}.

is dramatic, making x_{11} and x_{66} much more nearly equal; in CD_2Cl_2 the effect (if applicable), is to make the constants somewhat less equal than they were in the absence of the resonance. In all cases, x_{66} is slightly larger than x_{11}, as found for water.

A recent simple model for XH_2 systems, developed by Mills and Robiette (*9*) in a study of local mode and normal mode vibrational behavior in molecules, predicts for the XH_2 stretching vibrations that $x_{11} = x_{66} = x_{16}/4 = k_{1166}/4$ (numbering as for CH_2Cl_2). As can be seen in Table VIII, for CH_2Cl_2 the first three relations are closely obeyed when the Darling–Dennison constant k_{1166} is constrained to equal x_{16}. For this reason we consider that the parenthesized CH_2 stretching anharmonicity constants in Table VIII are the most physically realistic empirical values for methylene chloride.

Comparison of the anharmonicity constants in Table VIII with the well-established values for H_2O and D_2O reveals a remarkable isotopic correspondence. For water, all D_2O anharmonicity constants x_{ij} are almost precisely one half of their H_2O values (*10*). In Table VIII, either set of constants including the Darling–Dennison resonance are seen to bear a remarkably similar correspondence with the apparent sole exception of x_{12}. Direct comparison of the corresponding anharmonicity constants for H_2O, D_2O and CH_2Cl_2, CD_2Cl_2 is made in Table IX, the values given being based on equivalent molecular models, with Darling–Dennison resonance treated explicitly in the H_2 species, but not included in the D_2 species. We consider that a knowledge of such apparently simple relationships should prove useful to the advancement of our understanding of vibrational anharmonicity in polyatomic systems, and of the nature of molecular motions in multiply excited vibrations.

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