

## ARTICLE

# Coupling Among CH Stretching, Bending and Rocking Vibrational Modes in CH<sub>2</sub>Cl<sub>2</sub>

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Infrared absorption spectra of gaseous CH<sub>2</sub>Cl<sub>2</sub> in the regions of 1200–12000 cm<sup>-1</sup> were measured using a Bruker IFS 120HR Fourier transform spectrometer in conjunction with a multipass cell. 47 vibrational levels of overtone and combinational spectral lines of the CH stretching ( $\nu_1$ ,  $\nu_6$ ), bending ( $\nu_2$ ), and rocking ( $\nu_8$ ) modes were analyzed and assigned. Utilizing the normal mode model and considering the coupling among CH stretching, bending and rocking vibrations, values of the harmonic frequency  $\omega_i$ , the anharmonic constant  $x_{ij}$ , and the coefficients of Fermi and the Darling-Dennison resonances of  $\nu_1$ ,  $\nu_6$ ,  $\nu_2$  and  $\nu_8$  modes were also determined from experimental spectral data with nonlinear least-square fitting. These spectral constants reproduced the experimental levels very well. These results showed that Fermi resonance between CH stretching and rocking vibrations ( $k_{188} = -254.63$  cm<sup>-1</sup>) is stronger than that between CH stretching and bending vibrations ( $k_{122} = 54.87$  cm<sup>-1</sup>); and that Darling-Dennison resonances between CH stretching and bending vibrations ( $k_{1166} = -215.28$  cm<sup>-1</sup>) is also much stronger than that between CH bending and rocking vibrations ( $k_{2288} = -5.72$  cm<sup>-1</sup>).

**Key words:** Normal model, Darling-Dennison resonance, Fermi resonance

## I. INTRODUCTION

Even though both XH<sub>2</sub>Y<sub>2</sub> (X=C, Si, Y=F, Cl, Br, I) and H<sub>2</sub>X (X=O, S, Se etc.) molecules possess the C<sub>2v</sub>-symmetry, they differ on that XH<sub>2</sub>Y<sub>2</sub> has XH vibrational modes besides the XH stretching and bending vibrations. By investigating the effect of these vibrational modes on the XH stretching and bending vibrations, more precise potential energy surfaces and vibrational wave functions of these molecules can be obtained, so as to their dipole moments and vibrational intensities. Previous studies on these type of molecules mostly focused on the XH symmetric stretching mode  $\nu_1$ , the antisymmetric stretching mode  $\nu_6$  and the coupling between the XH stretching mode  $\nu_1$  and the bending mode  $\nu_2$  [1–4]. In those studies, the “frozen core” model [5], which regards XY<sub>2</sub> as a atom based on the mass difference between H atom and Y atom, was adopted. Amos *et al.* [6] went further to study the effects of the rocking motion of the CH<sub>2</sub> ( $\nu_8$ ) on the stretching and bending vibrations of CH bond in CH<sub>2</sub>F<sub>2</sub> molecule, combining with an *ab initio* theoretical calculations. However, because experimental data for CH<sub>2</sub>F<sub>2</sub> only contained overtones and combinations with the vibrational quantum number  $V$  less than 2, precise spectral parameters used to describe the intercoupling among the rocking vibration ( $\nu_8$ ) and  $\nu_1$ ,  $\nu_2$ ,  $\nu_6$  cannot be obtained. In order to reduce the complexity of the spectra of the methane type molecules, we chose the weightier atom Cl over the F atom, and we studied the vibrational states of CH<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> molecule in this work.

CH<sub>2</sub>Cl<sub>2</sub> is an important chemical reagent, its spectra have been investigated since the 1930s. Earlier works concerned mainly on recording and analysing the fundamental vibrations of CH<sub>2</sub>Cl<sub>2</sub>. Molecular force field method was employed in calculating the vibrational fundamentals of CH<sub>2</sub>Cl<sub>2</sub>, and the results were compared with experimental data. Shimanouchi *et al.* recorded the CH<sub>2</sub>Cl<sub>2</sub> fundamentals data and proposed a vibrational model [7, 8], which provided a remarkable reference for the subsequent researches. Duncan *et al.* [9] measured and analyzed gaseous CH<sub>2</sub>Cl<sub>2</sub> infrared spectra below 6100 cm<sup>-1</sup>, and assigned most of the bands. Halonen *et al.* measured the higher overtones spectra of CH<sub>2</sub>Cl<sub>2</sub> and analyzed the CH stretching and bending vibrations, and they pointed out that CH stretching vibrations in CH<sub>2</sub>Cl<sub>2</sub> molecules have local mode nature at high vibrational excitation [1, 10].

In this paper, we report the CH vibration spectra of gaseous CH<sub>2</sub>Cl<sub>2</sub> in the infrared and near infrared using a Fourier transform spectrometer (FTS) in conjunction with a 100 m multipass cell. The overtones and combinations of CH rocking ( $\nu_8$ ), stretching ( $\nu_1$ ,  $\nu_6$ ) and bending ( $\nu_2$ ) vibrations were assigned. Based on the fact that the vibration bands with close energies and the same symmetries interact each other, the Hamiltonian matrices used to calculate the above vibrations contain not only the vibrational anharmonic terms, but also the Fermi resonance and Darling-Dennison resonance terms. The anharmonic constants and coefficients of Fermi and Darling-Dennison resonances were obtained using nonlinear least-square fitting with the above Hamiltonian. The vibrational energy levels calculated with the above parameters agreed well with the experimental data.

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TABLE I Experimental conditions used to record the absorption spectrum of  $\text{CH}_2\text{Cl}_2$ 

Region / $\text{cm}^{-1}$	Gas pressure/Pa	Detector	Absorption length/m	Beamsplitter	Source
1200–6000	130	InSb	15	$\text{CaF}_2$	Globar
1200–6000	400/130	MCT	15	$\text{CaF}_2$	Globar
5500–10000	967/2157/6931	Ge-Diode	105	$\text{CaF}_2$	Tungsten
8800–12000	9129	Si Diode	105	Quartz	Tungsten

## II. EXPERIMENTAL

The purity of  $\text{CH}_2\text{Cl}_2$  gas is better than 99.5%. Absorption spectra of  $\text{CH}_2\text{Cl}_2$  gas were obtained with the FTS Bruker HR-120 equipped with a multipass cell. The spectral data in the regions of 1200–12000  $\text{cm}^{-1}$  covers CH overtone transitions with quantum number  $V=1-4$ . As shown in Fig.1, gas samples were filled in the multipass cell with a base length of 1.5 m. According to the Beer's law, absorptivity can be noticeably increased by increasing the light absorption pass length. Therefore, the detection sensitivity can be effectively improved by use of an adjustable multipass cell with the maximum path length is 105 m. In experiment, the following factors need to be considered: (i) in the wide range of spectra, absorption intensities decrease with the increase of vibrational quantum number; (ii) the overtone intensity is usually larger than that of the combination; (iii) the vibrational bands of different quantum number appear in same spectral region. Therefore, different experimental conditions were used for recording different vibrational spectra to the effect that every vibrational band has high signal-to-noise

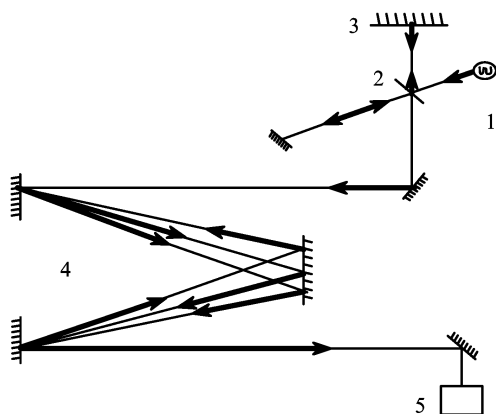


FIG. 1 Optical configuration of Bruker IFS 120HR FTIR spectrometer and multipass cell. 1: Sources; 2: Beamsplitter; 3: Scanning mirror; 4: Multipass cell

ratio (SNR), which means that the strong peaks are not saturated while the weak absorption features have enough intensity. In experiments, the vibrational bands with high SNR are obtained through changing the light absorption length and the pressure of samples, and the parameters are listed in Table I. The interferograms were recorded employing the interleaved rapid-scan method implemented with the FTS Bruker HR-120. The electronic filter was used to reduce noise. The Mertz mode was employed for manipulation of phase

correction. The Blackman-Harris-3-Term was adopted as apodization function in FTS. The resolution of all spectra is 0.2  $\text{cm}^{-1}$ . A part of gas phase infrared absorption spectra for  $\text{CH}_2\text{Cl}_2$  is showed in Fig.2.

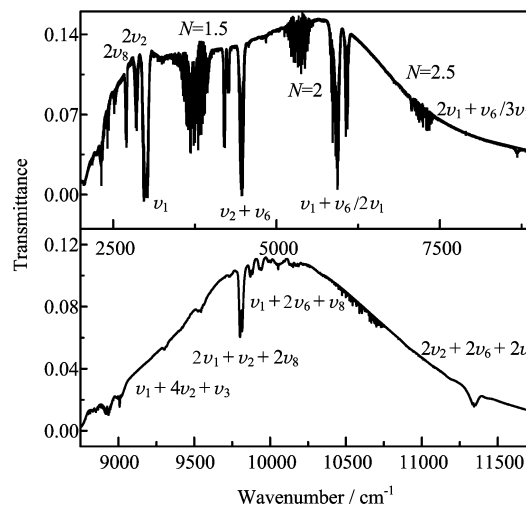


FIG. 2 Part of the infrared absorption spectrum of  $\text{CH}_2\text{Cl}_2$

## III. VIBRATIONAL SPECTRAL ASSIGNMENT

The overtone and combination energy levels of the CH vibrations are not the direct sum of the fundamental levels due to the anharmonicity of the vibrations and the interactions between the vibrational states. Hence, besides vibrational energies, absorption intensities of the vibrational states, band contours and symmetries should be simultaneously considered when the vibrational states are assigned.  $\text{CH}_2\text{Cl}_2$  molecule is an asymmetric top with  $C_{2v}$ -symmetry. Its dipole moment components at the three principal axes are non-zero. When the dipole moment varies along the principal inertia axes, the bands of A, B and C-type with  $B_2$ ,  $A_1$  and  $B_1$  symmetries, respectively, are produced. The nine vibrational modes and their fundamentals [5, 11, 12] of  $\text{CH}_2\text{Cl}_2$  are listed in Table II. Because the nine vibrational modes are all non-degenerate, the symmetries of the overtones and combinations energy levels can be obtained using symmetrical direct products of the normal modes. Therefore, we can determine the symmetries of the vibrational states on the basis of the experimental band types and assign them according to the energy levels positions. For example, the band contour of the vibrational band around 4267  $\text{cm}^{-1}$ , shown in

TABLE II Vibrational modes and fundamental frequencies of CH<sub>2</sub>Cl<sub>2</sub>

Vibrational modes	Symmetry	Fundamental frequency/cm <sup>-1</sup>
$\nu_1$ CH symmetric stretching vibration	A <sub>1</sub>	2997.66
$\nu_2$ CH <sub>2</sub> bending vibration	A <sub>1</sub>	1434.15
$\nu_3$ CCl symmetric stretching vibration	A <sub>1</sub>	712.9 [5, 11]
$\nu_4$ CCl <sub>2</sub> bending vibration	A <sub>1</sub>	281.5 [5, 11]
$\nu_5$ torsional vibration	A <sub>2</sub>	1153 [12] (inactive)
$\nu_6$ CH symmetric stretching vibration	B <sub>1</sub>	3055 [11]
$\nu_7$ CH <sub>2</sub> rocking vibration	B <sub>1</sub>	898.66 [4, 11]
$\nu_8$ CH <sub>2</sub> wagging vibration	B <sub>2</sub>	1268.86 [5, 11]
$\nu_9$ CCl symmetric stretching vibration	B <sub>2</sub>	759.82 [5, 11]

Fig.3(a), appears to be of a A-type, and is the same as that of the fundamental  $\nu_8$ ; therefore, this band has B<sub>2</sub>-symmetry, and must contain  $\nu_8$ , and the quantum number of  $\nu_8$  must be odd (to permit the B<sub>2</sub> symmetry). According to the energy level, this band is assigned as  $\nu_1+\nu_8$ . For another example, the vibrational band around 4467cm<sup>-1</sup> shown in Fig.3(a) is a C-type band. Because the symmetrical direct product of  $\nu_6$  and  $\nu_2$  is B<sub>1</sub>, which corresponds to a C-type band; furthermore, the energy level of  $\nu_6+\nu_2$  is about 4467 cm<sup>-1</sup>, thus the C-type band at 4467 cm<sup>-1</sup> is assigned as  $\nu_6+\nu_2$ . The assignments of these two bands are labeled in Fig.3(a), respectively. At higher vibrational energy region, the band types mentioned above should appear periodically. All of them are assigned and marked in Fig.3(b) and Fig.3(c) according to their energy, symmetry, and intensity.

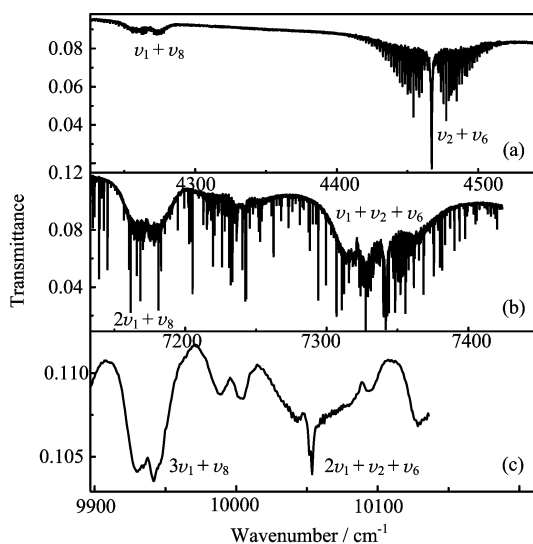


FIG. 3 Combination bands of the CH stretching with either bending  $\nu_2$  or the rocking  $\nu_8$  modes. a. 130 Pa, b. 2157 Pa, c. 9192 Pa.

According to Table II, the four vibrational modes, namely,  $\nu_1$ ,  $\nu_2$ ,  $\nu_6$ , and  $\nu_8$  possess higher fundamental frequencies, and their frequencies satisfy the following relation:  $\nu_1 \approx \nu_6 \approx 2\nu_2 \approx 2\nu_8$ . A Polyad number  $N$  is defined as  $N = n_1 + n_6 + (n_2 + n_8)/2$ , where  $n_i$  is vibrational quantum number of mode  $\nu_i$ . The energy levels with

the same  $N$  are close to each other, and the spectra related to the transitions of these energy levels are relatively congested. The overtones and combinations of other vibrational modes also congest in other spectral regions with lower fundamental frequencies and weak overtone absorptions compared with the stronger vibrations of C–H. Thus in the spectrogram we obtained, the stronger bands connect mostly with above four types of CH vibrational modes. Because of the spectra bands congestion in different parts, the  $N$  number is helpful to assignment of the spectra.

Similar to other studies [13], vibration intensity of the fundamental  $\nu_6$  (3055 cm<sup>-1</sup>) obtained by us is quite weak and overlapped with intense  $\nu_1$ . Therefore, for  $\nu_6$  the gaseous Raman spectra data [12] were adopted in this work. Based on the above considerations, the location and assignment of CH vibration have been determined, and then fitted with the vibration Hamiltonian.

#### IV. THEORETICAL MODELS

Because vibrational states with close energy levels and the same symmetries will couple with each other. Therefore, the harmonic oscillators approximation of the molecular vibrations can not fully describe the real vibrational energy levels. The normal vibration theory of molecular spectrum reveals that the higher order terms in the vibration Hamiltonian includes intercoupling among the vibrational states. Both the frequencies of  $\nu_2$  and  $\nu_8$  approach to half of  $\nu_1$  as in Table II, and besides,  $2\nu_2$  and  $2\nu_8$  have the same symmetry as  $\nu_1$ . Therefore,  $\nu_2$  and  $\nu_8$  will intercouple respectively with  $\nu_1$  through the cubic terms  $q_1 q_2^2$  and  $q_1 q_8^2$  in the expression of the potential energy ( $q$  is the normal coordinates). This kind of intercoupling is termed Fermi resonance [14]. Similarly, frequencies of  $\nu_2$  and  $\nu_1$  approach respectively to those of  $\nu_8$  and  $\nu_6$ , furthermore,  $2\nu_2$ ,  $2\nu_8$ ,  $2\nu_1$  and  $2\nu_6$  have the same symmetries (A<sub>1</sub>), so  $2\nu_2$  and  $2\nu_1$  will intercouple respectively with  $2\nu_8$  and  $2\nu_6$  through the quartic terms  $q_2^2 q_8^2$  and  $q_1^2 q_6^2$  in the expression of the potential energy. This intercoupling is called Darling-Dennison resonance [15]. As in Table II, the fundamental frequency of CCl bond is much smaller than that of CH, there is no obvious feature of coupling between CCl and CH modes, so the influence of CCl vibration on CH vibration was neglected in the

TABLE III Observed and calculated band centers results of the CH vibrational overtone and combination

Obs/cm <sup>-1</sup>	$\Gamma$	Assignment	(Cal-Obs)/cm <sup>-1</sup>	Obs/cm <sup>-1</sup>	$\Gamma$	Assignment	(Cal-Obs)/cm <sup>-1</sup>
1269.06	B <sub>2</sub>	$\nu_8$	1.94	7466.72	A <sub>1</sub>	$2\nu_6+\nu_2$	-1.72
1434.15	A <sub>1</sub>	$\nu_2$	-0.15	8189.74	A <sub>1</sub>	$4\nu_2+2\nu_8$	1.26
2526.58	A <sub>1</sub>	$2\nu_8$	-2.58	8307.66	A <sub>1</sub>	$\nu_1+2\nu_2+2\nu_8$	-3.66
2700.95	B <sub>2</sub>	$\nu_2+\nu_8$	-0.95	8339.48	B <sub>1</sub>	$\nu_6+2\nu_2+2\nu_8$	0.52
2853.66	A <sub>1</sub>	$2\nu_2$	0.34	8586.09	A <sub>1</sub>	$4\nu_2+\nu_1$	2.91
2997.33	A <sub>1</sub>	$\nu_1$	2.67	8602.40	B <sub>1</sub>	$4\nu_2+\nu_6$	-1.40
3055	B <sub>1</sub>	$\nu_6$	0.00	8679.68	A <sub>1</sub>	$3\nu_1$	-0.68
4116.86	B <sub>2</sub>	$2\nu_2+\nu_8$	1.14	8683.93	B <sub>1</sub>	$2\nu_1+\nu_6$	0.07
4267.23	B <sub>2</sub>	$\nu_1+\nu_8$	3.77	8742.24	A <sub>1</sub>	$2\nu_1+2\nu_2$	1.76
4467.05	B <sub>1</sub>	$\nu_2+\nu_6$	-1.05	8752.12	B <sub>1</sub>	$\nu_1+2\nu_2+\nu_6$	1.88
5520.41	A <sub>1</sub>	$2\nu_8+\nu_1$	3.59	8840.35	A <sub>1</sub>	$2\nu_6+2\nu_2$	-3.35
5557.45	B <sub>1</sub>	$2\nu_8+\nu_6$	-3.45	8925.55	A <sub>1</sub>	$\nu_1+2\nu_6$	-2.55
5683.53	B <sub>2</sub>	$\nu_1+\nu_2+\nu_8$	-5.53	9008.37	B <sub>1</sub>	$3\nu_6$	0.63
5827.14	A <sub>1</sub>	$2\nu_2+\nu_1$	-4.14	9418.99	B <sub>2</sub>	$\nu_1+2\nu_2+3\nu_8$	-2.99
5860.03	B <sub>1</sub>	$2\nu_2+\nu_6$	-1.03	9535.08	A <sub>1</sub>	$\nu_1+3\nu_2+2\nu_8$	-1.08
5910.84	A <sub>1</sub>	$2\nu_1$	-2.84	9545.65	B <sub>1</sub>	$\nu_6+3\nu_2+2\nu_8$	2.35
5935.12	B <sub>1</sub>	$\nu_1+\nu_6$	1.88	9810.37	A <sub>1</sub>	$2\nu_1+\nu_2+2\nu_8$	5.63
6071.96	A <sub>1</sub>	$2\nu_6$	2.04	9878.55	A <sub>1</sub>	$2\nu_6+\nu_2+2\nu_8$	-2.55
6958.70	B <sub>1</sub>	$2\nu_8+\nu_2+\nu_6$	4.30	9937.67	B <sub>2</sub>	$2\nu_6+2\nu_2+\nu_8$	4.33
7071.19	B <sub>2</sub>	$2\nu_2+\nu_1+\nu_8$	-1.19	9997.34	A <sub>1</sub>	$3\nu_1+\nu_2$	-5.34
7167.32	B <sub>2</sub>	$2\nu_1+\nu_8$	-0.32	10047.80	B <sub>2</sub>	$\nu_1+2\nu_6+\nu_8$	7.20
7236.51	B <sub>1</sub>	$3\nu_2+\nu_6$	1.49	11340.22	A <sub>1</sub>	$2\nu_6+2\nu_2+2\nu_8$	-0.22
7321.20	A <sub>1</sub>	$2\nu_1+\nu_2$	-1.20				
7341.56	B <sub>1</sub>	$\nu_1+\nu_2+\nu_6$	0.44				

Note: Root mean-square of the fitting residual  $\sigma=2.49$  cm<sup>-1</sup>

molecular vibration Hamiltonian. The wavefunctions  $|v_i v_j v_l v_m\rangle$  ( $i, j, l, m=1, 2, 6, 8$  and  $i \neq j \neq l \neq m$ ), which is in the form of product of singly excited harmonic oscillator function, are taken as the basis functions. The vibrational Hamiltonian  $H$  can be obtained from the perturbation theory, and the non-zero matrix elements of it are as below (in wavenumber units): The diagonal matrix elements:

$$H^0 = \sum_{i=1,2,6,8} \omega_i (v_i + \frac{1}{2}) + \sum_{i=1,2,6,8} \sum_{j \geq i} x_{ij} (v_i + \frac{1}{2})(v_j + \frac{1}{2}) \quad (1)$$

The off-diagonal elements including Fermi resonance terms:

$$H_{v_1, v_2; v_1-1, v_2+2}^F = \frac{k_{122}}{2} [v_1(v_2+1)(v_2+2)/2]^{\frac{1}{2}} \quad (2)$$

$$H_{v_1, v_8; v_1-1, v_8+2}^F = \frac{k_{188}}{2} [v_1(v_8+1)(v_8+2)/2]^{\frac{1}{2}} \quad (3)$$

The off-diagonal elements including Darling-Dennison resonance terms:

$$H_{v_1, v_6; v_1-2, v_6+2}^{DD} = \frac{k_{1166}}{4} [(v_6+1)(v_6+2)v_1(v_1-1)/2]^{\frac{1}{2}} \quad (4)$$

$$H_{v_2, v_8; v_2-2, v_8+2}^{DD} = \frac{k_{2288}}{4} [(v_8+1)(v_8+2)v_2(v_2-1)/2]^{\frac{1}{2}} \quad (5)$$

where  $\omega_i$  is the harmonic vibration frequency,  $x_{ij}$  is the anharmonic constant,  $v$  the vibration quantum number,  $k_{122}$  and  $k_{188}$  are the Fermi resonance coefficients between  $\nu_1$  and  $2\nu_2$ ,  $\nu_1$  and  $2\nu_8$  respectively,  $k_{1166}$  and  $k_{2288}$  are the Darling-Dennison resonance coefficients between  $\nu_1$  and  $\nu_6$ ,  $\nu_2$  and  $\nu_8$ , respectively. With the zero point level energy is subtracted from the diagonal element, the Hamiltonian matrix is diagonalized to give the eigenvalues. Then the spectroscopic constants  $\omega_i$ ,  $x_{ij}$ ,  $k_{122}$ ,  $k_{188}$ ,  $k_{1166}$  and  $k_{2288}$  are deduced by fitting the eigenvalues of Hamiltonian with the experimental vibrational band origins using Nelder-Mead method.

## V. RESULTS AND DISCUSSION

In this work, four CH vibrations with stronger interactions in CH<sub>2</sub>Cl<sub>2</sub> molecule have been studied. The optimizing directions are adjusted on the basis of the empirical relation:  $x_{11} \approx x_{66}$  [16] in the calculations. The observed CH vibrational band origins, the vibrational assignment with normal mode model, and the fits, are given in Table III and IV. Table III also gives a comparison between the observed and the calculated energy level positions, which clearly indicates that the present models reproduce the experimental levels well. The fitted potential energy surfaces parameters are classified into 3 types according to their properties: (i)  $k_{1166}$  is

TABLE IV Effective spectroscopic constants in  $\text{cm}^{-1}$ 

$\omega_1$	$\omega_2$	$\omega_6$	$\omega_8$	$x_{11}$	$x_{22}$
3134.22(24)	1467.11(35)	3226.74(41)	1313.92(73)	-34.23(19)	-4(70)
$x_{66}$	$x_{88}$	$x_{12}$	$x_{16}$	$x_{18}$	$x_{26}$
-35.46(19)	10.03(27)	-24.77(52)	-125.03(72)	-66.82(31)	-22.24(100)
$x_{28}$	$x_{68}$	$k_{122}$	$k_{1166}$	$k_{2288}$	$k_{188}$
4.19(41)	-55.01(39)	-54.87(26)	-215.28(72)	-5.72(23)	254.63(47)

Note: Uncertainties are given in parentheses

TABLE V Comparison of effective spectroscopic constants in  $\text{cm}^{-1}$  for three molecules with  $C_{2v}$  symmetry

	$\text{CH}_2\text{Cl}_2$	$\text{CH}_2\text{F}_2$ [6]	$\text{H}_2\text{O}$ [2, 17]
$\omega_1$	3134.22	3071.0	3693.8
$\omega_6$	3226.74	3140	
$\omega_2$	1467.11	1557.0	1614.5
$\omega_8$	1313.92	1464	
$k_{1166}$	-68.67	-119.0	168.8
$k_{122}$	11.62	160.1	95.9 [2, 17]
$k_{188}$	254.63	261.965	
$k_{2288}$	-5.72	-56.378	

used to depict the interaction between C–H stretching vibrations; (ii)  $k_{122}$  and  $k_{188}$  are employed to describe the interaction between stretching and bending, stretching and rocking vibrations, respectively; (iii)  $k_{2288}$  is used to depict the interaction between bending and rocking motions. Through the comparison of the results of  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_2\text{F}_2$  and  $\text{H}_2\text{O}$  molecules as shown in Table V, the following conclusions can be drawn:

(1) The  $k_{2288}$  of  $\text{CH}_2\text{F}_2$  is much larger than that of  $\text{CH}_2\text{Cl}_2$ , which indicates that the coupling between CH bending and rocking vibrations in  $\text{CH}_2\text{Cl}_2$  is weaker than that of  $\text{CH}_2\text{F}_2$ . In comparison with the stretching vibration, the coupling between these two types of molecules is relatively smaller. It is very instructive for the further studies, for example, the interaction terms depicted the coupling of bending ( $v_2$ ) and rocking ( $v_8$ ) vibrations can be reasonably approximated as an improved Hamiltonian is proposed.

(2) The Fermi resonance coefficient  $k_{122}$  of  $\text{CH}_2\text{Cl}_2$  is very small compared with that of  $\text{CH}_2\text{F}_2$  and  $\text{H}_2\text{O}$ , while the Darling-Dennison resonance coefficient  $k_{1166}$  is much larger. This indicates that the influence of bending vibration on stretching vibration in  $\text{CH}_2\text{Cl}_2$  is quite weak, but the coupling between the stretching vibrations is much stronger. This is just one of the reasons that the character of the local mode vibration in  $\text{CH}_2\text{Cl}_2$  molecule is more significant.

(3) Similar to those of  $\text{H}_2\text{O}$ , all four potential parameters  $k_{1166}$ ,  $k_{122}$ ,  $k_{188}$  and  $k_{2288}$  of  $\text{CH}_2\text{F}_2$  are much larger than those of  $\text{CH}_2\text{Cl}_2$ . Therefore, the coupling between the vibration modes of  $\text{CH}_2\text{F}_2$  is much stronger. This is why the spectra of  $\text{CH}_2\text{F}_2$  are so complicated.

To summarize from above discussions, spectra of

$\text{CH}_2\text{Cl}_2$  is more complicated as there are more vibrational degrees of freedom than those of  $\text{H}_2\text{O}$ , although both of them have the same  $C_{2v}$ -symmetry. Therefore, it is necessary to consider coupling of the rocking motion  $v_8$  in order to accurately calculate the vibrational spectra.

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