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Non-empirical analysis of isotopic shifts and resonance effects in the infrared high-resolution spectrum of freon-22 (CHF_2Cl), enriched with ^{13}C

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The IR transmittance spectrum of an isotopic mixture of chlorodifluoromethane (CHF_2Cl, Freon-22) with a 33% fraction of ^{13}C and a natural ratio of chlorine isotopes was measured in the frequency range $1400-740\,cm^{-1}$ with a resolution of $0.001\,cm^{-1}$ at a temperature of 20°C. An ab initio calculation of the structure and sextic potential energy surface and surfaces of the components of the dipole moment has been carried out by the the electronic quantum-mechanical method of Möller-Plesset, MP2/cc-pVTZ. Then the potential was optimized by replacing the harmonic frequencies with the frequencies calculated by the electronic method of coupled clusters, CCSD(T)/aug-cc-pVQZ. The fundamental and combination frequencies were calculated using the operator perturbation theory of Van Vleck (CVPTn) of the second and fourth order ($n = 2, 4$). Resonance effects were modeled using an additional variational calculation in the basis up to fourfold VCI excitation (4). The average prediction error for the fundamental frequencies of the ^{12}C isotopologues was $\sim 1.5\,cm^{-1}$. The achieved accuracy made it possible to reliably predict the isotopic frequency shifts of the ^{13}C isotopologues. It is shown that the strong Fermi resonance $\nu_4/2\nu_6$ dominates in the ^{12}C isotopologues and is practically absent in ^{13}C. The literature assumption [Spectrochim. Acta A, 44:553] about the splitting of ν_1 (CH) due to the resonance $\nu_1/\nu_2+\nu_7+\nu_9$ is confirmed. The coefficients of the polyadic quantum number are determined. The analysis made it possible to carry out a preliminary identification of the centers of the vibrational-rotational bands of isotopologues $^{13}CHF_2{}^{35}Cl$ and $^{13}CHF_2{}^{37}Cl$ in the spectrum of the mixture in preparation for individual analyzes of the vibrational-rotational structures of individual vibrational transitions.

Keywords: Chlorodifluoromethane, high-resolution spectrum, Fermi resonance, operator perturbation theory, hybrid potential energy surface.

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Introduction

Chlorodifluoromethane (CHF_2Cl, HCFC-22, Freon-22) is a widespread chemical that is used commercially in the synthesis of fluoropolymers, as a working fluid in refrigeration units, and as a foamer [1]. Freon-22 is present in the Earth's atmosphere [2–4] and can potentially affect chemical processes in the upper atmosphere [5]. Since the expected lifetime of CHF_2Cl in the troposphere is about 15.6 years [6], then upon discharge rate of this compound increasing [7], it can be expected that its role in chemistry of ozone destruction increases [5,8]. Thus, the important role of this compound in ecology, its possible effect on the Earth's ozone layer, and the need to monitor the presence of this substance in the atmosphere cause great interest in studying its spectra in the IR range.

The geometrical parameters of the Freon-22 molecule (r_0-, r_s-, r_z-structures) were obtained from microwave data provided by Cramb et al. (1988) [9], where the inverse harmonic vibrational problem was also solved. Later, microwave spectra were studied in detail by Kisiel et al. (1995) [10] and Blanco et al. (1996) [11]. A reliable equilibrium geometric structure of the molecule was recently established in the paper [12] based on a hybrid method that corrects the experimental rotational constants using the theoretical vibrational-rotational interaction constants.

Freon-22 molecule has C_s symmetry, all nine of its normal modes are active in IR absorption spectra and have a/c type contours for $\nu_1-\nu_6$ (A') or b type for $\nu_7-\nu_9$ (A''). For the first time, the low-resolution IR spectrum of Freon-22 in the gas phase was measured in the paper [13]. The assignment of the frequencies of fundamental and some combination vibrations and overtones was first performed in the paper [14], in which the low-resolution IR spectrum of CHF_2Cl was obtained in liquid argon. Further, similar studies of the spectra of matrix isolation in Ar, Kr, Xe were carried out in the paper [15]. The spectra of Raman scattering in the gas phase were studied in the papers [16,17], and in the liquid and solid phases — in the papers [18–22], while in the paper [16] absolute intensities and depolarization coefficients were measured. Spectra of medium resolution ($0.12-0.5\,cm^{-1}$) in a wide range ($15\,000-350\,cm^{-1}$), vibrational anharmonicity and Fermi resonances have been studied in detail by Brown et al.

(1988) [23]. The Fermi resonance $\nu_4/2\nu_6$ was detected, and a supposition about a random resonance $\nu_1/\nu_2+\nu_7+\nu_9$ was made [23].

The Freon-22 anharmonic force field was first obtained by Palmieri et al. (1995) [24], where harmonic force constants at the MP2 level were combined with cubic and quartic ones obtained by the Hartree−Fock method. Kuramshina et al. (1994) [25] obtained the Freon-22 harmonic force field using a combined method by solving an inverse regularized problem stabilized by nonempirical field at MP2/6-31G* level. By now, the calculation of the potential energy surface needs to be updated in accordance with modern standards (the MP2 method for the anharmonic part of the potential and the CCSD(T) coupled cluster method for harmonic frequencies).

Subsequently, the high-resolution IR spectra of CHF_2Cl were mainly measured (from 0.04 to $0.0007\,cm^{-1}$), which were obtained in the gas phase or in supersonic molecular beams for various fundamental vibrational-rotational bands at different temperatures [26–40]. The vibrational-rotational analysis of the bands of all fundamental vibrational transitions was completed by 2002 with the publication of study on ν_2 and ν_7 [36].

A summary of literature data on high-resolution spectroscopy is given in the book [41]. In the existing papers the spectral resolution of the order of $0.001\,cm^{-1}$ made it possible to measure individual lines of vibrational-rotational transitions, the Doppler widening of which was approximately $0.0015\,cm^{-1}$ at room temperature [38]. The publications also contained the theoretical analysis of the results obtained, the assignment of lines, the study of the Fermi ($\nu_4/2\nu_6$) [40] and Coriolis (ν_3/ν_8, ν_6/ν_9) resonances [38,33].

High-resolution spectra of CHF_2Cl isotopologues were obtained mainly for molecules with natural content of carbon, hydrogen, and chlorine isotopes. The natural concentration of the chlorine isotope ^{37}C1 is quite high (24.2%), which made it possible upon good spectral resolution of the units ($< 0.0024\,cm^{-1}$) and cooling of CHF_2Cl molecules to identify the vibrational-rotational lines of both components $^{12}CHF_2{}^{35}$C1 and $^{12}CHF_2{}^{37}$C1 [28,32,35–38]. However, due to a small isotopic shift between the components with ^{35}C1 and ^{37}C1 ($5.01-0.048\,cm^{-1}$ [38]) the PQR structure of the vibrational-rotational bands of chlorine isotopologues almost completely overlapped, which made it difficult to analyze the spectrum.

Magill et al. (1986) [26] obtained medium-resolution IR and Raman gas spectra (up to $0.04-0.002\,cm^{-1}$) of isotopologues (^{13}C- and D-substituted), carried out the assignment of the bands and investigated $\nu_4/2\nu_6$ resonance. It was shown that the isotopic shifts of the spectra of isotopologues substituted at ^{13}C are much larger than the shifts at ^{37}Cl, and are $25.5\,cm^{-1}$ for ν_3, $26.5\,cm^{-1}$ for ν_8 and $20.35\,cm^{-1}$ for ν_4 [26]. It can be expected that in the isotopic mixture close to equimolar one, the intensity of the vibrational-rotational lines $^{13}CHF_2Cl$, at least for the P-branches of bands ν_3, ν_8, and ν_4 will be comparable to the intensity of lines $^{12}CHF_2Cl$.

Earlier ^{13}C isotope-selective IR multiphoton dissociation of Freon-22 molecules under the action of pulsed radiation of CO_2 laser was studied in detail [42–46]. In the late 90s – early 2000s these works ended in the creation in Russia of a unique laser technology and the corresponding production for the enrichment of ^{13}C, where Freon-22 was the working substance [47,48]. The UV and IR photochemistry of Freon-22 and the effect of intramolecular vibrational redistribution in this molecule under the action of nano- and femtosecond laser pulses [49–53] were studied in detail.

The publications analysis shows the presence of significant gaps in the data concerning the positions of the centers of the vibrational bands of ^{13}C-substituted Freon-22, as well as more complete and reliable information about the effects of anharmonicity: Fermi resonances, intensities of „dark bands“, acquiring intensity due to the wave functions mixing with „bright bands“, isotopic shifts. There is an obvious need for a new study of such effects, based on the use of the most accurate modern non-empirical quantum mechanical calculations. Individual interest is shown to such study, and it is a necessary step for the preparation of a precision analysis of the vibrational-rotational spectra of ^{13}C-substituted Freon-22, which was not carried out before.

The main goal of our researches is to measure and interpret in detail the vibrational-rotational high-resolution IR spectra ($0.001\,cm^{-1}$) of $^{13}CHF_2Cl$ molecules in frequency range of $1400-740\,cm^{-1}$, which includes the bands of fundamental vibrations ν_2, ν_3, ν_4, ν_7 and ν_8. For this purpose the isotopic mixture of $^{12}CHF_2Cl$ and $^{13}CHF_2Cl$ containing 33% of ^{13}C was used.

Experimental part

Freon-22 enriched with ^{13}C up to 33% was synthesized by A.I. Sorokin (Perm Branch of JSC RSC „Applied Chemistry“). The declared content of the main substance was about 99%, which was confirmed by the results of chromatographic analysis. A container with Freon-22 enriched with ^{13}C was connected to a vacuum system, which was pumped out by a vacuum booster pump through a liquid nitrogen trap to a residual pressure of $7.5\cdot10^{-3}$ Torr. The same system was connected to a gas cell 122 mm long, $25\,cm^3$ in volume, with windows made of KBr, which had a vacuum indium seal. All elements of the vacuum system, including the container and cell, were made of stainless steel and Teflon. The cell was filled with CHF_2Cl at a pressure of 1 Torr and, after being disconnected from the vacuum system, was fixed in a special holder.

The infrared spectra of Freon-22 enriched with ^{13}C up to 33% were recorded on BRUKER IFS 125HR Fourier spectrometer with a resolution of $0.001\,cm^{-1}$, averaging over 620 scans at temperature 20°C. To reduce the partial pressure of carbon dioxide and water vapor before the

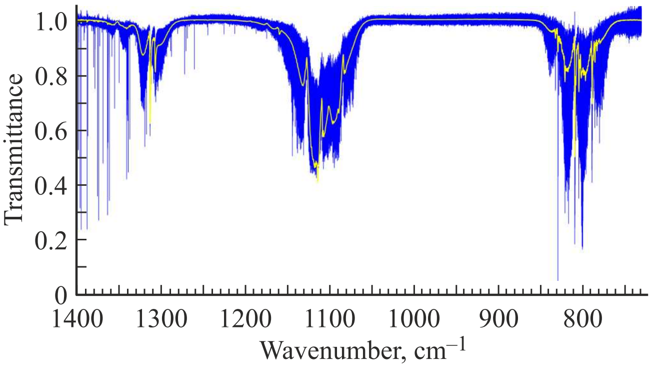

Figure 1. High-resolution infrared spectrum ($0.001\,\mathrm{cm}^{-1}$) of Freon-22 (CHF_2Cl) at pressure 1 Torr and cell length 122 mm with content of $^{13}C = 33\%$ (blue color); the light line shows the low-resolution IR spectrum ($0.1\,\mathrm{cm}^{-1}$) of the same isotopic mixture (yellow color).

Table 1. Experimental (r_s, r_z), semiempirical equilibrium (r_e [12]) and theoretical geometric parameters (Å, deg) of Freon-22 molecule

Parameter	r_s^a	r_z^a	MP2^b	CCSD(T)^c	CCSD(T)^d	r_e [12]
r (C–H)	1.098	1.098	1.0841	1.0862	1.0843	1.0850
r (C–F)	1.346	1.354	1.3379	1.3384	1.3352	1.3363
r (C–Cl)	1.742	1.742	1.7627	1.7640	1.7577	1.7560
∠(HCF)	—	—	109.983	110.037	109.99	109.97
∠(HCCl)	110.8	110.7	109.148	109.421	109.30	109.60
∠(FCCl)	110.5	111.0	109.69	109.611	109.68	109.62
∠(FCF)	107.5	106.6	108.336	108.107	108.20	108.06

Note. a — [9]; b — is present work, basis set cc-pVTZ; c is present work, basis set aug-cc-pVQZ; d is method/basis set: CCSD(T)(ae)/wCVQZ [12].

spectrum recording the volume of the Fourier spectrometer was evacuated by a vacuum pump to residual pressure of about 0.05 Torr. The spectra were recorded using liquid nitrogen cooled detectors based on CdHgTe and a KBr beam splitter. During processing the obtained spectra of Freon-22 were normalized to the transmission spectrum of an empty cell. Besides, the frequency scale in the range of $1496{-}829\,\mathrm{cm}^{-1}$ was corrected by 12 tabulated water lines [54] and two frequencies $^{12}CHF_2Cl$ measured by other authors in [28,38]. After correction the average deviation of these 14 frequencies was $-3.9 \cdot 10^{-6} \pm 2.5 \cdot 10^{-4}\,\mathrm{cm}^{-1}$, which is significantly less than the spectral resolution.

Figure 1 shows the IR spectrum of the isotopic mixture of $^{12}CHF_2Cl$ and $^{13}CHF_2Cl$ containing 33% of $^{13}CHF_2Cl$ with resolution $0.001\,\mathrm{cm}^{-1}$. In the same Figure, against the dark background of the high-resolution spectrum, the light line depicts the low-resolution IR spectrum ($0.1\,\mathrm{cm}^{-1}$) of the same isotopic mixture. In this spectrum, in ν_3 and ν_8 vibration bands, which for $^{12}CHF_2Cl$ merge into the total band centered at $1116\,\mathrm{cm}^{-1}$ and ν_4 centered at $809\,\mathrm{cm}^{-1}$, the isotopologue bands $^{13}CHF_2Cl$ can be clearly observed on long-wavelength branches.

Calculation procedure

The theoretical geometric structure of the Freon-22 molecule was optimized by non-empirical quantum mechanical methods (basis sets) MP2/cc-pVTZ and CCSD(T)/aug-cc-pVQZ using the Gaussian'09 software [55]. A comparison of the literature and theoretical geometrical parameters of the Freon-22 molecule obtained in this paper is given in the Table 1.

Further, for the MP2/cc-pVTZ method the second derivatives of the energy with respect to the Cartesian coordinates were obtained, which were then converted to internal coordinates and used to calculate the normal modes of all studied isotopologues. To obtain the anharmonic sextic force field of each of the isotopologues the numerical differentiation of the analytical second derivatives was used, they were calculated on a 9-point grid for one-dimensional differentiation and a 5-point grid for two-dimensional differentiation:

$$\frac{d}{dx}f(x) = \frac{1}{840h}[672(f_1 - f_{-1}) - 168(f_2 - f_{-2}) + 32(f_3 - f_{-3}) - 3(f_4 - f_{-4}),] \quad (1)$$

$$\frac{d^2 f(x)}{dx^2} = -\frac{1}{5040h^2} \times \begin{bmatrix} 14350 f_0 - 8064(f_1 + f_{-1}) + 1008(f_2 + f_{-2}) \\ -128(f_3 + f_{-3}) + 9(f_4 + f_{-4}) \end{bmatrix}, \quad (2)$$

$$\frac{d^3 f(x)}{dx^3} = \frac{1}{240h^3}[488(f_1 - f_{-1}) - 338(f_2 - f_{-2}) + 72(f_3 - f_{-3}) - 7(f_4 - f_{-4})], \quad (3)$$

$$\frac{d^4 f(x)}{dx^4} = \frac{1}{240h^4}[2730 f_0 - 1952(f_1 + f_{-1}) + 676(f_2 - f_{-2}) - 96(f_3 - f_{-3}) + 7(f_4 - f_{-4})]. \quad (4)$$

Thus, the maximum number of different indices in sextic force constants is four. The grid step was 0.02 in units of dimensional normal coordinates [Å·u$^{1/2}$]. The resulting force field, together with the rotational and Coriolis constants, was used to build Watson vibrational Hamiltonian.

The Schrödinger vibrational equation was solved using the operator version of the Van Vleck perturbation theory (CVPTn) of the second and fourth orders ($n = 2, 4$) [56–58]. Within the framework of CVPT the initial Hamiltonian in operator form, represented as the sum of a zero-order operator and perturbations, undergoes a sequence of K unitary transformations $U = U_K \dots U_2 U_1 H U_1^{-1} U_2^{-1} \dots U_K^{-1}$ which bring it to the required form:

$$\hat{H} = UHU^{-1} = U_K \dots U_2 U_1 H U_1^{-1} U_2^{-1} \dots U_K^{-1}. \quad (5)$$

The goal of this sequence of transformations is the commutability of the transformed operator $\hat{H}$ with the zero order operator H_0, except for resonance terms, which are processed separately under the variational problem VCI(m) in a restricted basis of wave functions. Our experience shows that it is sufficient to use bases with maximum total excitation levels from two to four vibrational quanta ($m = 2$, 3, 4).

The unitary transformations in the CVPT method are defined in exponential form, at that the Hermitian (self-conjugate) operator is the unitary transformation generator:

$$U_k = \exp(iS_k), \quad U_k^{-1}U_k = I, \quad S_k = -S_k^{\dagger}, \quad \langle S_k \rangle_{diag} = 0. \tag{6}$$

The CVPT(n) method is described in detail in the literature [56–59]. For example, the double-transformed Hamiltonian can be obtained after computing the sum of the operators:

$$\hat{H}^{(2)} = H_0 + H_1 + i[S_1, H_0] + H_2 + i[S_1, H_1] - \frac{1}{2}[S_1, [S_1, H_0]] + i[S_2, H_0]. \tag{7}$$

The form of the unitary transformation generators is found from single-type equations

$$i[S_K, H_0] = \hat{H}_K^{(K)} - \hat{H}_K^{(K-1)}. \tag{8}$$

A significant simplification of the CVPT formalism is achieved by transfer from the operators of coordinate and momentum to the creation/annihilation operators of vibrational quanta [57]:

$$q \to 2^{-1/2}(a^{\dagger} + a), \qquad p \to 2^{-1/2}i(a^{\dagger} - a). \tag{9}$$

In this case, the relevant part of the Hamilton operator can be reduced to a normally ordered form:

$$\hat{H}_K^{(K-1)} = \sum_j h_j \prod_{l=1}^{M} \left[(a_l^{\dagger})^{m_{jl}} (a_l)^{n_{jl}} + (a_l^{\dagger})^{n_{jl}} (a_l)^{m_{jl}} \right], \tag{10}$$

and to obtain the required form of the operator S_K, it is necessary to first remove from this operator polynomial the diagonal (d) and resonant (r) operators and apply the formula

$$S_k = -i \sum_{j \neq d,r} h_i \left(\sum_{l=1}^{M} (m_{jl} - n_{jl})\omega_l \right)^{-1} \times \prod_{l=1}^{M} \left[(a_l^{\dagger})^{m_{jl}} (a_l)^{n_{jl}} - (a_l^{\dagger})^{n_{jl}} (a_l)^{m_{jl}} \right]. \tag{11}$$

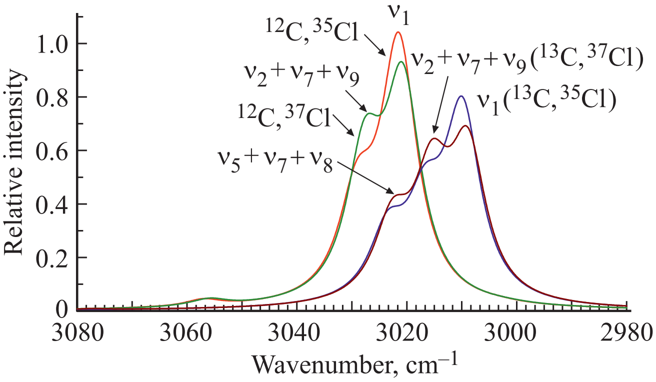

Figure 2. Superposition of calculated IR spectra of four CHF$_2$Cl isotopologues in the range of 3080−2980 cm^{-1}. Splitting of peaks ν_1 is due to random resonance $\nu_1/\nu_2 + \nu_7 + \nu_9$, and in case of ^{13}C isotopologues — also $\nu_1/\nu_5 + \nu_7 + \nu_8$ (see text). Color symbols: ^{12}C, ^{35}Cl — red, ^{12}C, ^{37}Cl — green, ^{13}C, ^{35}Cl — blue, ^{13}C, $^{\{}$37}Cl — brown.

The coefficient in parentheses in front of the operator in equation (11) is responsible for the smallness condition of the canonical transformation that ensures the convergence of the effective Dunham-type Hamiltonian. This coefficient is dimensionless and in practical calculations its certain threshold value $\Xi^{\dagger}$ is used:

$$\Xi_k = \left| h_k \left(\sum_{l=1}^{M} (m_{kl} - n_{kl})\omega_l \right)^{-1} \right| > \Xi^{\dagger}, \tag{12}$$

above which the possibility of vibrational resonance is assumed. The value of the frequency denominator in (12) is responsible for the energy difference between the interacting states, which can be used as an additional resonance criterion:

$$\Delta E = \left| \sum_{l=1}^{M} (m_{kl} - n_{kl})\omega_l \right|. \tag{13}$$

Practical calculation of anharmonic vibrational states and intensities of transitions in the IR spectrum was carried out using ANCO software [59–61] based on potential energy surfaces and dipole moment components obtained. The calculation method was similar to that used in previous studies [62–69]. For graphical simulation of the resulting spectra for a peak with transition energy E_j and IR intensity $I_j^{(IR)}$ (km/mol), a Lorentz-type contour was used,

$$L_j(x) = I_j^{IR} w\pi^{-1} \left[(E_j - x)^2 + w^2 \right]^{-1}, \tag{14}$$

with a fixed half-width $w = 4\,\text{cm}^{-1}$. Scanning of all calculated vibrational levels with a certain discretization step and accumulation of the total intensity into a one-dimensional data array forms the final form of the calculated spectrum. For all four isotopologues the sets of predicted energy levels and their relative intensities are presented graphically in Figs. 2−7 (ranges 3080−2980, 2300−2100, 1750−1500, 1370−1270, 1200−1000 and 850−750 cm^{-1}, respectively).

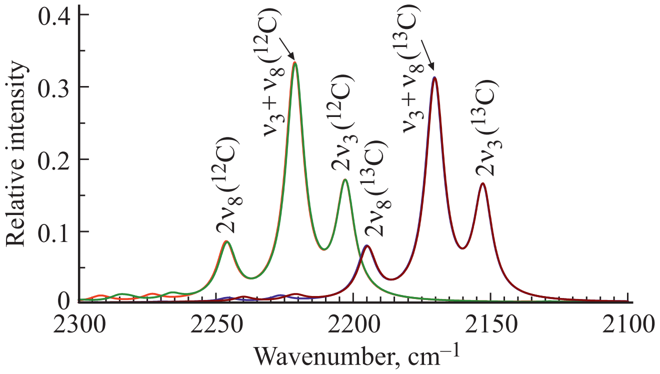

Figure 3. Superposition of calculated IR spectra of four CHF_2Cl isotopologues in the range of 2300–2100 cm^{-1}. Color symbols: $^{12}C, ^{35}Cl$ — red, $^{12}C, ^{37}Cl$ — green, $^{13}C, ^{35}Cl$ — blue, $^{13}C, ^{37}Cl$ — brown.

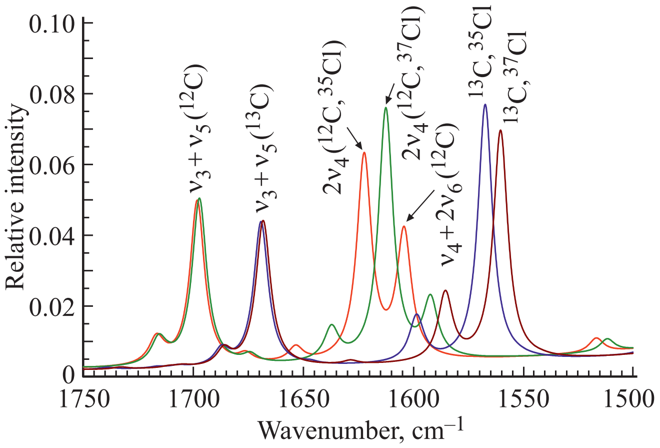

Figure 4. Superposition of calculated IR spectra of four CHF_2Cl isotopologues in the range of 1750–1500 cm^{-1}. Color symbols: $^{12}C,^{35}Cl$ — red, $^{12}C, ^{37}Cl$ — green, $^{13}C,^{35}Cl$ — blue, $^{13}C,^{37}Cl$ — brown.

Results and discussion

Theoretical fundamental frequencies

One of the main theoretical results of this study is the calculation of the sextic force field of four Freon-22 isotopologues in normal coordinates using a hybrid method of replacing harmonic frequencies with their analogs calculated by the high-precision coupled cluster method (CCSD(T)) using a fairly large basis set aug-cc-pVQZ. The calculation of the fundamental frequencies of vibrations of two ^{12}C-isotopologues, carried out using the second-order Van Vleck operator perturbation theory and supplemented by a variational problem in the fourfold excited basis VCI(4) to take into account resonance effects, shows that the theoretical values of the frequencies coincide with the experimental positions of the centers of the bands with a root-mean-square error 1.5 cm^{-1} (Tables 2 and 3). Noteworthy is that all errors have a systematic red shift, which clearly indicates the presence of unaccounted contributions to the calculated force field. The result obtained is undoubtedly a success in non-empirical calculations of the vibrational spectra of polyatomic molecules, which was difficult to predict at the end of the XXth century in the absence of implemented sufficiently advanced and economically viable quantum mechanical methods for the force field calculation. The actual error of fundamental frequencies prediction is only slightly below the threshold of „spectroscopic accuracy" equal to one wave number [70], and this result is achieved for five-atom molecules containing 48 electrons.

The resulting sextic force field and the numerical-analytical implementation of Van Vleck operator perturbation theory made it possible to calculate the fundamental frequencies in the fourth order. Their analysis shows that, with the exception of ν_1 for $^{13}C,^{37}Cl$ isotopologue, the frequency shifts do not exceed 0.8 cm^{-1} as compared with the second order, and the root-mean-square error is improved only slightly. This gives grounds to consider the results obtained in the second order of perturbation theory as sufficiently reliable and to take them as the basis of theoretical model for further theory comparison with experiment, and for making predictions. However, in the mentioned case ν_1 for ($^{13}C,^{37}Cl$) there is blue shift by 5.8 cm^{-1}, which is explained by the redistribution of the contributions of the wave functions of zero approximation at the resonance $\nu_1/\nu_2+\nu_7+\nu_9$.

Vibrational resonances and polyad quantum number

As the calculation within our theoretical model shows, a number of fundamental frequencies of the main molecule (^{12}C, ^{35}Cl) is subjected to resonant effects of various strength. The Table 4 gives a summary of the theoretically predicted vibrational resonances of the Freon-22 main molecule ($^{12}C,^{35}Cl$), ordered in descending order of the „resonance strength"parameter (12).

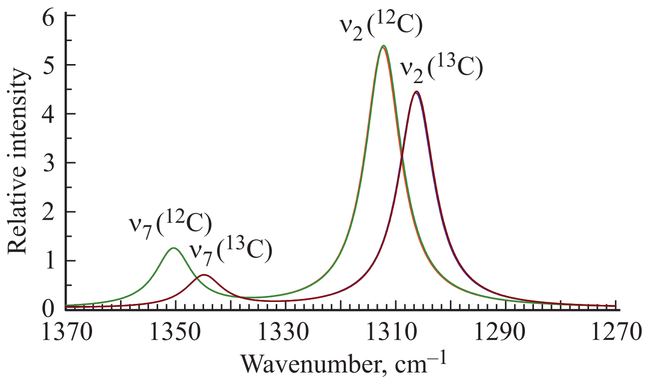

Figure 5. Superposition of calculated IR spectra of four CHF_2Cl isotopologues in the range of 1370–1270 cm^{-1}. Color symbols: $^{12}C,^{35}Cl$ — red, $^{12}C,^{37}Cl$ — green, $^{13}C,^{35}Cl$ — blue, $^{13}C,^{37}Cl$ — brown.

Table 2. Non-empirical harmonic (ω) and fundamental (ν) frequencies (cm^{-1}) of vibrations of Freon-22 ^{12}C-isotopologues, calculated using CVPT2/VCI(4) (PT2) and CVPT4/VCI(4) (PT4) methods with anharmonic hybrid potential MP2/cc-pVTZ and CCSD(T)/aug-cc-pVQZ (see text)

ν_k	Assignment	ω, MP2	ω, CC	ν, PT2	RMSE	ν, experiment	ν, PT4
A' ^{12}CHF$_2$^{35}Cl							
ν_1	ν(CH) symm. stretch.	3193.50	3156.16	3021.45	−0.19	3021.6335 [42]	3021.64
ν_2	δ(ClCH) bend.	1354.65	1340.89	1312.35	−0.74	1313.0936 [36]	1311.91
ν_3	ν(CF$_2$) symm. stretch.	1142.21	1130.91	1107.46	−1.27	1108.7293 [39]	1107.70
ν_4	ν(CCl) stretch.	831.47	822.94	806.52	−2.75	809.2726 [28]	806.57
ν_5	χ(CF$_2$) sciss.	607.04	601.65	595.02	−1.35	596.3714 [31]	594.99
ν_6	δ(FCCl) bend.	420.63	415.95	410.64	−2.29	412.9285 [34]	410.68
A'' ^{12}CHF$_2$^{35}Cl							
ν_7	ρ(CF$_2$) rock.	1402.35	1384.19	1350.39	−1.31	1351.7019 [36]	1350.23
ν_8	ν(CF$_2$) asymm. stretch.	1173.42	1157.07	1127.09	−0.20	1127.2851 [39]	1127.87
ν_9	χ(CF$_2$) twist.	372.85	367.91	364.26	−1.94	366.1972 [34]	364.25
A' ^{12}CHF$_2$^{37}Cl							
ν_1	ν(CH) symm. stretch.	3193.50	3156.16	3020.72	−0.68	3021.3995 [42]	3020.73
ν_2	δ(ClCH) bend.	1354.56	1340.81	1312.18	−0.71	1312.8941 [36]	1311.66
ν_3	ν(CF$_2$) symm. stretch.	1142.20	1130.90	1107.41	−1.27	1108.6813 [39]	1107.66
ν_4	ν(CCl) stretch.	828.42	819.88	801.35	−3.15	804.502 [28]	801.40
ν_5	χ(CF$_2$) sciss.	606.14	600.79	594.15	−1.25	595.4 [30]	594.12
ν_6	δ(FCCl) bend.	415.51	410.88	405.65	−2.27	407.9182 [34]	405.69
A'' ^{12}CHF$_2$^{37}Cl							
ν_7	ρ(CF$_2$) rock.	1402.34	1384.18	1350.37	−1.31	1351.6814 [36]	1350.16
ν_8	ν(CF$_2$) asymm. stretch.	1173.42	1157.06	1126.85	−0.28	1127.1227 [39]	1127.62
ν_9	χ(CF$_2$) twist.	370.87	365.96	362.35	−1.92	364.2667 [34]	362.35

If we consider the degrees of operators for vibrational modes as integer vector components, then the resulting set of vectors can be used to construct a vector of polyad quantum number coefficients orthogonal to resonance vectors [61,71] (in our case, the operator $3^{+2}\ 8^{-2}$ is linearly dependent):

$$P = 8\nu_1 + 3\nu_2 + 3\nu_3 + 2\nu_4 + 2\nu_5$$
$$+ \nu_6 + 3\nu_7 + 3\nu_8 + \nu_9.$$

Similar sets of polyad coefficients can be obtained for other isotopologues besides the main molecule. Preliminary analysis shows that a small variation in the strength of the resonances affects the final form of such polyad coefficients.

The Table 4 shows that ν_2, ν_4, ν_8 of the main molecule participate in Fermi resonances, and overtones $2\nu_2, 2\nu_3, 2\nu_7, 2\nu_8$ participate in Darling–Dennison resonances. Let us now consider in more detail three resonances involving the fundamental frequencies ν_1, ν_2, ν_4, ν_8. From theory point of view the interpretation of the structure of the doublet 3024.55(?)-3021.27(ν_1) with narrow splitting $\sim 3\,\text{cm}^{-1}$ is of great interest, this was discussed in the series of papers [23,27,32,72]. Mackenzie (1984) [72] identified these peaks as Q-branches, implicitly assuming resonance. In chronologically second paper [23] two assumptions were put forward about the nature of this doublet — interaction with „hot“ transition $(\nu_1 + \nu_9) - \nu_9$ or with three-quantum state $\nu_2 + \nu_7 + \nu_9$. A very detailed discussion of the nature of this doublet is given in subsequent paper by Amrein et

Table 3. Non-empirical harmonic (ω) and fundamental (ν) frequencies (cm^{-1}) of vibrations of Freon-22 ^{13}C-isotopologues, calculated using CVPT2/VCI(4) (PT2) and CVPT4/VCI(4) (PT4) methods with anharmonic hybrid potential MP2/cc-pVTZ and CCSD(T)/aug-cc-pVQZ (see text); experiment data were taken from the paper [26]

ν_k	Assignment	ω, MP2	ω, CC	ν, PT2	RMSE	ν, experiment	ν, PT4
A' ^{12}CHF$_2$^{35}Cl							
ν_1	ν(CH) symm. stretch.	3183.46	3146.29	3009.87	−0.73	3010.6	3009.94
ν_2	δ(ClCH) bend.	1348.86	1335.00	1306.33	−0.87	1307.2	1305.90
ν_3	ν(CF$_2$) symm. stretch.	1115.72	1104.64	1082.17	−1.33	1083.5	1083.45
ν_4	ν(CCl) stretch.	808.12	799.97	786.65	−2.25	788.9	786.66
ν_5	χ(CF$_2$) sciss.	602.72	597.38	591.07	−1.23	592.3	591.04
ν_6	δ(FCCl) bend.	420.39	415.69	410.48	−2.32	412.8	410.51
A'' ^{13}CHF$_2$^{35}Cl							
ν_7	ρ(CF$_2$) rock.	1395.95	1378.18	1344.85	−1.15	1346	1344.65
ν_8	ν(CF$_2$) asymm. stretch.	1146.06	1129.90	1101.32	0.32	1101	1102.05
ν_9	χ(CF$_2$) twist.	371.35	366.42	362.87	−0.13	363	362.86
A' ^{13}CHF$_2$^{37}Cl							
ν_1	ν(CH) symm. stretch.	3183.46	3146.2	3008.87	−1.73	3010.6	3014.70
ν_2	δ(ClCH) bend.	1348.76	1334.90	1306.19	−1.01	1307.2	1305.68
ν_3	ν(CF$_2$) symm. stretch.	1115.72	1104.63	1082.11	−1.39	1083.5	1082.41
ν_4	ν(CCl) stretch.	804.98	796.80	783.22	−2.28	785.5	783.24
ν_5	χ(CF$_2$) sciss.	601.85	596.55	590.22	−1.28	591.5	590.18
ν_6	δ(FCCl) bend.	415.27	410.63	405.50	−2.30	407.8	405.53
A'' ^{13}CHF$_2$^{37}Cl							
ν_7	ρ(CF$_2$) rock.	1395.94	1378.17	1344.84	−1.16	1346	1344.59
ν_8	ν(CF$_2$) asymm. stretch.	1146.05	1129.90	1101.12	0.12	1101	1101.89
ν_9	χ(CF$_2$) twist.	369.36	364.46	360.95	−2.05	363	360.93

al. (1988) [27], in which both previous ones are cited, and of the five possible explanations, (a) ν_1 interaction with „hot“ transition, (b) Coriolis resonance at high values J are assumed as most probable. Finally, Fraser et al. (1992) [32] as a result of a detailed analysis of the high-resolution vibrational-rotational spectrum stated that the issue of the nature of this splitting remains unresolved and requires additional experimental analysis at higher temperatures.

The non-empirical vibrational calculation carried out by us makes it possible to clarify the issue of the doublet nature of Q-branches 3024.55−3021.27 observed in the main molecule and resulting from the ν_1 resonance with the „dark“ transition. Indeed, the value of the anharmonic force constant $\varphi_{1279} = 4.2\,\mathrm{cm}^{-1}$ allows the appearance of a purely oscillatory resonance $\nu_1/\nu_2 + \nu_7 + \nu_9$, the possibility of which was specified by Brown et al. (1988) [23] and rejected by Amrein et al. (1988) [27]. Our calculation of CVPT2/VCI(4) confirms the presence of this vibrational resonance, although the calculated splitting ($7.7\,\mathrm{cm}^{-1}$) somewhat exceeds the experimental value. At that the predicted value $\nu_1 = 3021.4\,\mathrm{cm}^{-1}$ is close to the observed value. A similar resonance is also predicted for the ^{13}C, ^{37}Cl isotopologue. The calculation predicts another interesting effect — the formation of a resonant triplet $\nu_1/\nu_2 + \nu_7 + \nu_9/\nu_5 + \nu_7 + \nu_8$ in the case of both ^{13}C isotopologues, which can be seen in Fig. 2. This prediction must be compared with experimental data, which may be the subject of further studies.

Equally important is the Fermi resonance $\nu_4/2\nu_6$, which has the highest value of „resonance strength“ parameter $\Xi = 0.4906$ [61,73]. This resonance was studied in detail in a number of papers [14,26,23,28,24,40]. However, there were no data on this resonance behavior in ^{13}C isotopologues. The theoretical value of the

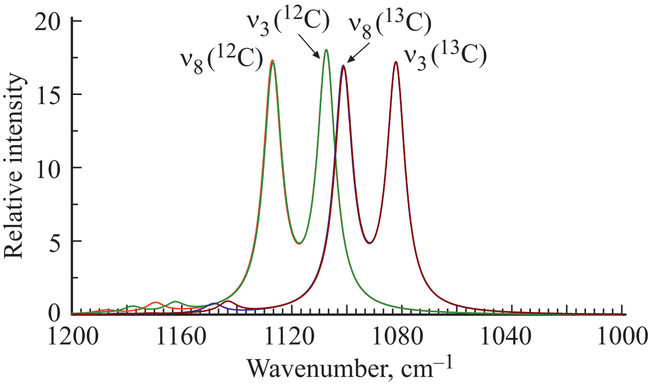

Figure 6. Superposition of calculated IR spectra of four CHF_2Cl isotopologues in the range of 1200−1000 cm^{-1}. Color symbols: $^{12}C,^{35}Cl$ — red, $^{12}C,^{37}Cl$ — green, $^{13}C,^{35}Cl$ — blue, $^{13}C,^{37}Cl$ — brown.

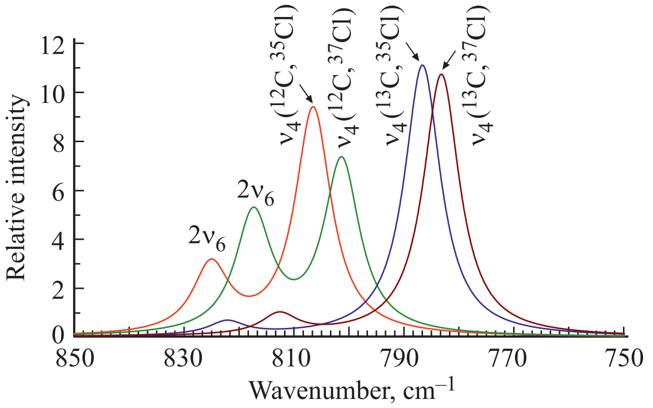

Figure 7. Superposition of calculated IR spectra of four CHF_2Cl isotopologues in the range of 850−750 cm^{-1}. Color symbols: $^{12}C,^{35}Cl$ — red, $^{12}C,^{37}Cl$ — green, $^{13}C,^{35}Cl$ — blue, $^{13}C,^{37}Cl$ — brown.

force constant $\varphi_{466} = 61.5\,\mathrm{cm}^{-1}$ is in good agreement with the experimentally found Fermi resonance constant $W = \varphi_{466}/4 = 15.5\,\mathrm{cm}^{-1}$ found in the paper [23]. In this study [23] a large number of hot transitions associated with partners of the Fermi resonance $\nu_4/2\nu_6$ were identified. In obtained high-resolution spectrum (Fig. 8) the previously observed [23] peaks 832.0 ($3\nu_6 - \nu_6$), 828.1 ($2\nu_6 + \nu_9 - \nu_9$) and 827.4 cm^{-1} ($2\nu_6 + \nu_5 - \nu_5$) of isotopologue ^{12}C, ^{35}Cl, and also peak 824.2 cm^{-1} ($3\nu_6 - \nu_6$) of the isotopologue ^{12}C, ^{37}Cl are also clearly visible. This range may contain similar peaks corresponding to hot transitions of ^{13}C isotopologues, but their detailed study is the subject of a separate paper. Concerning the Fermi resonance for ^{13}C isotopologues, the calculation shows its significant weakening when carbon is replaced by a heavier one, which can be seen in the simulated spectrum in Fig. 7. Comparison of the calculation (822.2 cm^{-1}) with the experimental spectrum makes it possible to assign the peak 820.8 cm^{-1} to the resonant overtone $2\nu_6$ of the isotopologue ^{13}C, ^{35}Cl.

Table 4. Theoretical characteristics of * vibrational resonances of Freon-22 ($^{12}C,^{35}Cl$)

№	$\bar{\omega}_j$	Δ_j	h_j	Ξ_j	$\hat{R}_j$
1	830.7	11.4	5.57	0.4906	$4^{+1}\ 6^{-2}$
2	3150.4	9.9	4.43	0.4469	$1^{-1}\ 5^{+1}\ 7^{+1}\ 8^{+1}$
3	1175.9	37.8	8.68	0.2297	$4^{+1}\ 8^{-1}\ 9^{+1}$
4	2289.1	49.9	6.31	0.1265	$3^{+2}\ 8^{-2}$
5	2508.0	19.0	2.35	0.1238	$2^{+1}\ 3^{-1}\ 7^{-1}\ 8^{+1}$
6	2727.0	87.9	10.73	0.1221	$2^{-2}\ 7^{+2}$
7	1292.3	98.4	10.86	0.1104	$2^{-1}\ 4^{+1}\ 6^{+1}$
8	1985.2	6.4	0.61	0.0947	$4^{+1}\ 5^{-1}\ 7^{-1}\ 8^{+1}$
9	1538.5	23.4	2.13	0.0911	$3^{+1}\ 6^{+1}\ 8^{-1}\ 9^{-1}$

* *Note.* $\bar{\omega}_j$ is average harmonic frequency of the states participating in the resonance; Δ_j is harmonic denominator in the expression for the S-operator (see equations (11)−(13)); h_j is constant in front of the (transformed) resonant operator; Ξ is „resonance strength“, quotient $h_j \cdot \Delta_j^{-1}$; $\hat{R}_j$ is a resonant operator (without factor h_j).

As can be seen from the Table 4, the theoretical calculation predicts the presence of a weak Fermi resonance $\nu_2/\nu_4 + \nu_6$, to which the force constant $\varphi_{246} = 30.8\,\mathrm{cm}^{-1}$ corresponds. In the paper [36] it is suggested that experimental evidence of resonance factors affecting ν_2 can be explained by the influence of $\nu_5 + \nu_9$. However, our analysis rather explains these experimental facts by the formation of the resonant triad $\nu_2/\nu_4 + \nu_6/3\nu_6$, in which the excited resonance $\nu_4/2\nu_6$ participates.

Although the theoretical model predicts the presence of the resonance $\nu_8/\nu_4 + \nu_9$ (Table 4), its experimental study is difficult due to the presence of the vibrational-rotational Coriolis resonance ν_3/ν_8, which was studied in detail in the papers [27,29,35,38,39]. According to our calculation, in main molecule $^{12}C,^{35}Cl$ the triad $\nu_8/\nu_4 + \nu_9/2\nu_6 + \nu_9$ (1127.1/1169.6/1187.1 cm^{-1}) is formed, at that the composite tone $\nu_4 + \nu_9$ increases intensity from 0.12 to 8.2 km/mol, and state $2\nu_6 + \nu_9$ — from 0.06 to 2.4 km/mol. Our high-resolution spectrum shows the presence of three Q-branches in this range with approximate wavenumbers 1159.3, 1160.7, 1174.6, and 1187.0 cm^{-1}, which can be interpreted as an experimental manifestation of the corresponding resonant states of a mixture of isotopologues, while in the low-resolution spectrum only 1159.3 cm^{-1} peak is sharp enough. The paper [26] shows in the low-resolution spectrum the presence of close in frequency peaks 1178 cm^{-1} for isotopologues ^{12}C and 1181.1 cm^{-1} for ^{13}C. We failed to find data on vibrational transitions in this region of the spectrum among high-resolution vibrational-rotational studies. This fact proves the importance of preliminary theoretical information about vibrational effects, which can be used in subsequent studies of the vibrational-rotational structure in this region of the spectrum.

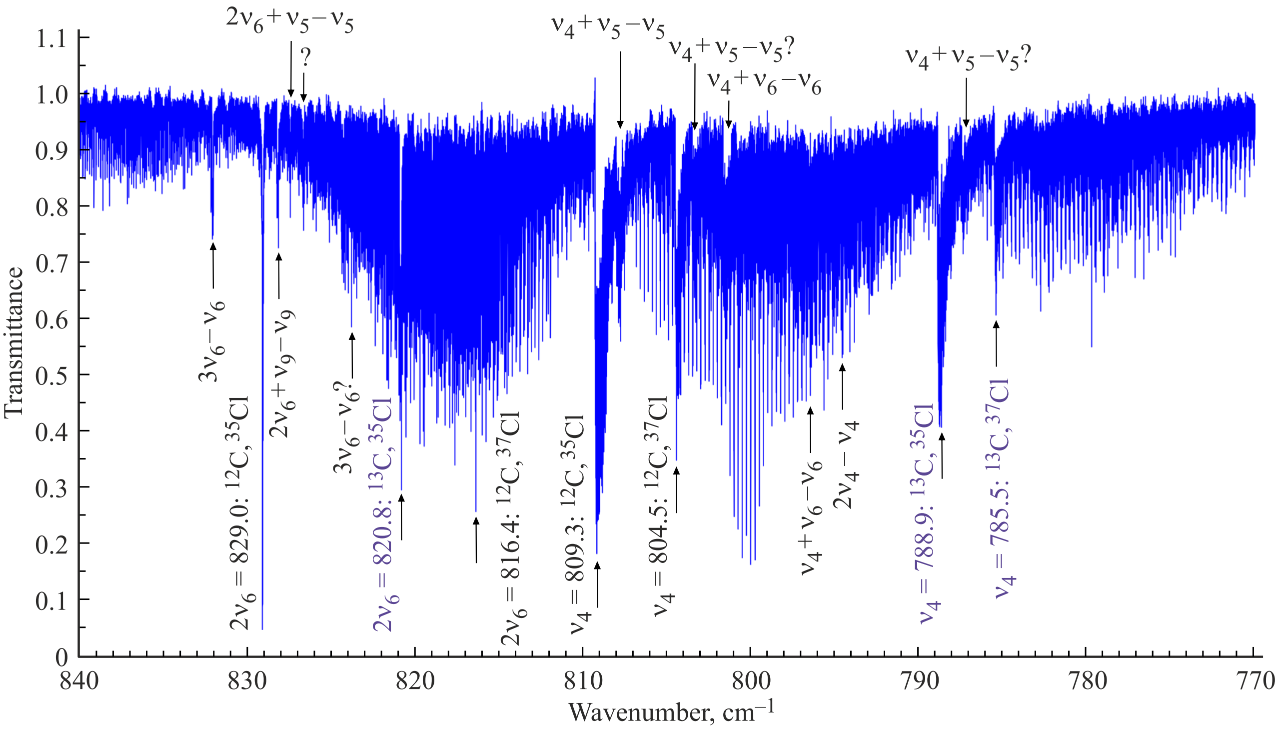

Figure 8. Fragment of high-resolution IR spectrum of Freon-22 enriched (33%) with ^{13}C isotopologues. In the Figure two peaks ν_4 and peak $2\nu_6$, related to ^{13}C isotopologues, are shown in purple. The assignment of number of „hot" transitions is according to Brown et al. (1988) [23].

Multiquantum transitions

As can be seen from Fig. 3, in the range of $2300-2100\,\mathrm{cm^{-1}}$, three combined transitions are observed for each isotopologue, $2\nu_8$, $\nu_3+\nu_8$ (A''), $2\nu_3$. All these transitions have intensity sufficient for experimental detection without borrowing from „bright" transitions. For example, for the main isotopologue the intensity is 4.18 km/mol. These transitions were observed experimentally (see spectrogram 10 in [23]): 2245, 2223.3 and $2205.3\,\mathrm{cm^{-1}}$, which agrees well with the calculation (^{12}C,^{35}Cl): 2246.3, 2221.3 and $2202.9\,\mathrm{cm^{-1}}$. Figure 4 illustrates an important area where a significant variability of the spectra depending on isotopes substitution is observed. This region of the spectrum was studied in the paper [23] (spectrogram 3), where a high level of correlation with our theoretical calculation is also observed.

Our experience shows [68] that three-quantum transitions often have an unperturbed intensity sufficient for experimental observation. Indeed, for the main molecule, for example, the state $\nu_4+2\nu_9$ $(1143.6684\,\mathrm{cm^{-1}})$ [39] identified experimentally during high-resolution spectrum analysis has a predicted intensity of 0.05 km/mol and a frequency of $1136.7\,\mathrm{cm^{-1}}$ with no intensity borrowing from the nearest „bright" bands. The transition $3\nu_9$ $(1098.7691\,\mathrm{cm^{-1}})$ [39], which is close in frequency, also has a small, but sufficient for observation, own theoretical intensity of 0.004 km/mol $(1093.0\,\mathrm{cm^{-1}})$, and also has no predicted intensity borrowing.

Conclusion

Freon-22 is a traditional object of close attention in terms of experimental vibrational and vibrational-rotational spectroscopy in the IR range. At the same time, for ^{13}C-substituted isotopologues (^{35}Cl, ^{37}Cl) there are no published studies of the structures of high-resolution vibrational-rotational bands, and the latest work on the anharmonic vibrational analysis is dated 1995 [24].

This study is the first publication in a series of works related to resonant polyads in a wide range of vibrational transitions and the analysis of vibrational-rotational bands of Freon-22 ^{13}C substituted isotopologues in the frequency range of $1400-740\,\mathrm{cm^{-1}}$. Using the hybrid method, a non-empirical anharmonic sextic force field was calculated, which ensures the coincidence of the predicted fundamental frequencies for two ^{12}C isotopologues with an error of about $1.5\,\mathrm{cm^{-1}}$. This made it possible to predict isotopic shifts for ^{13}C isotopologues. The calculation made it possible to reveal the most variable regions of the spectrum, in which isotope substitution gives the maximum separation of the peaks (for example, $1650-1550$ and $850-750\,\mathrm{cm^{-1}}$).

The anharmonic analysis of four molecules also provided detailed information on the nature and strength of resonance effects, which in turn is necessary for the interpretation of multiquantum transitions. In particular, the non-empirical calculation confidently predicts and explains the strong random resonance $\nu_1/\nu_2+\nu_7+\nu_9$ in the main molecule, leading to the doublet 3024.55 and 3021.27 cm^{-1} formation. The effectiveness of the method used for obtaining the hybrid force field and solution on its basis of the direct anharmonic oscillatory problem is demonstrated.

The performed analysis made it possible to preliminary identify the centers of the vibrational-rotational bands $^{13}CHF_2{}^{35}Cl$ and $^{13}CHF_2{}^{37}Cl$ in the spectrum of mixture while preparing for individual analyzes of the vibrational-rotational structures of individual vibrational transitions.

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Conflict of interest

The authors declare that they have no conflict of interest.

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