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Vibrational Anharmonicity and Harmonic Force Fields for Dichloromethane from Quantum-Chemical Calculations

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Anharmonic and related constants have been calculated for CH_2Cl_2, CD_2Cl_2, and $CHDCl_2$ by using the program Gaussian03 and B3LYP and MP2 models. Bases used were 6-311++G** and cc-pVTZ. The size of grid used in the B3LYP/6-311++G** model had a noticeable effect on resulting data. Features of the MP2/6-311++G** calculations suggested a deleterious effect of the absence of *f* functions in this basis set. The need for the replacement of second-order terms in the perturbation theory formulas for the vibrational anharmonic constants x_{ij} in the presence of Fermi resonance was explored, and minor resonances were found associated with the cubic constants ϕ_{122} and ϕ_{299} (d_0 isotopomer), ϕ_{122} and ϕ_{849} (d_2), and ϕ_{278} (d_1). Computed x_{ij} values for νCH and νCD motions agree quite well with earlier experimental data. Observed anharmonic frequencies, ν_{obsd}, were corrected to "observed" harmonic frequencies, ω_{obsd}, by using computed differences $\Delta = \omega_{\mathrm{QC}} - \nu_{\mathrm{QC}}$. These differences Δ are larger for the antisymmetric $\nu_{\mathrm{as}}CH_2$ mode than for symmetric $\nu_{\mathrm{s}}CH_2$ motion. This fact made it necessary to use differing scale factors for the two kinds of CH stretching force constants in a subsequent scaling of the harmonic force field to ν_{obsd}. Force field scaling was also carried out by refining to ω_{obsd}. In both approaches, the B3LYP models required differing scale factors for symmetric and antisymmetric CCl stretching force constants, indicating a failure to compute an accurate C−Cl stretch−stretch interaction force constant. The MP2/cc-pVTZ force field was preferred. Both scaled and unscaled harmonic force fields were used to calculate centrifugal distortion constants (CDCs) and contributions to the vibrational dependence of the rotational constants (alphas). Variations in the CDCs can, in part, be explained by the magnitudes of the frequencies used in the scaling process.

Introduction

The advent of quantum-chemical (QC) computer programs able to provide anharmonic vibrational data has greatly increased the possibilities for the analysis of vibrational spectra of small-to-medium-sized molecules. However, it remains true that only limited accuracy is obtained by the direct use of such programs merely to derive harmonic frequencies, if only readily accessible DFT or MP2 models are employed. In such circumstances, there is much merit in using such models to calculate anharmonicity constants x_{ij} and combining the latter with experimental anharmonic frequencies ν_{obsd} to obtain "observed" harmonic frequencies ω_{obsd},[1] where for mode *i*, we have $\omega_{i(\mathrm{obsd})} = \nu_{i(\mathrm{obsd})} + \Delta_i$ and $\Delta_i = -2x_{ii} - 0.5\sum x_{ij}$. The ω_{obsd} data obtained in this way can then be used to investigate and assess the quality of the harmonic force field yielded by the particular QC model employed. The usual procedure for achieving this objective involves scaling of the individual symmetry internal force constants. Such force-field scaling has in the past normally been carried out by fitting to observed anharmonic frequencies ν_{obsd}, with the result that the scale factors determined reflect the effects both of anharmonicity and of imperfections in the harmonic force field. However, the latter could be identified and studied separately if scaling were to be carried out instead by using ω_{obsd} data. A recent study of this kind involved calculations with B3LYP and MP2 models for the molecule difluorocyclopropane (DFCP) and its d_4 and d_2 isotopomers.[1]

A particular interest in the spectrum of the DFCP molecule was the apparent absence of significant Fermi resonances (FR) in the CH stretching region of the spectrum. When this simplification was combined with evidence indicating differing anharmonicity corrections Δ for the symmetric and antisymmetric CH stretching motions, the need became evident for differing scale factors for such motions if observed frequencies were to be fitted. It was also found in this work that fitting ω_{obsd} data was better achieved by MP2 calculations because of the smaller stretch/stretch interaction force constants yielded by this model, as compared with those from B3LYP calculations.

Dichloromethane (DCM) offers a favorable opportunity for extending this type of investigation, because (a) there is much precise experimental vibrational data available, including a large number of anharmonicity constants x_{ij} for the d_0 and d_2 species;[2−7] (b) the mid-infrared spectrum appears to be virtually free of perturbations such as FR (it has been described as that of an almost vibrationally unperturbed molecule);[2] and (c) both empirical[8,9] and low-level (HF/6-31G*) ab initio studies[10,11] have been made of the harmonic force field. In two of these studies,[8,10] force constants were refined to estimates of harmonic frequencies derived empirically through the use of Dennison's rules.[12] However, the reliability of such estimates of harmonic frequency needs careful scrutiny.

A further interest arising out of the above-mentioned DFCP study is the extent to which values of centrifugal distortion

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TABLE 1: Effect of Change of Grid Size on CH_2Cl_2 Harmonic Frequencies and Anharmonic Corrections Δ for the Model B3LYP/6-311++G Compared with the MP2/cc-pVTZ Model**

mode	ω_{dtz+}			ν_{dtz+}			$\Delta = \omega - \nu$			
	default	99302	ultrafine	default	99302	ultrafine	default	99302	ultrafine	mcct
1	3122.5	3121.7	3122.0	3003.1	3001.8	2998.2	119.4	119.9	123.9	122.4
2[a]	1457.0	1456.9	1457.0	1425.4	1422.8	1421.6	31.7	34.1	35.4	38.8
3	698.6	699.6	699.0	687.6	685.9	686.9	11.0	13.6	12.1	11.6
4	282.1	282.5	282.3	279.6	279.3	279.3	2.6	3.2	2.9	2.9
5	1178.0	1179.1	1179.5	1158.9	1155.4	1154.2	19.1	23.7	25.3	24.7
6	3201.3	3200.4	3200.7	3058.5	3058.4	3054.5	142.8	142.0	146.1	143.1
7	901.2	901.3	901.3	893.8	890.7	889.0	7.4	10.6	12.3	11.8
8	1301.9	1302.2	1302.6	1279.3	1276.7	1274.9	22.6	25.5	27.7	24.1
9	717.5	719.5	718.7	700.2	697.8	699.3	17.4	21.7	19.5	18.8

[a] 2,99 FR taken into account.

constants (CDCs) calculated from a particular QC model vary according to the method of calculation, that is, whether the force field used is unscaled or has been scaled in differing ways. Centrifugal distortion data for the ground state of DCM species were utilized by Duncan et al.[8,10] in the refinement of their empirical force field, but the current lack of information concerning the vibrational dependence of CDCs suggests a need for caution in their use for this purpose at the present time.

Yet another benefit to be gained from force field calculations is sets of vibration−rotation interaction alpha constants, which are needed inter alia if equilibrium-state rotational constants are to be determined and semi-experimental equilibrium geometries derived, as in recent studies.[13,14] Duncan has estimated the C−H and C−Cl equilibrium bond lengths in DCM, starting from a carefully determined r_z structure.[15]

Theoretical Section

MP2 and B3LYP calculations were performed by using the program Gaussian03 (G03).[16] Two types of basis set were employed: the Pople-type 6-311++G**[17] and the Dunning correlation-consistent set cc-pVTZ.[18,19] For convenience in the text and tables below, the following abbreviations are used: B3LYP/6-311++G** (dtz+), B3LYP/cc-pVTZ (dcct), MP2/6-311++G** (mtz+), and MP2/cc-pVTZ (mcct). Convergence in the prior geometry optimizations was controlled by the tight option.

In our initial studies with the two DFT models, a grid of 99 radial shells, each containing 302 angular points,[20] was employed, as in previous work from our laboratories.[1,21] However, a calculation performed accidentally with the G03 default grid settings (50 shells, 194 points)[20] revealed that whereas the harmonic frequencies were virtually unaffected by the change of grid, significant changes occurred in certain of the anharmonicity constants and hence of the anharmonic corrections Δ. This sensitivity might have been anticipated from an earlier theoretical study by Boese et al. of the quality of calculation needed to yield accurate DFT-based anharmonic force fields.[22] Their results indicated a need for a grid fineness far larger than that available from G03 if a precision of the order of 1 cm^{-1} was to be achieved.[22] However, our own test calculations with the dtz+ model, utilizing the largest grid fineness option available (ultrafine grid, ufg = 99 shells, 590 points[20]) and a comparison with results from the mcct model, suggested that the problem was not a major one, with uncertainties in Δ from this source unlikely to exceed 2−3 cm^{-1}.

Table 1 shows the changes in harmonic frequency ω_{QC} and anharmonicity correction $\Delta = \omega_{QC} - \nu_{QC}$ for CH_2Cl_2 from the dtz+ model with three of the grid sizes available from G03—default, fine (99,302), and ultrafine (99,590). These Δs are compared with those from the mcct model. Whereas the harmonic dtz+ frequencies all agree with each other to within about 1 cm^{-1}, values of Δ can vary by up to 6 cm^{-1}, as in the case of Δ_5. Values of ν_{QC} vary accordingly. With the exception of Δ_2, Δ_6, and Δ_8, the effect of increasing grid fineness is to lead to Δ values well within 3 cm^{-1} of those from the mcct model. We note that Δ increases uniformly with grid fineness only in five cases, Δ_1, Δ_2, Δ_5, Δ_7, and Δ_8. In other modes, both increases and decreases in Δ are found. The ufg option was used for all DFT calculations unless otherwise indicated.

We were careful to ensure that Cartesian coordinates derived from energy optimizations in G03 were transformed into the principal axis system before passing these coordinates to the vibration−rotation module.[1]

All G03 calculations were performed on a Beowulf computation cluster at Oberlin College or on PC-type computers.

For the calculation of harmonic force constants in a symmetry coordinate basis and subsequent scaling, the G03 output of Cartesian-based force constants was input into the program ASYM40.[23] Such calculations were performed first by using values of ν_{obsd}, corrected where appropriate for FR, and second on ω_{obsd}, where $\omega_{obsd} - \nu_{obsd} = \Delta_{QC}$, as given directly by the G03 calculation.[24] In such calculations, each x_{ii} or x_{ij} constant involves a series of terms, determined by second-order perturbation theory,[26] each of which involves a different cubic or quartic force constant ϕ_{ijk} or ϕ_{ijkl}, the former being multiplied by a function involving several frequencies ω_i.

In concluding this section, we note a limitation of the program ASYM40 through which scaling of the QC-based force fields is achieved. This program utilizes the Pulay procedure whereby each off-diagonal symmetry force constant is scaled by the geometric mean of the scale factors for the corresponding two diagonal force constants.[27] Despite theoretical support for such a procedure,[28] experimental evidence indicates its invalidity in certain cases. Thus, MP2 and B3LYP values of the νCH/νCH valence interaction force constants differ by a factor of 2 or more, where only a variation of the order of 10% can result from scaling to the mean of the factors for the diagonal CH stretching force constants.[1,29] In butadiene, there is evidence for a similar variation in the interaction constant between the stretchings of the two double bonds.[21] Other cases have been noted earlier.[30]

Fermi Resonance Assessment. The issue of FR arises from the presence within the second-order perturbation expressions for the anharmonicity constants x_{ii} and x_{ij} of terms involving $\phi^2_{iij}/(2\omega_i - \omega_j)$ and $\phi^2_{ijk}/(\omega_1 + \omega_j - \omega_k)$ that tend to become infinite in the event that $2\omega_i \approx \omega_k$ (type-one FR) or $\omega_i + \omega_j \approx \omega_k$ (type-2 FR), respectively. The remedy is to remove the offending term from the second-order expressions and thence

TABLE 2: Assessment of FR in CH_2Cl_2, CD_2Cl_2, and $CHDCl_2$ (cm^{-1})

FR	model[a]	$\lvert\phi_{ijk}\rvert$	$\delta\omega_{QC}$[b]	$\delta\nu_{dp}$[c]	FRtest[d]	$\nu^* - \nu$[e]	$\delta\nu_{FR}$[f]
				CH_2Cl_2			
1,22	dtz+	220.63	207.93	145.1	1.030	14.6	18.5
1,22	dcct	214.71	197.47	140.1	1.078	14.6	18.1
1,22	mtz+	225.55	211.41	147.5	1.070	15.0	19.0
1,22	mcct	204.67	189.78	131.1	1.003	13.8	17.5
2,99	dtz+	32.65	19.58	28.1	0.591	3.4	2.2
2,99	dcct	31.98	28.11	33.9	0.184	2.3	1.8
2,99	mtz+	27.31	−155.43	−145.3	0.001	−0.3	−0.3
2,99	mcct	28.15	−109.92	−103.0	0.002	−0.5	−0.5
				CD_2Cl_2			
1,22	dtz+	149.61	124.14	96.9	1.023	11.3	12.7
1,22	dcct	146.29	116.12	91.7	1.142	11.5	12.7
1,22	mtz+	150.51	125.45	99.9	1.015	11.3	12.5
1,22	mcct	139.53	110.49	85.3	1.098	11.0	12.4
8,49	dtz+	26.89	1.26	3.58	4131.6	72.0	7.9
8,49	dcct	26.30	−6.09	−2.49	33.20	−14.2	−8.1
8,49	mtz+	25.41	−39.21	−41.6	0.108	−2.1	−1.9
8,49	mcct	23.79	−59.58	−57.6	0.024	−1.2	−1.2
				$CHDCl_2$			
2,78	dtz+	55.87	170.00	140.4	0.031	2.3	2.7[g]
2,78	dcct	55.41	190.79	161.4	0.021	2.0	2.3[g]
2,78	mtz+	59.52	110.45	80.4	0.146	4.0	5.2[g]
2,78	mcct	55.73	174.70	144.6	0.028	2.2	2.6[g]
2,77	mcct	38.96	−166.25	−176.9	0.002	−0.6	−0.5
3,45	mcct	15.37	−189.41	−198.3	0.000	−0.2	−0.2
7,68	mcct	15.41	53.30	49.4	0.006	0.6	0.6
7,69	mcct	14.54	197.35	193.5	0.000	0.1	0.1
8,69	mcct	20.47	−143.60	−139.9	0.001	−0.4	−0.4

[a] DFT models (dtz+ and dcct) with ultrafine grid (ufg). [b] Separation between the harmonic frequencies of the interacting levels from the G03 program. In the Appendix to ref 31, $\delta\omega_{QC}$ is denoted by Δ. [c] Separation between the deperturbed anharmonic frequencies of the interacting levels from the G03 program ($\bar{\Delta}$ in ref 31). [d] FRtest = $\phi_{iik}^4/256\delta\omega_{QC}^3$ (type-1 resonance) or $\phi_{ijk}^4/64\delta\omega_{QC}^3$ (type-2 resonance), eqs A24 and A25, with change of sign, in ref 31. [e] Contribution to anharmonic frequency from the second-order term involved the FR (eqs A17 and A23 in ref 31 with change of sign). [f] Upward FR shifts on the deperturbed fundamentals, as calculated by G03. [g] These upward shifts are reduced in the G03 output by up to 0.5 cm^{-1} by a further small shift due to resonance with the level $2\omega_7$ lying above ω_2, as exemplified by the mcct result shown.

to calculate x_{ii}* and x_{ij}* values. Then, so-called deperturbed anharmonic frequencies $2\nu_i$*, ν^*_j, $\nu_i + \nu_j$*, ν_k* are computed by using the x_{ii}* and x_{ij}* values, as well as x_{ij} values unaffected by the FR. Here, asterisks indicate that the resonant terms have been omitted. Finally, the effective Hamiltonian matrix is diagonalized for the pairs of interacting levels to obtain $2\nu_i$, ν_j, $\nu_i + \nu_j$, and ν_k values comparable with their experimental counterparts. This procedure is well described by Martin et al. in the Appendix to their paper on the anharmonic force field of ethylene.[31]

Although the presence of a strong FR is readily recognized from the unusual values of x_{ii} or x_{ij} that result if only second-order theory is employed, it is hard, if not impossible, to find a simple criterion for the recognition of a weak FR. The decision here will be influenced by factors such as the precision required from the calculation and the amount of additional labor involved in diagonalizing the effective Hamiltonian matrix. Martin et al. suggest that a measure of the need to invoke an FR is provided by the quantity $\phi^4_{iij}/256\Delta^3$ in the case of a type-one resonance (eq A24 in ref 31, with change of sign) or $\phi^4_{ijk}/64\Delta^3$ for a type-two resonance (eq A25 in ref 31, with change of sign).[31] In these two expressions, Δ is the separation between the harmonic levels concerned. To avoid confusion with our use of Δ_i for the difference $\omega_i - \nu_i$, we will write $\delta\omega_{QC}$ instead of Δ. Similarly, we replace the symbol $\bar{\Delta}$ used by Martin et al. for the separation of the deperturbed anharmonic levels by $\delta\nu_{dp}$. We note that the discussion in ref 31 assumes that $\Delta \approx \bar{\Delta}$, which we show below may be far from being the case. Martin et al.'s eq A24 (or A25) is a simple (approximate) measure of the difference between the second-order perturbation theory equations and diagonalization for a given vibrational level.

G03 has the ability to identify terms appropriate for an FR calculation by selecting, first, the minimum magnitude of the cubic potential constant, ϕ_{iij} or ϕ_{ijk}, the default value (FX3MIN) of which is 10 cm^{-1}, and second, the maximum magnitude of the separation $\delta\omega_{QC}$. The default value of the latter is 10 cm^{-1}, but its value may be changed to x through use of the keyword DelFre = x.[32] Table 2 shows the results of a search conducted by G03 for FRs in CH_2Cl_2, CD_2Cl_2, and $CHDCl_2$ with DelFre ≈ 200 cm^{-1} and FX3MIN = 10 cm^{-1}. For the isotopomers d_0 and d_2, two modest FRs are discerned in each species, resulting from the cubic constants: ϕ_{122} and ϕ_{299} in d_0 affecting ν_1 and ν_2, and ϕ_{122} and ϕ_{849} in d_2 affecting ν_1 and ν_8. Table 2 lists first the cubic potential constants ϕ_{ijj} and ϕ_{ijk}; second, the separation of the harmonic frequencies $\delta\omega_{QC}$; third, the separation $\delta\nu_{dp}$ of the anharmonic frequencies after removal of the appropriate second-order terms from the x_{ii} or x_{ij} involved; fourth, the test quantity proposed by Martin et al. (A24 or A25 in their paper, with a change of sign), which we will call FRtest here; fifth, the change $\nu^* - \nu$ in the anharmonic frequency consequent on the removal of the above-mentioned second-order terms; and sixth, the shift $\delta\nu_{FR}$ in the fundamental frequency resulting from diagonalizing the Hamiltonian matrix for the pair of levels. In the event that second-order theory was perfectly adequate to describe the contribution of the ϕ term to the anharmonicity of the frequency involved, the entries in the fifth and sixth columns would be identical, and FRtest would approach zero.

TABLE 3: Comparison of Observed and QC-Calculated[a] Values of Anharmonicity (x_{ij}) and Darling−Dennison (K_{1166}) Constants (cm^{-1}) Associated with CH/CD Stretching in CH_2Cl_2, CD_2Cl_2, and $CHDCl_2$

		QC calculated value[a]				observed value	
parameter	species	dtz+[b]	dcct	mtz+	mcct	(1)[c]	(2)[d]
x_{11}	CH_2Cl_2	−29.2 (−29.1)	−28.9	−28.8	−28.4	−30.0(−42.7)	
x_{11}	CD_2Cl_2	−15.5	−15.2	−15.3	−15.0	−13.8(−16.1)	
x_{16}	CH_2Cl_2	−120.1 (−120.3)	−118.9	−117.8	−115.6	−117.2[e]	
K_{1166}	CH_2Cl_2	−127.7 (−127.8)	−126.1	−125.2	−122.2	−117.2[e]	
x_{16}	CD_2Cl_2	−62.8	−62.1	−61.7	−60.4	−59.7[e]	
K_{1166}	CD_2Cl_2	−69.1	−67.8	−69.5	−67.9	−59.7[e]	
x_{66}	CH_2Cl_2	−34.4(−34.6)	−34.0	−33.4	−32.8	−32.2(−19.5)	
x_{66}	CD_2Cl_2	−20.3	−20.1	−19.7	−19.4	−18.8(−16.5)	
x_{11}	$CHDCl_2$	−62.5	−61.9	−60.9	−59.7		−61.3
x_{22}	$CHDCl_2$	−33.1	−32.6	−32.5	−31.8		−33.2
x_{12}	$CHDCl_2$	−2.1	−2.1	−1.9	−2.3		−4.3

[a] Model specification: d, B3LYP; m, MP2; tz+, 6-311++G**; cct, cc-pVTZ. [b] Values in parentheses were obtained with the default grid. [c] (From ref 2) The values of x_{11} and x_{66} were derived by using an effective Hamiltonian model and including the Darling−Dennison resonance between $2\nu_1$ and $2\nu_6$. In parentheses are empirical values of x_{11} and x_{66} that ignore this resonance. The observed data cited were obtained by ignoring the very small FR between ν_1 and $2\nu_2$ in CH_2Cl_2 identified by these authors. [d] This work, determined by using the observed band centers for ν_1, ν_2, and $\nu_1 + \nu_2$ reported in ref 4. [e] From ref 2, where the constraint $K_{1166} = x_{16}$ was imposed, as in local mode theory.

The gross features for CH_2Cl_2 and CD_2Cl_2 seen in Table 2 are as follows. There is a marked contrast among the cubic constants between the large values of ϕ_{122} associated with the CH stretching mode ω_1 and the much smaller values for ϕ_{299} and ϕ_{849}, the latter both associated with bending modes. Despite the large $\delta\omega$ values, ∼200 cm^{-1} for the 1,22 FR in d_0, the FRtest values of about 1 suggest failures of the second-order perturbation theory of the order of 1 cm^{-1}. The FR shift (column six) is about 18 cm^{-1}, and the second-order term, which has been removed to make way for this shift, is less than the above amount by about 3.7 cm^{-1}.

If the magnitude of the FR were to be gauged by the extent to which the second-order expression proves deficient, we would say that the FR affecting ν_1 is weak. This judgment would be intuitively acceptable to the experimentalist and would also appear to be in accord with an experimental estimate of 1.9 cm^{-1} for the FR shift on ν_1.[2] A further source of disquiet about the description of the situation comes when one realizes that the main reason why second-order theory gives a smaller anharmonic correction to ν_1 is the marked difference between $\delta\omega_{QC}$ and $\delta\nu_{dp}$. This difference indeed entirely accounts for the differences between columns 5 and 6 for the 1,22 FRs. In one sense, there is no reason to regard the second-order term in ϕ_{122} as deficient in form. One can, however, argue that the diagonalization treatment has the merit of greater accuracy because of its more realistic estimate of the level separations. Elsewhere in Table 2, we see examples of marked effects of the differences in $\delta\omega_{QC}$ between the different models. Both DFT models make ω_8 in d_2 almost coincide with $\omega_4 + \omega_9$, resulting in enormous values of $\phi^4{}_{489}/64\delta\omega_{QC}{}^3$, where there is no doubt of the failure of second-order theory. By contrast, in both MP2 models, excellent agreement is seen between $\nu^* - \nu$ and $\delta\nu_{FR}$ in the fifth and six columns. The same is true for the 2,99 FR in d_0.

As shown in Table 2, a similar survey of FR was conducted in $CHDCl_2$ with DelFre = 200 cm^{-1}. This survey yielded the following numbers of resonances: dtz+ and dcct (7); mtz+ (3) and mcct (6). Only one FRtest value exceeded 0.03, that of 0.146 for the 2,78 resonance in the mtz+ model. Table 2 shows the data for this resonance for all four models and also for the other five resonances identified by the mcct model. The effect of the 2,78 resonance on the value of ν_2 is negligible, 1.2 cm^{-1} at worst. The nearest level that might interact with the CH stretch ν_1 lies well over 400 cm^{-1} above ν_1, so that FR involving ν_1 can be ruled out here in d_1, unlike the situation with ν_1 in d_0 and d_2. As can be seen from the mcct results, the effects of all the other FRs were quite trivial. However, for simplicity, the Δ values for all models listed below for $CHDCl_2$ include the effects of all the resonances found by using DelFre = 200 cm^{-1}.

Overall, we discern very little to upset the earlier judgment[2] that "the mid-infrared spectrum of DCM (and its isotopomers) is that of an almost unperturbed molecule."

Comparison of Theoretical and Experimental Anharmonicity Constants x_{ij}. Tables 3 and 4 compare our calculated values of the anharmonicity constants x_{ij} with those previously derived from experiment.[2−4] Table 3 selects those quantities associated purely with CH/CD stretching, namely, x_{11}, x_{16}, and x_{66} for the d_0 and d_2 species and x_{11}, x_{12}, and x_{22} for the d_1 species. None of these is affected by the 1,22, 2,99, or 8,49 FRs discussed above. However, as for all systems with symmetrically equivalent hydrogen-stretching modes, the experimental x_{11} and x_{66} must be determined in an analysis that includes the Darling−Dennison resonance between $2\nu_1$ and $2\nu_6$.[33−38] Thus, the experimental values of x_{11} and x_{66} in Table 3 are taken from the analysis of Duncan et al., which includes this resonance.[2] Experimental values of x_{11} and x_{66} derived without the above resonance are also included in Table 3 (in parentheses) so as to illustrate the magnitude of the effect, which is particularly marked for the d_0 isotopomer. The Darling−Dennison resonance parameter, K_{1166}, may be computed ab initio by using a second-order perturbation theory formula, analogous to those for x_{ij}, involving the cubic and quartic force constants and the harmonic wavenumbers.[39,40] Note that no resonant terms due to $\nu_1 \approx \nu_6$ occur in the second-order perturbation theory formula for x_{ij}.

Three other groups have measured overtone spectra of CH_2Cl_2 complementary to those reported by Duncan et al.,[2] Baggott et al.,[6] Marom et al.[7] and Liu et al.[3] All of these latter works focus on the very high overtone regions where the $\nu_1/2\nu_2$ resonance tunes in. In any case, the data of Baggott et al.[6] and Marom et al.[7] do not provide any x_{ij} not already deduced by Duncan et al., whereas the constants derived from the analyses of the later data are not comparable with those of Duncan et al. because of the differing effective Hamiltonian models used (curvilinear internal coordinates in one case[6] and a normal mode model omitting the essential K_{1166} Darling−Dennison resonance in the other).[7] The analysis of Liu et al.,[3] which involved optimizing the model parameters in a least-squares fitting procedure, apparently contains errors: the reported values of x_{18} (−66.82

TABLE 4: Comparison of Observed and Calculated Values of Anharmonicity Constants x_{ij} (cm^{-1}) for CH_2Cl_2 and CD_2Cl_2 (excluding CH/CD Stretching)[a]

	CH_2Cl_2[b]					CD_2Cl_2[a]				
i, *j*	dtz+[c]	dcct[c]	mtz+[c]	mcct[c]	obsd[d]	dtz+[c]	dcct[c]	mtz+[c]	mcct[c]	obsd[d]
1, 2	−2.7	−2.4	−1.7	−3.8	**−12.1**	4.4	5.1	5.2	4.3	**−0.5**
1, 2*	−31.9	−31.5	−31.7	−31.4	**−13.7**	−18.1	−17.9	−17.4	−17.7	**−2.7**
1, 3	−0.3	−0.3	−0.5	−0.5		−0.5	−0.4	−0.7	−0.7	−1.2
1, 4	0.5	0.5	0.4	0.4		0.3	0.4	0.2	0.2	**−8.2**
1, 8	1.6	0.7	3.1	0.1	−0.5	9.9	8.7	**16.4**	10.5	
1, 9	2.2	2.5	1.4	1.7	**−2.5**	0.7	0.8	−0.5	−0.4	1.1
2, 2	−7.5	−8.1	−7.7	−7.3	−8.2	−5.6	−6.0	−5.7	−5.5	−5.7
2, 2*	−0.2	−0.8	−0.1	−0.4	−7.3	0.05	−0.3	0.0	0.0	**−5.3**
2, 6	−20.3	−20.4	−20.3	−21.3	−21.3	−11.3	−11.3	−11.4	−11.8	−12.6
2, 7	−11.4	−11.6	−12.3	−11.7	−14.0	−6.4	−6.5	−6.9	−6.7	−9.8
2, 8	−2.7	−2.6	−3.2	−3.0	−3.0	−2.3	−2.3	−2.3	−2.6	−2.6
2, 9	**3.9**	**1.5**	−2.4	−3.2	−5.8	−1.9	−1.9	−0.9	−1.0	
2, 9*	−2.9	−3.0	−1.8	−2.3						
3, 3	−2.0	−2.0	−2.1	−2.1		−1.7	−1.7	−1.8	−1.8	**−6.4**
3, 8	−1.5	−1.3	−1.3	−1.0	**2.9**	−1.3	−1.1	−1.7	−1.1	1.4
3, 9	−6.6	−6.4	−6.0	−5.5	**−2.1**	−5.6	−5.5	−4.7	−4.4	−2.3
4, 8	−0.4	−0.3	−0.3	−0.3	−0.4	**71.0**	**−15.2**	−3.4	−2.5	**2.0**
4, 8*						−1.0	−1.0	−1.3	−1.3	
4, 9	−3.3	−3.2	−3.2	−3.2	−0.8	**−74.5**	**11.6**	−0.1	−0.9	1.3
4, 9*						−2.5	−2.5	−2.1	−2.1	
5, 6	−5.7	−6.1	−5.9	−6.8	−4.9	−3.1	−3.3	−3.0	−3.5	−1.0
5, 7	3.3	3.9	2.0	4.3	**8.9**	1.5	−1.8	0.8	2.1	5
5, 8	−14.6	−12.9	**−17.4**	−12.2	**−5.7**	−8.0	−7.1	−10.1	−7.3	
6, 7	−3.8	−3.9	−3.9	−4.3	−6.7	−1.4	−1.5	−1.4	−1.7	−1.7
6, 8	−10.5	−10.7	−11.0	−11.1	−12.1[e]	−5.3	−5.3	−4.7	−4.6	
8, 8	−5.7	−4.9	−7.6	−4.7	**−0.1**	−6.0	−5.3	−6.3	−6.1	
8, 9	−6.7	−6.4	−5.4	−5.6		**67.2**	**−18.8**	−6.3	−5.0	
8, 9*						−4.8	−4.6	−4.2	−3.8	
9, 9	−5.3	−4.7	−3.9	−3.6		−2.9	−2.9	−3.0	−2.9	**−10.3**
9, 9*	−3.6	−3.6	−4.1	−3.9						

[a] Deperturbed values, indicated by an asterisk, are included for x_{rs} excluding contributions from ϕ_{122} and ϕ_{299} in CH_2Cl_2, ϕ_{122} and ϕ_{849} in CD_2Cl_2. [b] For ^{12}C, ^{35}Cl species. Apparently anomalous values are in bold. [c] Model specification: d, B3LYP; m, MP2; tz+, 6-311++G**; cct, cct-pVTZ. [d] From ref 2, except where noted. [e] This work, as determined by using the observed band centers for ν_6, $2\nu_8$, and $\nu_6 + 2\nu_8$ reported in ref 3.

cm^{-1}) and x_{68} (−55.01 cm^{-1}) for CH_2Cl_2 are highly implausible. The cause seems to be several mis-matches between the assignments of the observed data, which we believe to be correct, and those of their calculated counterparts, which are wrong. For example, by using Liu et al.'s Hamiltonian and model parameters,[3] we find that Liu et al.'s calculated eigenvalue of 4271 cm^{-1} actually corresponds to the A_2 symmetry $\nu_6 + \nu_8$ combination and not the B_2 symmetry $\nu_1 + \nu_8$ combination. Nevertheless, Liu et al.'s observed band centers provide information on at least one x_{ij} constant not otherwise available. By using the observed band centers for ν_6, $2\nu_8$ and $\nu_6 + 2\nu_8$ (and ignoring the weak 1,88 FR), we obtain $x_{68} = -12.1$ cm^{-1}.

Baggott et al. have measured overtone spectra of $CHDCl_2$ and analyzed the data in terms of the harmonically coupled local mode model.[4] By using the observed band centers for ν_1, ν_2, and $\nu_1 + \nu_2$ and ignoring weak resonances, we obtain the x_{ij} values reported in the last column of Table 3.

In general, agreement between the ab initio and empirical values in Table 3 is quite good. For the dtz+ model only, we include in parentheses the x_{11}, x_{16}, and x_{66} values obtained with the default grid for CH_2Cl_2. The effect of grid fineness seen here is very slight. Curiously, values obtained with the 99302 fine grid differ appreciably from those obtained with either the Ultrafine or default grids. Table 3 includes a comparison of calculated and observed values of the Darling−Dennison constant K_{1166}. The analysis of Duncan et al. included the constraint $K_{1166} = x_{16}$ implied by local mode theory.[34] Our QC calculations appear to support this assumption quite well.

Table 4 contains the remaining x_{ij} values for which experimental data are available for either the d_0 or d_2 isotopomer. Where a term in an x_{ij} induces a FR, both x_{ij} and x_{ij}* are listed, as in the cases of x_{12}, x_{22}, x_{29}, x_{48}, x_{49}, x_{89}, and x_{99}. (x_{ij}* is the second-order perturbation value from which the FR term has been removed). Throughout Table 4, apparently anomalous data are indicated in bold. The values of x_{12} and to a lesser extent x_{22} in Table 4 differ markedly from x_{12}* and x_{22}* in all the QC models for both d_0 and d_2 because of the large ϕ_{122} values ($0.5\phi_{122} = k_{122} = 102.3$ cm^{-1} for CH_2Cl_2 and the mcct model). On the other hand, the *x* values are only slightly different in the corresponding experimental analyses (without and with the 1,22 resonance included) because the experimental FR parameter, k_{122} ($0.5\phi_{122} = 32.5$ cm^{-1} for CH_2Cl_2)[2] is relatively small. The reason for the discrepancy between the QC and experimental FR terms almost certainly arises from the fact that in many systems, the ab initio normal mode cubic force constant k_{122} is a poor approximation to its empirical counterpart because higher-order effects can become important.[41] Typically, the observed effective FR interaction constant is significantly smaller in magnitude than the raw QC cubic force constant.[41] In the light of this observation, it is not surprising that the empirical x_{12} values for both CH_2Cl_2 and CD_2Cl_2 should lie between the QC x_{12} and x_{12}* values. In the case of x_{22}, agreement between theory and experiment is in fact rather good.

Continuing down Table 4, agreement between theory and experiment is fair for x_{29} for the two MP2 models where FR is absent or negligible. Disagreement >3 cm^{-1} for x_{14} and x_{33} in

TABLE 5: Estimation of "Observed" Harmonic Frequencies (ω_{obsd}) from QC Values of Harmonic (ω_{QC}) and Anharmonic (ν_{QC}) Frequencies (cm^{-1})

$^{12}CH_2{}^{35}Cl_2$

		ω_{QC}				$\Delta = \omega_{QC} - \nu_{QC}$[b]				$\omega_{obsd} = \nu_{obsd} + \Delta$				
mode	ν_{obsd}[a]	dtz+	dcct	mtz+	mcct	dtz+	dcct	mtz+	mcct	dtz+	dcct	mtz+	mcct	ω_{obsd} emp[c]
A_1 1	2995.8[d]	3122.0	3120.9	3162.0	3157.0	120.0	119.3	117.7	118.6	3115.8	3115.1	3113.5	3114.4	3122.6
2	1435.0	1457.0	1461.7	1475.3	1483.6	35.4	37.4	36.6	38.8	1470.4	1472.4	1471.6	1473.8	1464.3
3	712.9	699.0	698.8	750.8	740.6	12.1	11.8	12.2	11.6	725	724.7	725.1	724.5	723.8
4	281.5	282.3	277.5	301.4	289.0	2.9	2.7	3.0	2.9	284.4	284.2	284.5	284.4	284.3
A_2 5	1153	1179.5	1170.2	1209.3	1193.5	25.3	25.5	19.1	24.7	1178.3	1178.5	1172.1	1177.7	1176.5
B_1 6	3055	3200.7	3197.3	3238.8	3238.4	146.1	145.0	144.4	143.1	3201.1	3200.0	3199.4	3198.1	3182.3
7	898.66	901.3	900.6	933.1	917.0	12.3	12.0	15.7	11.8	911.0	910.7	914.4	910.5	917.0
B_2 8	1268.9	1302.6	1286.2	1358.3	1302.2	27.7	25.1	33.5	24.1	1296.5	1294.0	1302.3	1293.0	1294.8
9	759.82	718.7	716.8	815.4	796.8	19.5	18.9	19.1	18.8	779.3	778.7	779.0	778.6	771.4

$^{12}CD_2{}^{35}Cl_2$

		ω_{QC}				$\Delta = \omega_{QC} - \nu_{QC}$[f]				ω_{obsd}[e] $= \nu_{obsd} + \Delta$				
mode	ν_{obsd}[a,e]	dtz+	dcct	mtz+	mcct	dtz+	dcct	mtz+	mcct	dtz+	dcct	mtz+	mcct	ω_{obsd} emp.[c]
A_1 1	*2204.27*[d]	2262.1	2260.7	2293.9	2289.2	57.0	56.7	53.7	55.8	*2261.2*	*2260.9*	*2257.9*	*2260.1*	2272.5
2	1060.81	1069.0	1072.3	1084.2	1089.4	21.3	22.2	20.3	21.5	1082.1	1083.0	1081.1	1082.3	1076.7
3	687.6	671.8	671.9	719.5	710.8	10.1	9.9	10.3	9.6	697.7	697.5	697.9	697.2	697.7
4	279	279.7	275.0	298.7	286.3	2.6	2.6	2.9	2.7	281.6	281.6	281.9	281.7	281.8
A_2 5	825	838.6	832.1	859.9	848.7	14.2	14.3	11.1	13.8	839.2	839.3	836.1	838.8	837.0
B_1 6	*2303.72*	2384.9	2382.3	2411.2	2411.2	80.8	80.2	79.9	79.2	*2384.5*	*2383.9*	*2383.6*	*2382.9*	2375.4
7	713	712.6	711.8	739.6	725.7	7.9	7.7	9.6	7.5	720.9	720.7	722.6	720.5	724.5
B_2 8	961.04	975.7	962.4	1034.7	987.6	10.4	24.9	24.1	18.3	*971.5*	*986.0*	985.2	979.4	975.8
9	730.26	694.7	693.6	775.2	760.9	15.5	15.3	14.9	14.3	745.8	745.5	745.1	744.6	740.9

$^{12}CHD^{35}Cl_2$.

		ω_{QC}				$\Delta = \omega_{QC} - \nu_{QC}$[h]				ω_{obsd}[e] $= \nu_{obsd} + \Delta$				
mode	ν_{obsd}[d,g]	dtz+	dcct	mtz+	mcct	dtz+	dcct	mtz+	mcct	dtz+	dcct	mtz+	mcct	ω_{obsd} emp.[c]
A′ 1	*3024.8*	3164.0	3161.6	3202.8	3200.3	140.0	139.2	137.3	136.5	*3164.8*	*3164.0*	*3162.1*	*3161.3*	3149.5
2	*2251.5*	2321.0	2319.1	2350.2	2347.6	71.6	70.7	69.8	70.8	*2323.1*	*2322.2*	*2321.3*	*2322.3*	2321.2
3	1286	1301.1	1305.0	1319.1	1324.8	30.7	32.0	29.6	30.8	1316.7	1318.0	1315.6	1316.8	1309.5
4	782.5	781.6	780.9	813.7	800.0	10.2	9.9	12.3	10.1	792.7	792.4	794.8	792.6	796.4
5	692.5	678.0	678.0	723.8	714.2	10.5	10.3	10.6	9.6	703.0	702.8	703.1	702.1	702.7
6	280	281.1	276.3	300.0	287.7	2.8	2.7	2.9	2.8	282.8	282.7	282.9	282.8	282.8
A″ 7	1223.5	1251.9	1238.1	1299.41	1256.9	26.9	26.2	28.4	23.6	1250.4	1249.7	1251.9	1247.1	1247.9
8	890.4	899.1	890.2	940.3	916.0	17.2	16.4	16.2	17.1	907.6	906.8	906.6	907.5	904.4
9	739.8	704.0	702.5	786.6	771.9	17.2	16.7	15.5	15.5	757.0	756.5	755.3	755.3	750.7

[a] From ref 2. [b] Incorporating the effects of the 1,22 and 2,99 resonances. [c] Ref 8 obtained by using empirical corrections for anharmonicity. [d] Including corrections for FR with $2\nu_2$, ref 2, but excluding the further resonance suggested in ref 8. [e] In italics, data not used in the scale factor refinements. [f] Incorporating the effects of the 1,22 and 8,49 resonances. [g] ν_1, ν_2 from ref 4, ν_3 to ν_9 from ref 5. [h] Incorporating the effects of the 2,78 and other very small resonances.

d_2 has no obvious explanation. The same is true of x_{38}, x_{39}, x_{57}, and x_{58} in d_0. With x_{48}, x_{49}, and x_{89} in d_2, we encounter the difficulties imposed by the 8,49 FR. Experimental values are reported only for x_{48} and x_{49}, and these differ a little from the MP2 results but enormously from the DFT ones where a spurious coincidence of the two levels (Table 2) leads to a very large FR. A final disagreement without current explanation is that of about 7 cm^{-1} between experiment and all four QC models for the value of x_{99}. In the hope of assisting future experimental investigations, we include a complete set of x_{ij} values from the mcct model in the Supporting Information, Tables S1 (CH_2Cl_2), S2 (CD_2Cl_2), and S3 ($CHDCl_2$)

Estimation of "Observed" Harmonic Frequencies. Table 5 lists the experimental fundamental frequencies ν_{obsd}, the G03-based harmonic frequencies ω_{QC}, anharmonicity corrections $\Delta = \omega_{QC} - \nu_{QC}$, and ω_{obsd} values computed from the ν_{obsd} and Δ values. Among the ω_{QC} values, the usual differences between DFT and MP2 values are seen, the latter always being higher than the former. The effect of change of basis set is small between the two DFT models but quite large between certain of the MP2 ω_{QC} values, notably for ω_8 in d_0 and d_2 and ω_7 in d_1. Suspicion here must fall on the mtz+ values.

In general, the values of Δ in Table 5 agree quite well across the four models, but we note anomalies in certain of the mtz+ values, namely, Δ_5, Δ_7, and Δ_8 in d_0, Δ_8 in d_2, and Δ_7 in d_1. These are associated with cubic and quartic force constants in the mtz+ model that are out of line with the corresponding dtz+, dcct, and mcct ones. Another anomaly is the difference between the dtz+ and dcct Δ_8 values in d_2. This anomaly is readily traced to the accidental, very large 8,49 FR in both B3LYP models that is entirely missing (see Table 2) in the MP2 calculations. The corresponding $\omega_{8(obsd)}$ values for both the dtz+ and dcct models were omitted from the subsequent scale factor refinements. The oddities in both ω_{QC} and Δ data from the mtz+ model are plausibly attributed to the absence of *f* functions in the Pople-type 6-311++G** basis set. (*f* functions are included

TABLE 6: Scale Factors[a] for QC-Based Harmonic Force Fields in Symmetry Coordinate Space for Dichloromethane, Scaled to Observed (ν_{obsd}) or Harmonically Corrected Observed (ω_{obsd}) Frequencies

type of motion	symm. coord.[b]	dtz+[c]		dcct[c]		mtz+		mcct	
		ν_{obsd}	ω_{obsd}	ν_{obsd}	ω_{obsd}	ν_{obsd}	ω_{obsd}	ν_{obsd}	ω_{obsd}
ν_sCH_2	$S_1(a_1)$	0.9207(68)	0.9960(57)	0.9215(72)	0.9963(59)	0.8977(59)	0.9696(45)	0.9005(45)	0.9732(19)
$\nu_{as}CH_2$	$S_6(b_1)$	0.9104(66)	1.0003(58)	0.9128(72)	1.0017(59)	0.8896(59)	0.9758(47)	0.8899(44)	0.9753(19)
$\Delta\nu CH_2$		−0.0103(4)[d]	0.0043(4)[d]	−0.0087(4)[d]	0.0054(4)[d]	−0.0081(4)[d]	0.0062(4)[d]	−0.0106(4)[d]	0.0021(4)[d]
δ_sCH_2	$S_2(a_1)$	0.9774(40)	1.0225((34)	0.9721(44)	1.0190(35)	0.9500(36)	0.9931(27)	0.9416(27)	0.9868(11)
wCH_2	$S_9(b_2)$	0.9640(43)	1.0010(45)	0.9893(48)	1.0227(48)	0.8693(36)	0.9148(27)	0.9489(27)	0.9855(12)
τCH_2	$S_5(a_2)$	0.9645(44)	1.0034(37)	0.9801(49)	1.0200(39)	0.9150(39)	0.9424(28)	0.9403(30)	0.9766(12)
ρCH_2	$S_7(b_1)$	0.9993(45)	1.0215(36)	1.0006(48)	1.0243(37)	0.9283(38)	0.9569(27)	0.9633(29)	0.9830(12)
ν_sCCl_2	$S_3(a_1)$	1.0566(55)	1.0921(45)	1.0499(61)	1.0846(48)	0.9156(44)	0.9463(23)	0.9295(34)	0.9586(14)
$\nu_{as}CCl_2$	$S_8(b_2)$	1.1049(45)	1.1570(38)	1.1109(49)	1.1616(39)	0.8785(34)	0.9183(25)	0.9162(26)	0.9566(11)
$\Delta\nu CCl_2$		0.0483(100)	0.0649(83)	0.0610(110)	0.0770(87)	−0.0371(78)	−0.0280(48)	−0.0133(60)	−0.0020(25)
δ_sCCl_2	$S_4(a_1)$	0.9830(48)	1.0012(43)	1.0229(56)	1.0409(42)	0.8669(39)	0.8841(28)	0.9517(32)	0.9698(13)
ΣWSE[e]		1.79	1.07	2.15	1.15	1.53	0.76	0.85	0.13
mean[f]		0.9868	1.0328	0.9956	1.0412	0.9012	0.9446	0.9313	0.9743
σ_d[g]		0.0615	0.0614	0.0614	0.0519	0.0282	0.0342	0.0246	0.0112

[a] Dispersions in parentheses are based on 1% uncertainties in all frequencies utilized except for where otherwise stated. [b] As defined in ref 8, Table 1, except for (a) an interchange of S_2 and S_3, (b) reversal of the relative signs in the pairs S_6, S_7 and S_8, S_9. [c] Ultrafine grid. [d] Error resulting from uncertainties of ±1 cm^{-1} on the two CH stretching frequencies. [e] Sum of weighted squares of frequency errors ε = obsd − calc. [f] Mean scale factor. [g] Standard deviation of mean.

TABLE 7: Unscaled and Scaled Values of Valence Coordinate CH and CCl Stretch/Stretch Interaction Force Constants in Dichloromethane: HCH and ClCCl Angles

	$f'_{CH/CH}$/ aJ Å^{-2}				$f'_{CCl/CCl}$/ aJ Å^{-2}			
		scaled on				scaled on		
model	unsc.	ν_{obsd}	ω_{obsd}	∠HCH/ °	unsc.	ν_{obsd}	ω_{obsd}	∠ClCCl/ °
dtz+	0.0394	0.0631	0.0275	112.03	0.4860	0.4497	0.4305	113.23
dcct	0.0436	0.0638	0.0289	112.10	0.4827	0.4259	0.4215	113.00
mtz+	0.0328	0.0520	0.0145	110.97	0.4500	0.4732	0.4719	113.12
mcct	0.0287	0.0556	0.0222	111.54	0.4400	0.4305	0.4252	112.51

in the cc-pVTZ basis.) Difficulties attributed to such an absence of *f* functions were first observed in molecules containing multiple bonds[42–44] but were also detected in DFCP.[1] DCM may constitute the first instance of the inadequacy of a Pople-type basis in a simple sp^3-type organic molecule. The effect of the absence of *f* functions is much less marked in DFT calculations, both here and in DFCP.[1]

Finally, in this section, it is interesting to compare our ω_{obsd} values with those in the last column of each section of Table 5, which were deduced earlier by Duncan et al. by using empirical means.[8] Agreement is quite good overall, the main differences lying in the CH and CD stretching frequencies, where Duncan et al. employ only a constant anharmoncity factor, whereas all the models clearly agree on a larger Δ value for the antisymmetric stretch. This last feature, which was found also in DFCP and methyl halides,[1] constitutes further evidence of a need for differing scale factors for the two types of CH stretching force constant, as discussed below. A curious observation is that the Δ_1 value for the single CH stretch in $CHDCl_2$ lies distinctly closer to that for the antisymmetric stretch ω_6 in CH_2Cl_2 than to the average of the Δ_1 and Δ_6 values, as intuition might have led one to expect. This relationship was also a feature of the DFCP calculations.[1] Analysis of the $\Delta_6 - \Delta_1$ difference in CH_2Cl_2 by using the mcct data, with no allowance for FR, shows that the result arises from three terms involving respectively $2(x_{66} - x_{11})$ (38%), $0.5(x_{26} - x_{12})$ (38%), and $0.5(x_{68} - x_{18})$ (24%). The second of these differences stems largely from two terms in x_{12} involving respectively ϕ_{111}, ϕ_{122}, and (ϕ_{122}).[2]

Scaling of the Symmetrized Harmonic Force Fields. For simplicity, we employed throughout a set of symmetry coordinates identical with those of Duncan et al.[8] except for an interchange of S_2 and S_3 and changes of relative signs within the pairs S_6, S_7 and S_8, S_9. Table 6 includes the conventional descriptions of these coordinates. Simultaneous refinement to the d_0, d_2, and d_1 frequencies was effected by assembling coordinates S_{1-4}, S_6, and S_7 into an A′ block; similarly S_5, S_8, and S_9 into an A″ block. No problem arose from any failure of the program to distinguish A_1 from B_1 or A_2 from B_2 frequencies within the respective A′ and A″ blocks.

To maximize the chance of identifying deficiencies in the QC-based force fields, we used the maximum number (9) of scale factors (sf) possible with ASYM40. In the case of the CH and CCl stretching coordinates, this choice introduces differing scale factors for the symmetric stretching constants $F_s = f + f'$ and the antisymmetric stretching constants $F_{as} = f - f'$, where f and f' are the principal and interaction valence constants concerned, respectively. A consequence of this procedure is that if differing scale factors are found for a pair of F_s and F_{as} constants, the scaled value of f' may be different from its unscaled value by an amount that may be markedly different from the mean of the two scale factors involved in the two symmetry force constants. This outcome could indicate that there are problems with the data used, but it might alternatively mean that the QC calculation of f' is deficient. Indeed, one might judge the worth of a particular QC model by its ability to yield similar scale factors for similar types of motion.

Inspection of the resulting scale factors listed in Table 6 and of the associated values of f' for both CH and CCl bonds given in Table 7 shows instances of both kinds of behavior, successful and less successful calculations of f'. Table 7 includes also the calculated HCH and ClCCl angles in order to show that these are little affected by the nature of the model and therefore should

TABLE 8: Comparison of Scaled QC Force Fields in Symmetry Coordinates for Dichloromethane (aJ Å^{-2}, aJ rad^{-2})

	ν_{obsd}				ω_{obsd}				ω_{emp}[a]
F	dtz+	dcct	mtz+	mcct	dtz+	dcct	mtz+	mcct[b]	HF/6-31G*
1,1	5.085	5.087	5.076	5.079	5.500	5.500	5.482	5.490	5.486
1,2	0.134	0.136	0.130	0.131	0.142	0.145	0.138	0.139	0.121
2,2	0.604	0.601	0.605	0.597	0.632	0.630	0.632	0.626	0.611
1,3	0.141	0.153	0.108	0.109	0.149	0.161	0.114	0.115	0.134
2,3	−0.340	−0.340	−0.319	−0.323	−0.354	−0.356	−0.332	−0.336	−0.321
3,3	3.832	3.795	3.852	3.791	3.961	3.927	3.981	3.910	3.845
1,4	−0.013	−0.014	−0.025	−0.022	−0.014	−0.015	−0.027	−0.022	−0.011
2,4	−0.224	−0.224	−0.220	−0.218	−0.231	−0.231	−0.227	−0.225	−0.230
3,4	0.249	0.239	0.258	0.248	0.256	0.245	0.264	0.254	0.271
4,4	1.055	1.060	1.018	1.037	1.075	1.079	1.038	1.056	1.061
5,5	0.602	0.601	0.601	0.601	0.626	0.625	0.619	0.624	0.621
6,6	4.959	4.959	4.972	4.968	5.445	5.442	5.453	5.445	5.433
6,7	0.022	0.025	0.045	0.045	0.023	0.027	0.048	0.048	0.025
7,7	0.851	0.842	0.849	0.830	0.871	0.862	0.875	0.850	0.837
8,8	2.932	2.943	2.905	2.930	3.070	3.078	3.037	3.059	3.050
8,9	0.597	0.604	0.525	0.552	0.622	0.628	0.550	0.575	0.533
9,9	0.681	0.681	0.663	0.669	0.707	0.704	0.697	0.695	0.682

[a] Force field scaled to "empirical" harmonic frequencies, ref 10. [b] Preferred force field.

TABLE 9: Frequency Fit (ε = obsd − calc, cm^{-1}) and PEDs in Symmetry Coordinates for DCM Isotopomers from the MP2/cc-pVTZ Model

	d_0				d_2			d_1			
mode	ω_{obsd}	ε	PED	motion[a]	ω_{obsd}	ε	PED	mode	ω_{obsd}	ε	PED
A_1 1	3114.4	0.0	$100S_1$	ν_sCH_2	2260.1	1.8	$100S_1$	A′ 1	3161.3	2.2	$44S_1$, $56S_6$
2	1473.8	−0.4	$111S_2$	δ_sCH_2	1082.3	0.0	$110S_2$, $5S_3$	2	2322.3	5.3	$56S_1$, $44S_6$
3	724.5	−1.3	$92S_3$, $19S_4$	ν_sCCl_2	697.2	0.6	$89S_3$, $19S_4$	3	1316.8	0.4	$105S_2$, $6S_7$
4	284.4	0.2	$12S_3$, $86S_4$	δ_sCCl_2	281.7	0.0	$11S_3$, $88S_4$	4	792.6	−0.1	$6S_2$, $16S_3$, $81S_7$
A_2 5	1177.7	−1.7	$100S_5$	τCH_2	838.8	0.1	$100S_5$	5	702.1	0.8	$77S_3$, $17S_4$, $13S_7$
B_1 6	3198.1	0.0	$100S_6$	$\nu_{as}CH_2$	2382.9	1.6	$99S_6$	6	282.8	−0.2	$12S_3$, $87S_4$
7	910.5	0.0	$100S_7$	ρCH_2	720.5	0.0	$99S_7$	A″ 7	1247.1	0.7	$33S_5$, $75S_9$
B_2 8	1293.0	−0.5	$111S_9$	wCH_2	979.4	−0.6	$22S_8$, $118S_9$	8	907.5	1.8	$60S_5$, $20S_8$, $43S_9$
9	778.6	−0.2	$116S_8$, $7S_9$	$\nu_{as}CCl_2$	744.6	0.2	$96S_8$	9	755.3	−0.1	$7S_5$, $97S_8$
ΣWSE[b]		0.06				0.01				0.06	

[a] τ, twist; ρ, rock; w, wag. [b] Sum of weighted squares of errors.

TABLE 10: Reproduction (ϵ = obsd - calc) of CH and CD Stretching Frequencies in $CHDCl_2$ and CD_2Cl_2 by Force Fields Fitting Exactly the Symmetric and Antisymmetric Frequencies of CH_2Cl_2 (cm^{-1})

	$CHDCl_2$				CD_2Cl_2			
	ε_1 (νCH)		ε_2(νCD)		ε_1(ν_sCD_2)		ε_6($\nu_{as}CD_2$)	
model	ν_{obsd}	ω_{obsd}	ν_{obsd}	ω_{obsd}	ν_{obsd}	ω_{obsd}	ν_{obsd}	ω_{obsd}
dtz+	−2.4	3.4	4.5[a]	4.3	9.7[a]	3.3	1.5[a]	−0.9
dcct	−2.4	3.5	4.9[a]	4.4	9.8[a]	4.1	1.6[a]	−0.6
mtz+	−2.3	2.8	4.6[a]	4.0	7.0[a]	−0.6	4.0[a]	1.9
mcct	−2.3	2.2	4.8[a]	5.3	7.9[a]	1.8	3.4[a]	1.6

[a] Based on refinement value × 1.011.

make similar contributions to the ν_{as}/ν_s splittings. Variations such as those found are unlikely to have a significant influence on the analysis below of the changes in f'.

Starting with the CCl stretching scale factors, we see in the case of the two B3LYP models a marked difference between sf_3 and sf_8, with $sf_3 < sf_8$. This difference is present in the scaling to both ν_{obsd} and ω_{obsd}. By contrast, for the two MP2 models, especially for the mcct model, the above scale factors are more similar, with $sf_3 > sf_8$. As a consequence, f'_{CCl} falls markedly upon scaling with both B3LYP models but either rises (mtz+) or is little changed (mcct) on scaling with the MP2 ones. If we multiply the unscaled mcct value of f'_{CCl} (0.4400) by the average of the two ω_{obsd} scale factors (0.9575), we obtain 0.4213, which is very close to the 0.4252 obtained from the ω_{obsd} refinement, independently of the method of scaling. The mcct result is seen to be quite the best of the four. The impression is also given that the smaller values of f'_{CCl} given by the MP2 models are more realistic than the larger ones from the DFT calculations. Another merit of the MP2 calculations here is that the MP2 sf_3 and sf_8 scale factors lie close to the overall average sf value, also given in Table 6, whereas from the B3LYP model, the sf_3 and sf_8 values are markedly larger than the average. A similar effect has been previously noted for the B3LYP CF stretching constants in DFCP.[1]

We now examine the scale factors for CH bond stretching. Table 6 shows that when scaling is based on ν_{obsd} data, sf_1 is larger than sf_6 in all models. This difference has the effect of nearly doubling the value of f'_{CH} (Table 7). There is little doubt that this result is the consequence of the inherent difference in the anharmonicities associated with ν_1 and ν_6, as quantified in their Δ values. On scaling to ω_{obsd}, sf_6 becomes slightly larger than sf_1, in consequence of which f'_{CH} falls slightly from its unscaled value. The mcct calculation gives the closest agreement between sf_1 and sf_6, which we take to be evidence in favor of the lower value of f'_{CH} yielded by MP2 models, as found in DFCP.[1] Among the scale factors for the CH bending modes, one can discern a general tendency to uniformity on passing from ν_{obsd} to ω_{obsd} scaling. Overall, the most consistent set of factors is that from the mcct ω_{obsd} scaled force field. The latter also gives the best fit to data as given by ΣWSE (sum of weighted squares of errors) of all the calculations.

TABLE 11: Comparison of Some Calculated and Observed Heavy Isotope Harmonic Frequency Shifts (cm^{-1}) $\delta\omega$ Downwards from $^{12}CH_2{}^{35}Cl_2$ and $^{12}CD_2{}^{35}Cl_2$

	$^{13}CH_2\ {}^{35}Cl_2$				$^{12}CH_2{}^{35}Cl^{37}Cl$				$^{12}CD_2{}^{35}Cl^{37}Cl$			
	mcct[a]	Expt[b]	SQM[c]	GHFF[c]	mcct[a]	expt[b]	SQM[c]	GHFF[c]	mcct[a]	expt[b]	SQM[c]	GHFF[c]
A_1 1	5.75	6.94	6.00	6.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	3.81	4.06	3.79	3.86	0.02	0.0	0.02	0.01	0.01	0.00	0.00	0.01
3	18.04	17.93	17.90	17.82	3.02	2.95	2.98	3.08	3.28	3.17	3.22	3.28
4	1.31	1.33	1.29	1.34	3.39	3.45	3.40	3.37	3.31	3.14	3.30	3.29
A_2 5	0.00	0.00	0.00	0.00	0.17	0.2	0.16	0.17	0.24	-	0.23	0.24
B_1 6	13.08	12.69	13.00	12.54	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	9.08	9.27	9.02	9.26	0.30	0.30	0.29	0.30	0.37	0.40	0.36	0.38
B_2 8	4.70	4.37	5.07	4.37	0.15	0.16	0.14	0.17	0.06	-	0.07	0.06
9	21.98	21.80	21.72	21.93	2.29	2.24	2.32	2.24	2.54	2.49	2.65	2.53

[a] This work. [b] Ref 8. These experimental shifts are based on observed frequency shifts $\delta\nu$ adjusted to harmonic values by using Dennison's rules and empirical estimates of anharmonicity. [c] SQM, scaled quantum mechanical; GHFF, general harmonic force field, ref 10.

Among the scale factors for the CH bending modes, one can discern a general tendency to uniformity on passing from ν_{obsd} to ω_{obsd} scaling. Overall, the most consistent set of factors is that from the mcct ω_{obsd} scaled force field. The latter also gives the best fit to data as given by ΣWSE (sum of weighted squares of errors)[23] of all the calculations.

Symmetry Force Fields and Frequency Fit. Table 8 lists the symmetry force constants from the four models, in each case scaled to both anharmonic (ν_{obsd}) and harmonic (ω_{obsd}) frequencies. The earlier scaled HF/6-321G* force field of Duncan et al.[10] is included for comparison. There is little evidence for any major effect of basis set, but certain off-diagonal constants, particularly $F_{1,3}$, $F_{1,4}$, $F_{6,7}$, and $F_{8,9}$ change markedly on a percent basis from the B3LYP to the MP2 models. There are smaller differences in a number of off-diagonal constants between the mcct model and the HF/6-31G* results. The changes here in $F_{6,7}$ and $F_{8,9}$ slightly reduce the apparently significant differences seen previously between the ab initio and empirical force field values.[10]

Table 9 shows the fit to the frequencies of the d_0, d_2, and d_1 isotopomers obtained with our preferred mcct force field. The accompanying potential energy distributions (PED), also shown, vary little with model. The quality of the frequency fit obtained from the mcct model is so good that it seems unlikely that a more sophisticated type of calculation, involving off-diagonal constants refined independently of the diagonal ones, would result in a significant change in the force field. As mentioned above, such a calculation is not feasible with ASYM40.

The frequency fit in the CH and CD stretching regions merits closer attention. The relevant data are shown in Table 10. Remembering that ν/ω_1 and ν/ω_6 in d_0 are fitted exactly in all cases, we show only the reproduction of ν/ω_1 for d_1 and the three ν/ω_{CD} values in d_1 and d_2. All four models yield a value for $\nu_1(d_1)$ about 2 cm^{-1} above its observed value of 3024.8 cm^{-1}. A closer fit would result if the FR correction of 1.9 cm^{-1} incorporated in the observed value[2] of 2995.8 cm^{-1} for ν_1 d_0 were to be increased slightly. As discussed above, $\nu_1(d_1)$ appears to be entirely unaffected by FR. By contrast, $\omega_1(d_1)$ is predicted slightly lower by 2−3 cm^{-1} than the estimated $\omega_{1(obsd)}$ values. This difference might reflect some slight error in the QC calculations of the anharmonicity corrections Δ, including the analysis of the FR in $\nu_1(d_0)$. The predictions of anharmonic ν_{CD} values in both d_1 and d_2 all involve the prior application of the usual fudge factor[1] of 1.011 to the refinement predictions to account for overcorrection of ν_{CD} from scaling to ν_{CH}. This adjustment is seen to work quite well for $\nu_1(d_1)$ and $\nu_6(d_2)$ and less well so for the symmetric stretching mode $\nu_1(d_2)$. This difference was to be expected from the similar behavior found earlier in DFCP.[1] The fit to ω_{obsd} values of ω_{CD} modes is generally better than that to ν_{obsd}, particularly for $\omega_1(d_2)$. Again, the MP2 models perform better than the B3LYP ones.

A number of heavy isotope frequency shifts are known from the work of Duncan et al.,[2] and Table 11 compares some of our mcct computed values with "experimental", scaled SCF, and empirical force fields.[8,10] Some uncertainty is associated with the experimental frequency-shift values because these are based on observed (anharmonic) $\delta\nu$ data, which were subsequently increased by anharmonic corrections based on Dennison's rules. Error in the latter treatment may account for the discrepancy between the mcct and experimental values of $\delta\omega_6$, for example. The largest discrepancy, for $\delta\omega_1$, was evident in the earlier work and was explained by a very weak resonance in the ^{12}C species between two essentially coincident levels at about 2997 cm^{-1} due to ν_1 and $\nu_3 + 2\nu_5$.[10] There is undoubtedly a resonance here, but our mcct anharmonicity constants suggest a more plausible origin for the level involved, namely, $4\nu_9$, which in the absence of any resonance with $2\nu_9 + \nu_2$ would be expected at about 2996 cm^{-1}. By contrast, $\nu_3 + 2\nu_5$ is predicted to lie close to 3009 cm^{-1}. The small shifts from $^{35}Cl_2$ to $^{35}Cl^{37}Cl$ species are well reproduced in all cases.

Finally, we note that the values of $\omega_8(d_2)$ for the dtz+ and dcct models (971.5 and 986 cm^{-1}, respectively, Table 5), which were omitted from the refinements on account of the undue influence of the 8,49 FR, are in fact predicted at 974.6 and 971.5 cm^{-1}, respectively. This outcome suggests that error in Δ_8 due to the 8,49 FR resided mainly in the dcct model value.

Centrifugal Distortion Constants. Table 12 compares observed values[9] of centrifugal distortion constants (CDCs) for d_0 and d_2 with those calculated with ASYM40 from our four models, each force field being either unscaled or scaled to ν_{obsd} or ω_{obsd}. Unscaled values computed with G03 are in essential agreement with those from ASYM40. Also included are the values from the scaled HF/6-31G** model of Duncan et al.[10] The variations found are considerable. Some features are understandable. In general, higher frequencies imply tighter bonding and lower values of the resulting CDCs. The marked fall in all frequencies in the two MP2 models from an unscaled force field to one scaled to ν_{obsd} is accompanied by the expected rise in CDC value in each case. This change is then reversed on passing from a force field scaled to ν_{obsd} to one scaled to ω_{obsd}, again as expected. This latter change is also seen with both B3LYP models. With the latter, however, passing from an unscaled force field to one scaled to ν_{obsd} has a variable effect, which can be explained by the presence of scale factors both less and greater than unity.

TABLE 12: Observed and Computed Centrifugal Distortion Constants (kHz) for $^{12}CH_2{}^{35}Cl_2$ and $^{12}CD_2{}^{35}Cl_2$

	expt[a]	dtz+[b]			dcct[b]			mtz+[b]			mcct[b]			HF/6-31G*[c]
		unsc.	sc./ν_{obsd}	sc./ω_{obsd}	unsc.	sc./ν_{obsd}	sc./ω_{obsd}	unsc.	sc./ν_{obsd}	sc./ω_{obsd}	unsc.	sc./ν_{obsd}	sc./ω_{obsd}	sc./ω_{est}
							d$_0$							
Δ_J	1.3921	1.2787	1.2672	1.2388	1.3466	1.3021	1.2739	1.2072	1.3692	1.3373	1.3264	1.4048	1.3738	1.385
Δ_{JK}	−26.176	−23.931	−25.527	−25.327	−25.591	−25.560	−25.380	−23.145	−27.360	−27.074	−25.834	−26.758	−26.494	−25.92
Δ_K	473.16	483.76	490.32	480.90	496.81	485.25	476.26	449.78	516.88	506.29	468.93	493.72	484.00	465.7
δ_J	0.17699	0.1539	0.1557	0.1528	0.1643	0.1600	0.1572	0.1476	0.1700	0.1667	0.1665	0.1752	0.1719	0.1752
δ_K	5.365	5.0137	4.8305	4.6933	5.2255	4.9062	4.7717	4.5213	5.2056	5.0584	4.8871	5.2213	5.0773	5.05
							d$_2$							
Δ_J	1.2977	1.1912	1.1799	1.1533	1.2538	1.2122	1.1858	1.1232	1.2732	1.24342	1.2332	1.3063	1.2774	1.287
Δ_{JK}	−15.844	−14.635	−15.613	−15.511	−15.707	−15.673	−15.582	−13.950	−16.516	−16.369	−15.726	−16.274	−16.138	−15.77
Δ_K	204.05	208.44	211.86	207.676	214.60	210.10	206.09	192.24	221.04	216.39	202.19	212.97	208.65	201.2
δ_J	0.19014	0.1663	0.1680	0.1650	0.1774	0.1727	0.1696	0.1592	0.1834	0.1798	0.1792	0.1887	0.1852	0.1884
δ_K	4.079	3.7454	3.6263	3.5276	3.9101	3.6772	3.5816	3.4003	3.9340	3.8243	3.6786	3.92622	3.8212	3.81

[a] From ref 9. [b] From QC-based quadratic force fields either unscaled or scaled to ν_{obsd} or ω_{obsd}, as computed with ASYM40. [c] From ref 10.

A puzzling feature concerns the values of Δ_K from the scaled mtz+ model force fields, which are markedly higher than those from the other models. Smaller variations are seen widely in the other CDCs with change of model. These high values of Δ_K (mtz+) are surprising, because the frequency data used for scaling are either identical, as in the case of the use of ν_{obsd}, or else very similar, as for the ω_{obsd} force fields. This outcome suggests that we may be seeing an effect of the small variations in off-diagonal symmetry force constants between different models noted above. Such variations could also arise both from the differing scaling applied to the diagonal symmetry constants imposed by the Pulay-type program or from inherently different force constants, as identified among the f'_{CH} and f'_{CCl} constants discussed above.

It would be premature to choose a model on the basis of agreement with experimental CDC values, because the former apply to the equilibrium state and the latter to the ground state. Little or nothing is known as yet concerning the vibrational dependence of CDCs.[45] On other grounds, we prefer the mcct force field, and we note that the associated mcct (ω_{obsd}) CDCs agree with the experimental values within 2% except for δ_K where the disagreement is greater, ~ 6%. From this point of view, the earlier scaled HF/6-31G** values from Duncan et al.[10] are at least as good as those from our mcct model.

If a program to calculate the vibrational dependence of the CDCs were to become available, CDC data could then be safely used in refining harmonic symmetry force fields. With such assistance, it might be possible to identify flaws in the QC estimation of off-diagonal force constants in the different models. As indicated above, to refine force constants in this way would require a program more flexible than that of ASYM40.

Although we have seen and discussed differences of less than 20% in the CDCs found between the various QC models without and with scaling, we note that taken together, the computed CDCs are a marked improvement over assuming CDCs are zero, as is done for the rigid rotor model in rotational spectroscopy. Using computed CDCs when fitting rotational lines to a Hamiltonian improves the fit of the *A*, *B*, and *C* rotational constants. If experimental CDCs are available for the normal species, this fitting procedure can be improved by scaling CDCs for the normal species with ratios of predicted CDCs (isotopomer/normal) to give the CDCs for isotopomers.[8]

Vibration−Rotation Constants. Another goal of this research is determining a semiexperimental equilibrium (r_e) structure for DCM. For this purpose, vibration−rotation constants (alphas) are needed from QC calculations. G03 provides alphas if care is taken to supply Cartesian coordinates in the PAS to the vibration−rotation module of the software. (See the Theoretical Section.) An improved method of computing the harmonic contributions to the alphas uses scaled QC force fields.[46] Cubic force fields come directly from G03.[46] We have made such calculations of alphas for DCM and its isotopomers. These results will be reported in a subsequent paper on the semiexperimental structure after improved measurements are made of microwave lines of several isotopomers.

Conclusions

1. Limitations on the grid size available in Gaussian 03 for DFT calculations may introduce significant error into anharmonic calculations. A procedure is outlined for circumventing a deficiency in the G03 code encountered in calculations of vibrational quantities.

2. Anomalies in both harmonic and anharmonic data from the MP2/6-311++G** model suggest that Pople-type basis sets lacking *f* functions may be unsuitable for molecules such as DCM.

3. The incidence of FR is explored throughout the fundamental regions of the spectra of the d_0, d_2, and d_1 isotopomers and found to be slight.

4. Agreement between computed and observed anharmonic constants associated with CH and CD stretching modes is quite good.

5. Anharmonic corrections $\Delta = \omega_{QC} - \nu_{QC}$ in general agree quite well between the various models. Δ values for antisymmetrric CH stretching are greater than those for symmetric CH stretching, resulting in a need for differing scale factors in harmonic force fields scaled to ν_{obsd}.

6. Scaling of the harmonic force fields by refining to both ν_{obsd} and ω_{obsd} data shows anomalies in the B3LYP force fields, pointing to error in the computed νCCl/νCCl interaction force constant. The B3LYP νCCl scale factors are also noticeably higher than average. The mcct force field is preferred and gives a very good account of harmonic and anharmonic fundamental frequencies.

7. Centrifugal distortion constants calculated from the harmonic force fields vary some according to the manner of calculation and the model concerned. They are, however, useful in fitting rotational constants to rotational transitions.

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Supporting Information Available: Anharmonic constants x_{ij} from the MP2/cc-pVTZ model for CH_2Cl_2 (Table S1), CD_2Cl_2 (Table S2), and $CHDCl_2$ (Table S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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