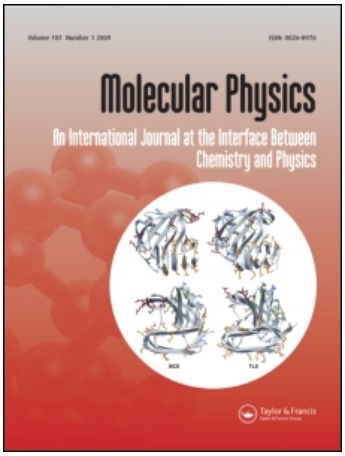

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INVITED ARTICLE

High resolution infrared spectroscopy and global vibrational analysis for the CH_3D and CHD_3 isotopomers of methane†

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We report infrared spectra of CH_3D and CHD_3 in the range 2900 to 9000 cm^{-1} measured with the Zürich high resolution Fourier transform infrared (FTIR) interferometer Bruker IFS 125 prototype (ZP 2001) at 80 K in a collisional-cooling cell with optical paths ranging from 5 to 10 m. In all, 57 new ro-vibrational bands of CH_3D and 40 for CHD_3 were assigned and analysed. Using a strategy of the direct assignment of the $J=0$ states of excited vibrational levels, precise experimental values of the band centres with uncertainties in the range of about 0.0001 to 0.0003 cm^{-1} were obtained. Including 15 previously known band centres of CH_3D and 12 previously known band centres of CHD_3, these data were used as the initial information for the determination of the harmonic frequencies, anharmonic coefficients, and vibrational resonance interaction parameters in an effective hamiltonian. A joint set of 64 parameters reproduces the 124 experimental vibrational energies of both molecules up to 6500 cm^{-1} with a root mean deviation of $d_{rms}=0.73\,cm^{-1}$. The results are discussed in relation to intramolecular dynamics on a global potential hypersurface of methane, intramolecular vibrational redistribution, and the spectroscopy of the atmospheres of the earth and planetary systems.

Keywords: infrared spectroscopy; vibration–rotation spectra; CH_3D; CHD_3; overtone and combination bands; spectroscopic parameters; isotopes; methane; FTIR; intramolecular quantum dynamics; potential hypersurfaces; resonances

1. Introduction

Methane is the prototypical hydrocarbon with fundamental importance ranging from the theory of chemical bonding [1,2], rotational dynamics in symmetrical molecules [3], our understanding of the structure of potential hypersurfaces [4–9], unimolecular reaction rate theory [10,11], fundamental bimolecular reaction dynamics [12–15], to even the fundamental physics of chirality and parity violation [16–19]. Methane has also been studied in the context of accurate multidimensional calculations of vibrational dynamics [4,20–25]. Apart from these fundamental aspects methane plays a central role in various fields of science and technology. We might mention here combustion and environmental processes, atmospheric chemistry in the context of the greenhouse effect, planetary science and astrophysics. In all these contexts the understanding of the methane spectra is essential.

The present work is part of a large effort to unravel methane's rovibrational spectra and dynamics up to high vibrational excitations. Our recent work on the spherical top isotopomers $^{12}CH_4$ and $^{13}CH_4$ provides also a guide to the extensive literature impossible to cite in completeness here [26–29]. Recently, we have provided high resolution analyses for the isotopomer CD_2H_2 giving a rather complete picture of vibrational state dynamics covering the spectral range from low excitations to about 6500 cm^{-1} [30–32]. This asymmetric top molecule has many advantages for such an initial study of deutero isotopomers. Here we turn our attention to the symmetric top isotopomers CH_3D and CD_3H. These isotopomers are of interest for a number of reasons. CH_3D is obviously the most abundant deutero isotopomer in natural environments allowing for its detection in the Earth's atmosphere and also in an astrophysical context. CD_3H has been a prototype for anharmonic intramolecular quantum dynamics arising from the strong and very selective coupling between the CH stretching and CH bending modes [33,34]. The isolated CH chromophore in this molecule

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†Dedicated to R.N. Zare on the occasion of his 70th birthday.

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provides a spectroscopic window to this mode selective dynamics by allowing analyses extending to excitations exceeding 2 eV (18,500 cm^{-1}), achieved already more than two decades ago [7,20], similar to the case of CF_3H [35,36]. However, these early results were mostly limited to the levels of the CH chromophore itself, excluding other modes. In addition, the spectra taken then were of limited resolution. Recent progress has allowed us to derive highly accurate vibrational level positions including excitation of all modes. The experimental approach involves spectra recorded at sufficiently low temperature either in supersonic jet expansions [29,37] or collisional-cooling cells [32] in such a way that a correct and precise assignment of transitions to the $J=0$ rotational level of the excited state checked by combination differences in the lower state is possible. By adding the known rotational energy of the lower level of the transition in the vibrational ground state, one obtains a direct and precise result depending on the resolution of the spectra and the signal-to-noise level in the spectra for the excited vibrational level energies. The main advantage of this strategy is to avoid a complete global rovibrational analysis of large numbers of interacting levels. Such a complete global analysis has been done successfully for the main isotopomer $^{12}CH_4$ only recently up to the octad region around 4500 cm^{-1} consisting of 35 interacting levels [26]. We are able now to present correct and precise assignments using our direct approach for 57 newly observed vibrational levels of CH_3D in addition to 15 previously known band centres and for 37 vibrational levels of CD_3H in addition to 10 band centres previously analysed. Our new results extending to 6500 cm^{-1} and beyond will provide benchmarks for the understanding of the vibrational dynamics of these isotopomers. A preliminary account of some of our results has been presented in [38,39]. A few bands of CH_3D were subsequently also analysed in [40].

2. Experimental

The Fourier transform infrared (FTIR) spectra of CH_3D and CD_3H have been recorded in the wavenumber range from 2800 to 9000 cm^{-1} with the Zürich FTIR spectrometer Bruker IFS 125 prototype 2001 [41–43]. The nominal instrumental resolution, defined by $1/d_{MPOD}$ (maximum optical path difference) ranged from 0.0027 to 0.0048 cm^{-1} resulting in essentially Doppler limited spectra. The Doppler widths at 80 K range from about 0.004 cm^{-1} at 2800 to 0.0096 cm^{-1} at 6600 cm^{-1}. About 100 spectra were typically co-added in each spectral region. A multi-reflection collisional cooling cell based on White optics and embedded in a Dewar was used for recording the cold spectra [43] similar to the design described in [44–46]. Optical path lengths ranging from 5 to 10 m were used for the measurements. More details of the experimental setup and procedures can be found in [43].

Most of the CH_3D and CD_3H spectra were taken at about 80 K. The total sample pressure of a mixture of CH_3D/CD_3H and He in the cell ranged from 2.8 to 3.5 mbar in most cases. In addition, spectra with a pressure of 0.5 mbar were recorded in order to measure the strong lines without saturation. Pressure broadening can be neglected under these conditions. All spectra were self-apodised. The aperture used was 1 mm. Table 1 summarises the experimental parameters. The wavenumbers were calibrated with OCS at room temperature (2900 to 3600 cm^{-1}) [47] and with $^{12}CH_4$ from 3000 to 6000 cm^{-1} [26,48]. The deuterated samples were purchased from Cambridge Isotope Laboratories. The identity, chemical and isotopic purity (specified to be better than 98%) was obvious from the spectra.

The absolute wavenumber accuracy of non-blended, unsaturated and not too weak lines (about 10,100 assignments) can be estimated to be better than 10^{-4} cm^{-1} in the range from 2800 to 6600 cm^{-1}.

3. Theoretical background: symmetry and Hamiltonian model

3.1. *Point group and molecular symmetry group for the C_{3v} isotopomers of methane*

CH_3D is a prolate symmetric top and CHD_3 is an oblate symmetric top with an equilibrium geometry

Table 1. Experimental setup for the regions 2900–6500 cm^{-1} of the infrared spectrum of CH_3D and CHD_3.

Region /cm^{-1}	Resolution /cm^{-1}	Windows	Source	Detector	Beamsplitter	Opt. filter /cm^{-1}	Aperture /mm	ν_{mirror} /(kHz)	Electr. filter /cm^{-1}	Calib. gas
2800–3700	0.0027	KBr	Globar	InSb	CaF_2	3000–3600	1.0	40	2600–3700	OCS [47]
3300–4300	0.0033	KBr	Tungsten	InSb	CaF_2	3400–4400	1.0	40	2800–5500	
4100–6000	0.0033	KBr	Tungsten	InSb	CaF_2	4100–6000	1.0	40	3200–6300	$^{12}CH_4$ [26,48]
5100–6500	0.0048	KBr	Tungsten	InSb	CaF_2	5500–6200	1.0	40	3600–7800	

corresponding to the C_{3v} point group of order 6 (Figure 1).

This point group is isomorphous to the molecular symmetry group M_{S6}, which is a subgroup of the permutation inversion group S_3^* applicable to both isotopomers of methane if the tunnelling substructure of the levels of methane and parity are considered explicitly [49,50].

Table 2 provides the character table for C_{3v} and M_{S6} as well as the induced representation $\Gamma_m \uparrow S_3^*$ generated by the motional species Γ_m in M_{S6}. This is thus the structure of sublevels of A_1, A_2, and E in C_{3v} (M_{S6}) including tunnelling, motional and parity assignment for S_3^* (letter symbol with exponent + for positive parity, − for negative parity providing the symmetry

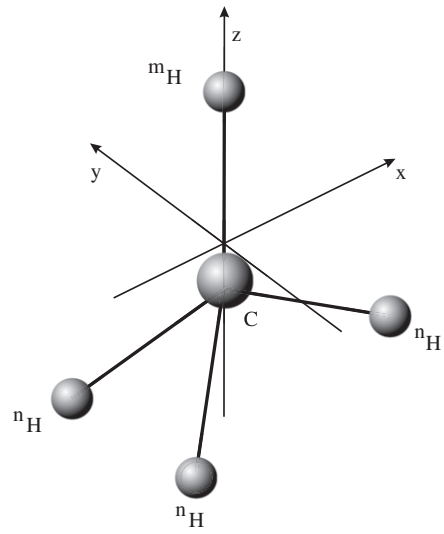


Figure 1. Equilibrium structure of the CH_3D molecule and axes definitions used in the present work ($n=1$, $m=2$ für CH_3D, a similar definition applies to CHD_3 with $n=2$, $m=1$, but a shift of the centre of mass).

Table 2. Character table for C_{3v} and the isomorphous group M_{S6} with the induced representations $\Gamma(M_{S6}) \uparrow S_3^*$. The point group operations C_3, σ_v follow standard notation [51] and for the permutations the common cyclic notation is used [49,50,52] with a star indicating space inversion operations. For the irreducible representations the conventional point group labels are used, whereas the species in S_3^* indicate pure permutational species by the letter symbol and parity by the exponent + or − (see [49,50,52,53] for this convention).

$\Gamma(C_{3v})$ $\Gamma(M_{S6})$	E E	$2C_3$ 2(123)	$3\sigma_v$ $3(12)^*$	$\Gamma_m \uparrow S_3^*$
A_1	1	1	1	$(A_1^+) + A_2^-$
A_2	1	1	−1	$A_2^+ + (A_1^-)$
E	2	−1	0	$E^+ + E^-$

property under the space inversion operation, $\hat{P}$ or E^*). At the resolution of our experiments the tunnelling substructure cannot be observed and thus one might usually label all rovibronic levels by the species A_1, A_2, E in C_{3v}. However, because of the generalised Pauli principle and approximate separability of rovibrational and nuclear spin wavefunctions, the total allowed symmetry species are the product of the 'motional' (rovibronic or rovibrational) species Γ_m and nuclear spin species Γ_{ns} with $\Gamma_m \otimes \Gamma_{ns} = A_2^{\pm}$ for the protons (Fermions), say in CH_3D. The 2^3 nuclear spin functions for the three protons form a reducible representation $D_R = 4A_1^+ + 2E^+$, where the four A_1^+ functions correspond to total (H_3) nuclear spin $I=3/2$ ($-3/2 \leqslant M_I \leqslant +3/2$) and the two E^+ functions to total (H_3)-nuclear spin $I=1/2$ (with $M_I=\pm 1/2$). One can write the (H_3)-nuclear spin multiplets as $^4A_1$ and ^2E. Thus the motional (rovibronic) wave functions of species A_2^+ and A_2^- occur combined with nuclear spin species A_1^+ and total (H_3)-nuclear spin ($I=3/2$) and the motional species E^+ and E^- occur with nuclear spin species E^+ (and $I=1/2$). The $A_1^{\pm}$ motional species have no Pauli-allowed partner among the nuclear spin functions and thus are forbidden by the generalised Pauli principle in the case of CH_3D. This is indicated by the parentheses in $\Gamma_m \uparrow S_3^*$ in Table 2. From this consideration one sees that assigning a symmetry species in S_3^* to the levels of the C_{3v} molecule, CH_3D provides actually additional information. A_1 levels (in C_{3v}) are actually pure A_2^- in S_3^*, with well-defined negative parity, and similarly A_2 levels in C_{3v} result in A_2^+ with pure positive parity and no tunnelling doublet structure. For levels of symmetry species E in C_{3v} one finds a non-resolved tunnelling doublet E^+ and E^- with levels of different parity (and both combining with (H_3)-nuclear spin $I=1/2$ and thus an extra degeneracy of 2 from $m_I=\pm 1$). Of course, in all cases the further nuclear spin from the one deuteron in CH_3D (with $I_D=1$) has to be added to the considerations.

Completely analogous considerations apply to CHD_3 where the 3^3 nuclear spin functions of (D_3) form a reducible representation corresponding to the (D_3)-nuclear spin multiplet notation $^7A_1^+(I=3) + {}^3A_1^+(I=1) + {}^1A_2^+(I=0) + {}^5E^+(I=2) + {}^3E^+(I=1)$ [49]. These spin functions for the boson D combine with the motional functions to give Pauli-allowed overall totally symmetric symmetry species $A_1^{\pm}$. Thus all levels in C_{3v} (A_1, A_2, E) result in tunnelling doublets of different parity $A_1^{\pm}$, $A_2^{\pm}$ and $E^{\pm}$ in S_3^* and a more complex D_3-nuclear spin multiplet structures as given by the reducible representation indicated above. Again, the extra nuclear spin (1/2) from the single H has to be considered in addition.

Table 3. Values of the fundamental band centres of the CH_3D molecule (in cm^{-1}).

ν	Γ	$\nu_0^{exp.}/cm^{-1}$	Ref.	Assignment
ν_1	A_1	2969.512	[25]	CH_3 s-stretch
ν_2	A_1	2200.041	[25]	CD stretch
ν_3	A_1	1306.848	[54]	CH_3 s-deform
ν_4	E	3016.713	[25]	CH_3 d-stretch
ν_5	E	1472.022	[54]	CH_3 d-deform
ν_6	E	1166.103	[54]	CH_3 rock

Table 4. Values of the fundamental band centres of the CHD_3 Molecule (in cm^{-1}).

ν	Γ	$\nu_0^{exp.}/cm^{-1}$	Ref.	Assignment
ν_1	A_1	2992.786	[This work][a]	CH stretch
ν_2	A_1	2142.583	[56]	CD_3 s-stretch
ν_3	A_1	1004.548	[55]	CD_3 s-deform
ν_4	E	2250.828	[56]	CD_3 d-stretch
ν_5	E	1292.500	[55]	CD_3 rock
ν_6	E	1035.920	[55]	CD_3 d-deform

Note: [a]Ref. [20] gave 2992.75 cm^{-1} with an estimated measurement (and calibration) uncertainty of 0.02 cm^{-1}, in essential agreement with the present much more accurate result.

In practice in assigning symmetry species, one uses first the conventional C_{3v} symmetry species for both CH_3D and CD_3H and then derives the substructure of the almost degenerate levels and the corresponding nuclear spin statistical weights from the induced representation in Table 2 and the considerations given above.

The electric dipole selection rules take a very simple form in S_3^*: conservation of nuclear spin symmetry and change of parity in the optical transition, thus

$$A_1^+ \leftrightarrow A_1^- \tag{Ia}$$

$$A_2^+ \leftrightarrow A_2^- \tag{Ib}$$

$$E^+ \leftrightarrow E^- \tag{Ic}$$

with all other transitions being electric dipole forbidden with the approximation of nuclear spin symmetry conservation [49,50,52,53]. For magnetic dipole transitions one has no change of parity in the transition, but these are extremely weak in the infrared spectra and not analysed here.

3.2. *The effective rotational–vibrational Hamiltonian*

The nine vibrational normal modes q_λ of both molecules have the symmetry species A_1 or E in C_{3v}, three nondegenerate modes q_λ $(\lambda = 1, 2, 3) \in A_1$ and three doubly degenerate modes q_{μ_1} and q_{μ_2} $(\mu = 4, 5, 6) \in E$. Tables 3 and 4 summarise the six vibrational fundamentals as known today for the CH_3D and CHD_3 isotopomers.

The presence of degenerate modes in the C_{3v} symmetric methane isotopomers leads to a more complicated picture of ro-vibrational spectra than for CH_2D_2 [32], especially in excited overtone and combination bands largely governed by symmetry. It is therefore suitable to make use of the symmetry properties of these molecules [3], applying theorems and results of the theory of irreducible tensorial sets, [57,58], for the construction of the molecular hamiltonian, ro-vibrational eigenfunctions, and the various matrix elements as adapted to the C_{3v} type molecules, see e.g. [58,59].

On the other hand, the presence of numerous and strong resonance interactions between different vibrational states of both CH_3D and CHD_3 leads to the necessity to use even in a preliminary analysis of infrared spectroscopic data a Hamiltonian model which takes into account explicitly all strong resonance interactions. Using C_{3v} symmetry, the Hamiltonian takes the following form [59]

$$H^{\text{v.-r.}} = \sum_{v\Gamma, v'\Gamma'} H^{v\Gamma, v'\Gamma'}, \tag{1}$$

where the summation extends over all interacting vibrational states; $\Gamma = A_1, A_2, E$ is the symmetry species of the vibrational state. The diagonal operators $H^{v\Gamma, v\Gamma}$ describe the rotational structures of the corresponding vibrational state and can be written in the following form:

$$H_{\text{diag.}} = \sum_v H^{vA_1, vA_1} + \sum_v H^{vA_2, vA_2} + \sum_v H^{vE, vE}. \tag{2}$$

The operators H^{vA_i, vA_i} $(i = 1, 2)$ which describe the rotational–vibrational structures of nondegenerate vibrational states have the form:

$$\begin{aligned} H^{vA_i, vA_i} &= |vA_i\rangle\langle vA_i|\{E^{va_i} + B^{va_i}(J_x^2 + J_y^2) + C^{va_i}J_z^2 - D_J^{va_i}J^4 \\ &\quad - D_{JK}^{va_i}J^2J_z^2 - D_K^{va_i}J_z^4 + H_J^{va_i}J^6 + H_{JK}^{va_i}J^4J_z^2 \\ &\quad + H_{KJ}^{va_i}J^2J_z^4 + H_K^{va_i}J_z^6 + L_J^{va_i}J^8 + \cdots \\ &\quad + [(\epsilon'^{va_i}J_z + \epsilon_J'^{va_i}J_zJ^2 + \epsilon_K'^{va_i}J_z^3 + \cdots), (J_+^3 + J_-^3)]_+ \\ &\quad + h'^{va_i}(J_+^6 + J_-^6) + \cdots\}. \end{aligned} \tag{3}$$

Here B^{va_i}, C^{va_i}, $D_J^{va_i}$, $D_{JK}^{va_i}$, $D_K^{va_i}$, $H_J^{va_i}$, $H_{JK}^{va_i}$, $H_{KJ}^{va_i}$, $H_K^{va_i}$, $L_J^{va_i}$, ... are the rotational constants and centrifugal distortion parameters, respectively (it should be mentioned that the notations B and C for the rotational parameters are used in the spectroscopic literature for the oblate symmetric top molecules, like CHD_3; for the prolate symmetric top molecules, like CH_3D, the

notation A is used instead of C). The operators $(J_+^3 + J_-^3)$ connect rotational states $|JK\rangle$ and $|JK'\rangle$ with different values of the quantum numbers K, namely $\Delta K = K - K' = \pm 3$. They account, in particular, for the A_1/A_2 splittings of $K=3$ levels, and the operators J_+ and J_- have the form of $J_\pm = J_x \mp \mathrm{i}J_y$. The parameters $\epsilon_J'^a$ and $\epsilon_K'^a$ describe the J and K dependence of the main ϵ'^a parameter. The expression $[\ldots,\ldots]_+$ denotes an anticommutator.

For doubly degenerate vibrational states the $H^{vE,vE}$ operator is

$$H^{vE,vE} = H_1^{vE,vE} + H_2^{vE,vE} + H_3^{vE,vE}, \tag{4}$$

where

$$\begin{aligned} H_1^{vE,vE} &= (|vE_1\rangle\langle vE_1| + |vE_2\rangle\langle vE_2|)\big\{E^{ve} + B^{ve}(J_x^2 + J_y^2) + C^{ve}J_z^2 \\ &\quad - D_J^{ve}J^4 - D_{JK}^{ve}J^2J_z^2 - D_K^{ve}J_z^4 + H_J^{ve}J^6 + H_{JK}^{ve}J^4J_z^2 \\ &\quad + H_{KJ}^{ve}J^2J_z^4 + H_K^{ve}J_z^6 + L_J^{ve}J^8 + \cdots \\ &\quad + [(\epsilon'^{ve}J_z + \epsilon_J'^{ve}J_zJ^2 + \epsilon_K'^{ve}J_z^3 + \cdots), (J_+^3 + J_-^3)]_+\big\}, \end{aligned} \tag{5}$$

$$\begin{aligned} H_2^{vE,vE} &= (|vE_1\rangle\langle vE_2| - |vE_2\rangle\langle vE_1|)\{2(C\zeta)^{ve}J_z + \eta_J^{ve}J_zJ^2 \\ &\quad + \eta_K^{ve}J_z^3 + \eta_{JJ}^{ve}J_zJ^4 + \eta_{JK}^{ve}J_z^3J^2 \\ &\quad + \eta_{KK}^{ve}J_z^5 + \eta_{JJJ}^{ve}J_zJ^6 + \eta_{JJK}^{ve}J_z^3J^4 \\ &\quad + \eta_{JKK}^{ve}J_z^5J^2 + \eta_{KKK}^{ve}J_z^7 + \cdots\}, \end{aligned} \tag{6}$$

and

$$\begin{aligned} H_3^{vE,vE} &= (|vE_2\rangle\langle vE_2| - |vE_1\rangle\langle vE_1|)\{[\mathrm{i}A^{ve}, (J_+ - J_-)]_+ \\ &\quad + [B^{ve}, (J_+ + J_-)]_+ + [C^{ve}, (J_+^2 + J_-^2)]_+ \\ &\quad + [\mathrm{i}D^{ve}, (J_-^2 - J_+^2)]_+ + [F^{ve}, (J_+^4 + J_-^4)]_+ \\ &\quad + [\mathrm{i}G^{ve}, (J_-^4 - J_+^4)]_+\} \\ &\quad + (|vE_1\rangle\langle vE_2| + |vE_2\rangle\langle vE_1|)\{[A^{ve}, (J_+ + J_-)]_+ \\ &\quad + [\mathrm{i}B^{ve}, (J_- - J_+)]_+ + [\mathrm{i}C^{ve}, (J_+^2 - J_-^2)]_+ \\ &\quad + [D^{ve}, (J_+^2 + J_-^2)]_+ + [\mathrm{i}F^{ve}, (J_+^4 - J_-^4)]_+ \\ &\quad + [G^{ve}, (J_+^4 + J_-^4)]_+\}, \end{aligned} \tag{7}$$

$$\begin{aligned} A^{ve} &= \frac{1}{2}\alpha^{ve} + \frac{1}{2}\alpha_J^{ve}J^2 + \alpha_K^{ve}J_z^2 + \frac{1}{2}\alpha_{JJ}^{ve}J^4 \\ &\quad + \alpha_{JK}^{ve}J^2J_z^2 + \alpha_{KK}^{ve}J_z^4 + \cdots \\ &\quad + \alpha_{JJK}^{ve}J^4J_z^2 + +\alpha_{JKK}^{ve}J^2J_z^4 + \cdots, \\ B^{ve} &= \beta^{ve}J_z + \beta_J^{ve}J_zJ^2 + \beta_K^{ve}J_z^3 + \beta_{JJ}^{ve}J^4J_z + \beta_{JK}^{ve}J^2J_z^3 + \cdots, \\ C^{ve} &= \frac{1}{2}\gamma^{ve} + \frac{1}{2}\gamma_J^{ve}J^2 + \gamma_K^{ve}J_z^2 + \frac{1}{2}\gamma_{JJ}^{ve}J^4 + \gamma_{JK}^{ve}J^2J_z^2 + \cdots \\ &\quad + \gamma_{JJK}^{ve}J^4J_z^2 + \cdots, \\ D^{ve} &= \delta^{ve}J_z + \delta_J^{ve}J_zJ^2 + \delta_K^{ve}J_z^3 + \delta_{JJ}^{ve}J_zJ^4 + \delta_{JK}^{ve}J^2J_z^3 + \cdots, \\ F^{ve} &= \frac{1}{2}\kappa^{ve} + \frac{1}{2}\kappa_J^{ve}J_z^2 + \kappa_K^{ve}J_z^2 + \frac{1}{2}\kappa_{JJ}^{ve}J^4 + \kappa_{JK}^{ve}J^2J_z^2 + \cdots, \\ G^{ve} &= \theta^{ve}J_z + \theta_J^{ve}J_zJ^2 + \theta_K^{ve}J_z^3 + \theta_{JJ}^{ve}J_zJ^4 + \theta_{JK}^{ve}J^2J_z^3 + \cdots. \end{aligned} \tag{8}$$

In Equation (5) the $E^{ve}, B^{ve}, \ldots, \varepsilon'^{ve}$ parameters have the same meaning as the corresponding ones in Equation (3) with only one exception: although the operators $(J_+^3 + J_-^3)$ connect rotational states $|JK\rangle$ and $|JK'\rangle$ with $\Delta K = K - K' = \pm 3$, they do not split A_1/A_2 levels. The operator $H_2^{vE,vE}$ describes the $k-l$ splittings; other types of operators, $(J_+^n \pm J_-^n)$, connect rotational states $|JK\rangle$ and $|JK'\rangle$ where $\Delta K = K - K' = \pm n$. Of these, the operators with $n = 2m$ provide the $A_1 - A_2$ splittings of energy levels with $K = m$.

The Fermi-type resonance operators $H^{v\Gamma,v'\Gamma}$ connect vibrational states of the same symmetries and formally have the same form as expressions (3)–(8). However, the vibrational operators $|v\Gamma_\sigma\rangle\langle v\Gamma_{\sigma'}|$ in these formulae should be exchanged by $|v\Gamma_\sigma\rangle\langle v'\Gamma_{\sigma'}|$, and the parameters $E^{va_i}, B^{va_i}, \ldots, \theta_{JK}^{ve}, \ldots$ in Equations (3)–(8) should be exchanged by the corresponding resonance operators $E^{va_i,v'a_i}, B^{va_i,v'a_i}, \ldots, \theta_{JK}^{ve,v'e}, \ldots$.

Finally, the Coriolis-type interaction operators which connect vibrational states of different symmetries, have the following form:

$$\begin{aligned} H^{vA_1,v'E} &= |vA_1\rangle\langle v'E_1|\{[\mathrm{i}A^{va_1,v'e}, (J_+ - J_-)]_+ \\ &\quad + [B^{va_1,v'e}, (J_+ + J_-)]_+ \\ &\quad + [C^{va_1,v'e}, (J_+^2 + J_-^2)]_+ + [\mathrm{i}D^{va_1,v'e}, (J_-^2 - J_+^2)]_+ \\ &\quad + [F^{va_1,v'e}, (J_+^4 + J_-^4)]_+ + [\mathrm{i}G^{va_1,v'e}, (J_-^4 - J_+^4)]_+\} \\ &\quad + |vA_1\rangle\langle v'E_2|\{[A^{va_1,v'e}, (J_+ + J_-)]_+ \\ &\quad + [\mathrm{i}B^{va_1,v'e}, (J_- - J_+)]_+ \\ &\quad + [\mathrm{i}C^{va_1,v'e}, (J_+^2 - J_-^2)]_+ + [D^{va_1,v'e}, (J_+^2 + J_-^2)]_+ \\ &\quad + [\mathrm{i}F^{va_1,v'e}, (J_+^4 - J_-^4)]_+ + [G^{va_1,v'e}, (J_+^4 + J_-^4)]_+\}. \end{aligned} \tag{9}$$

and

$$\begin{aligned} H^{vA_2,v'E} &= -|vA_2\rangle\langle v'E_2|\{[\mathrm{i}A^{va_2,v'e}, (J_+ - J_-)]_+ \\ &\quad + [B^{va_2,v'e}, (J_+ + J_-)]_+ \\ &\quad + [C^{va_2,v'e}, (J_+^2 + J_-^2)]_+ + [\mathrm{i}D^{va_2,v'e}, (J_-^2 - J_+^2)]_+ \\ &\quad + [F^{va_2,v'e}, (J_+^4 + J_-^4)]_+ + [\mathrm{i}G^{va_2,v'e}, (J_-^4 - J_+^4)]_+\} \\ &\quad + |vA_2\rangle\langle v'E_1|\{[A^{va_2,v'e}, (J_+ + J_-)]_+ \\ &\quad + [\mathrm{i}B^{va_2,v'e}, (J_- - J_+)]_+ \\ &\quad + [\mathrm{i}C^{va_2,v'e}, (J_+^2 - J_-^2)]_+ + [D^{va_2,v'e}, (J_+^2 + J_-^2)]_+ \\ &\quad + [\mathrm{i}F^{va_2,v'e}, (J_+^4 - J_-^4)]_+ + [G^{va_2,v'e}, (J_+^4 + J_-^4)]_+\}. \end{aligned} \tag{10}$$

The operators $A^{va_iv'e}, B^{va_iv'e}, \ldots$, etc., can be derived from Equation (8) by replacing the parameters

Table 5. Elements of the G-reduction matrix for the C_{3v} point group.[a]

Element	Value
${}^{(J)}G^{m}_{NA_1}$	$\frac{(-\mathrm{i})^J}{2^{1/2}}(1+\delta_{N,0})^{-1/2}(\delta_{m,3N}+(-1)^{(J+3N)}\delta_{m,-3N})$
${}^{(J)}G^{m}_{NA_2}$	$\frac{(-\mathrm{i})^{J+1}}{2^{1/2}}(1-2\delta_{N,0})(1+\delta_{N,0})^{-1/2}(\delta_{m,3N}+(-1)^{(J+3N+1)}\delta_{m,-3N})$
${}^{(J)}G^{m}_{NE1}$	$\frac{(-\mathrm{i})^{J}}{2^{1/2}}(\delta_{m,3N+1}+(-1)^{(J+3N+1)}\delta_{m,-(3N+1)})$
${}^{(J)}G^{m}_{NE2}$	$\frac{(-\mathrm{i})^{J+1}}{2^{1/2}}(\delta_{m,3N+1}+(-1)^{(J+3N)}\delta_{m,-(3N+1)})$
${}^{(J)}G^{m}_{(N+1+\{(J-1)/3\})E1}$	$\frac{(-\mathrm{i})^{J}}{2^{1/2}}(\delta_{m,3N+2}+(-1)^{(J+3N)}\delta_{m,-(3N+2)})$
${}^{(J)}G^{m}_{(N+1+\{(J-1)/3\})E2}$	$\frac{(-\mathrm{i})^{J-1}}{2^{1/2}}(\delta_{m,3N+2}+(-1)^{(J+3N+1)}\delta_{m,-(3N+2)})$

Note: [a]The index N takes the following values: $N=0, 1, \ldots, \{J/3\}$ for the states of A_1 and A_2 symmetry; $N=0, 1, \ldots, \{(J-1)/3\}$ for the states of E symmetry. The nomenclature of the rotational states is illustrated also in Figure 2.

$\alpha, \beta, \ldots$ by $\alpha^{va_i,v'e}$, $\beta^{va_i,v'e}, \ldots$, etc. $(i=1,2)$. The last type of Coriolis resonance interactions has the following form:

$$\begin{aligned} H^{vA_1,v'A_2} &= |vA_1\rangle\langle v'A_2|\{2(C\zeta)^{va_1,v'a_2}J_z \\ &+\eta_J^{va_1,v'a_2}J_zJ^2+\eta_K^{va_1,v'a_2}J_z^3+\eta_{JJ}^{va_1,v'a_2}J_zJ^4+\eta_{JK}^{va_1,v'a_2}J_z^3J^2 \\ &+\eta_{KK}^{va_1,v'a_2}J_z^5+\eta_{JJJ}^{va_1,v'a_2}J_zJ^6+\eta_{JJK}^{va_1,v'a_2}J_z^3J^4 \\ &+\eta_{JKK}^{va_1,v'a_2}J_z^5J^2+\eta_{KKK}^{va_1,v'a_2}J_z^7+\cdots\}. \end{aligned} \tag{11}$$

3.3. *Symmetrised rotational–vibrational functions*

Since the C_{3v} symmetry group has three irreducible representations A_1, A_2, and E (with the two components E_1 and E_2), every vibration–rotation wave functions should be symmetric (A_1), antisymmetric (A_2), or be transformed under symmetry operations according to one from two lines (E_1 or E_2) of the irreducible representation E. Thus every vibration–rotation state function should have the form [58,59]

$$|v\gamma_v, JK\gamma_r, m\gamma s\rangle \equiv (|v\gamma_v\rangle \otimes |JK\gamma_r\rangle)^{\gamma}_{s}. \tag{12}$$

It should be mentioned that the sets of indices $v\gamma_v$, $JK\gamma_r$, and $m\gamma s$ are single valued and determine every vibration–rotation state function. In Equation (12) γ_v, γ_r, and γ denote symmetries of vibrational, rotational, and vibrational–rotational states, respectively; s is the line of the irreducible representation γ. The index m distinguishes between the vibrational–rotational states of the same symmetry; $0 \le K \le J$ with total angular momentum quantum number J; the symbol $\otimes$ denotes a direct tensorial product.

In accordance with [58,59], the pure rotational functions $|Jk\gamma_r\sigma\rangle$ can be written with the help of elements of the so-called G-reduction matrix (for the C_{3v} point symmetry group they are presented in Table 5) in the form

$$|Jk\gamma_r\sigma\rangle = \sum_k {}^{(J)}G^{k}_{\gamma rs}|Jk\rangle. \tag{13}$$

Here the index s denotes the line of the 'rotational' irreducible representation γ_r; $|Jk\rangle$ denotes the $(m=0)$ part of the usual well-known rotational functions [3,60]

$$|Jkm\rangle = \exp(-\mathrm{i}k\varphi)d^{j}_{km}(\vartheta)\exp(-\mathrm{i}m\psi). \tag{14}$$

In Equations (13) and (14), $J \ge k \ge -J$. Since for a free molecule the index m in the functions (14) is nonessential, we omitted it both in Equation (13) and further on in this paper.

For molecules belonging to the C_{3v} symmetry group, using the data from Table 5, one can write the rotational functions (13) in an explicit form as

$$2^{1/2}|JK\gamma_r\sigma\rangle = C^{l}_{JK\gamma_r\sigma}\{|JK\rangle + (-1)^{l}(-1)^{J+K}|J-K\rangle\}, \tag{15}$$

where the coefficients $C^{l}_{JK\gamma_r\sigma}$ are presented in Table 6.

In order to take into account the definition of the so-called tensorial product of two irreducible tensorial values [57,61], we write

$$(A^{\Gamma}\otimes B^{\Gamma'})^{\gamma}_{\sigma} = ([\gamma])^{1/2}\sum_{ss'}\begin{pmatrix}\gamma & \Gamma & \Gamma' \\ \sigma & s & s'\end{pmatrix}A^{\Gamma}_{s}B^{\Gamma'}_{s'}, \tag{16}$$

and using Equation (15), the symmetrised vibrational–rotational functions (12) can be written in a more traditional form. In this case:

(1) For the A_1- (or A_2)-type vibrational states the ro-vibrational wavefunctions have the simple form of the usual products of vibrational

Table 6. Coefficients $C^{l}_{JK\gamma_r\sigma}$ of symmetrised rotational functions.

$\gamma_1\sigma_1$	$\gamma_2\sigma_2$	$\gamma_3\sigma_3$	Value	$\gamma_1\sigma_1$
even	0	A_1	0	$(-\mathrm{i})^J 2^{1/2}$
odd	0	A_2	1	$-(-\mathrm{i})^{J+1}2^{1/2}$
any	3, 6, 9, ...	A_1	0	$(-1)^J$
		A_2	1	$(-1)^{J+1}$
	1, 4, 7, ...	E_1	0	$(-1)^J$
		E_2	1	$(-1)^{J+1}$
	2, 5, 8, ...	E_1	0	$(-1)^J$
		E_2	1	$(-1)^{J-1}$

Table 7. Coefficients $A^{\gamma_r\sigma}_{JKm\gamma s}$ and $B^{\gamma_r\sigma}_{JKm\gamma s}$ of symmetrised rotational–vibrational functions.

J	K	$m\gamma s$	$\gamma_r\sigma$	$A^{\gamma_r\sigma}_{JKm\gamma s}$	$B^{\gamma_r\sigma}_{JKm\gamma s}$
any	$k \neq 0, 3, 6, 9, \ldots$	A_1	E_1	1	
			E_2		1
		A_2	E_1		-1
			E_2	1	
		E_1	E_1	-1	
			E_2		1
		E_2	E_1		1
			E_2	1	
any	$k = 3, 6, 9, \ldots$	$1E_1$	A_1	1	
			A_2		1
		$1E_2$	A_1		-1
			A_2	1	
		$2E_1$	A_1	1	
			A_2		1
		$2E_2$	A_1		1
			A_2	-1	
even	$k = 0$	E_1	A_1	$2^{1/2}$	
		E_1	A_1		$2^{1/2}$
odd	$k = 0$	E_2	A_2		$2^{1/2}$
		E_2	A_2	$-2^{1/2}$	

functions $|vA_1\rangle$ (or $|vA_2\rangle$) and pure rotational functions (15),

$$|vA_1, JK, \gamma\sigma\rangle = |vA_1\rangle|JK\gamma_r\sigma\rangle, \tag{17}$$

or

$$|vA_2, JK, \gamma\sigma\rangle = |vA_2\rangle|JK\gamma_r\sigma'\rangle, \tag{18}$$

respectively. In Equation (18), $\gamma_r = A_1$ when $\gamma = A_2$ and $\gamma_r = A_2$ when $\gamma = A_1$; furthermore one has $\gamma_r\ \sigma = E1$ when $\gamma\sigma = E2$ and $\gamma_r\sigma = E2$ when $\gamma\sigma = E1$.

(2) For the E-type vibrational states ro-vibrational functions have a more complicated form,

$$2^{1/2}|vE, JK, m\gamma_r s\rangle = \sum_{\gamma_r\sigma} A^{\gamma_r\sigma}_{JKm\gamma s}|vE1\rangle|JK\gamma_r\sigma\rangle + \sum_{\gamma_r\sigma} B^{\gamma_r\sigma}_{JKm\gamma s}|vE2\rangle|JK\gamma_r\sigma\rangle, \tag{19}$$

where the coefficients $A^{\gamma_r\sigma}_{JKm\gamma s}$ and $B^{\gamma_r\sigma}_{JKm\gamma s}$ are presented in Table 7. In Equation (16) $[\gamma]$ denotes the dimension of the irreducible representation γ, namely $[A_1] = [A_2] = 1$ and $[E] = 2$;

$$\begin{pmatrix} \gamma & \Gamma & \Gamma' \\ \sigma & s & s' \end{pmatrix}$$

are 3Γ symbols of the corresponding symmetry group. Table 8 presents non-zero 3Γ symbols for the C_{3v} symmetry group.

Table 8. Non-zero 3Γ symbols $\begin{pmatrix} \gamma_1 & \gamma_2 & \gamma_3 \\ \sigma_1 & \sigma_2 & \sigma_3 \end{pmatrix}$ of the C_{3v} symmetry group.[a]

$\gamma_1\sigma_1$	$\gamma_2\sigma_2$	$\gamma_3\sigma_3$	Value	$\gamma_1\sigma_1$	$\gamma_2\sigma_2$	$\gamma_3\sigma_3$	Value
A_1	A_1	A_1	1	A_2	E_1	E_2	$1/2^{1/2}$
A_1	A_2	A_2	1	E_1	E_1	E_1	$-1/2$
A_1	E_1	E_1	$1/2^{1/2}$	E_1	E_2	E_2	$1/2$
A_1	E_2	E_2	$1/2^{1/2}$				

Note: [a]Other non-zero 3Γ symbols are connected with the values given in the table by the relations

$$\begin{pmatrix} \gamma_1 & \gamma_2 & \gamma_3 \\ \sigma_1 & \sigma_2 & \sigma_3 \end{pmatrix} = \begin{pmatrix} \gamma_2 & \gamma_3 & \gamma_1 \\ \sigma_2 & \sigma_3 & \sigma_1 \end{pmatrix} = (-1)^{\gamma_1+\gamma_2+\gamma_3}\begin{pmatrix} \gamma_1 & \gamma_3 & \gamma_2 \\ \sigma_1 & \sigma_3 & \sigma_2 \end{pmatrix},$$

where $(-1)^{A_1} = (-1)^{E} = +1$; $(-1)^{A_2} = -1$.

4. Analysis of the experimental data

The spectra of both the CH_3D and CHD_3 species were measured in the region of 2900–9000 cm^{-1}. The corresponding overviews of the recorded spectra are shown in Figures 3 and 4. The regions of very strong absorbance in both figures correspond to the fundamental bands. In Figure 3, the bands ν_1 and ν_4 are clearly pronounced near 3000 cm^{-1}. Similarly, the fundamental band ν_1 is clearly seen in Figure 4. The weaker, but, as a rule, also well-recognised bands belong to doubly excited first overtone and combinational bands (they are marked on Figures 3 and 4). The total number of such bands as seen in absorption is 21 (27 if one takes into account the presence of both allowed subbands of symmetries A_1 and E in the bands $2\nu_4$, $2\nu_5$, $2\nu_6$, $\nu_4+\nu_5$, $\nu_4+\nu_6$, and $\nu_5+\nu_6$) for any of the two symmetric top methane isotopomers. A number of weak bands, belonging to triple excitations of vibrational quanta and appearing, as a rule, by strong resonance interactions with stronger first overtone and combinational bands, also can be seen in the pictures of the overview spectra. As is well known, at higher excitations the Fermi resonance polyad system of the CH chromophore in CHD_3 (involving ν_1 and ν_5) becomes dominant in absorption [20]. In total, we were

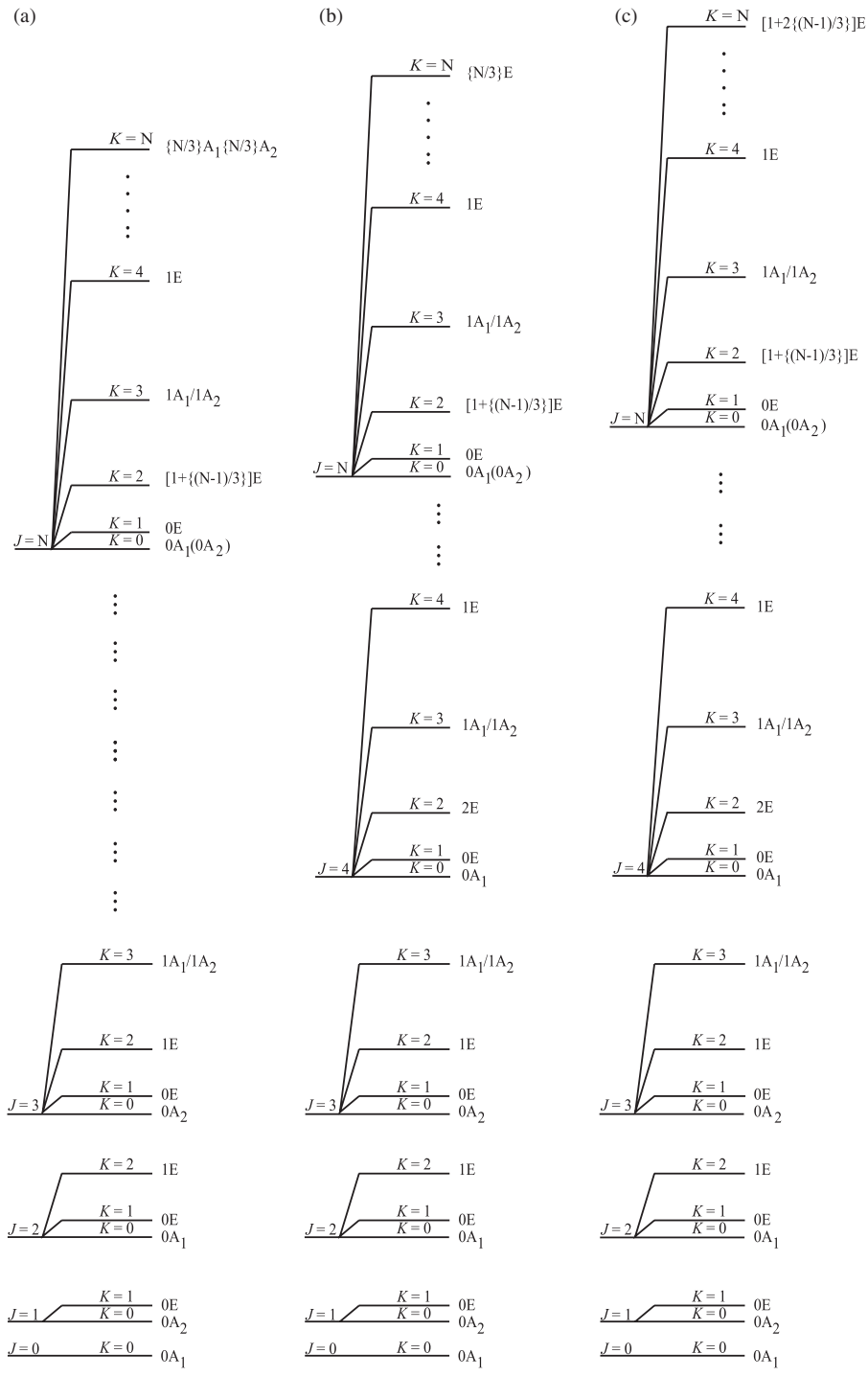


Figure 2. Nomenclature of states of different rotational symmetry species in C_{3v} for a given value of quantum number J: (a) J is divisible by 3; (b) $J-1$ is divisible by 3; (c) $J+1$ is divisible by 3. It should be noted that the indices $n\Gamma$ determine uniquely the K index and vice versa; for nA indices $K=3n$ at $0 \leq n \leq \{J/3\}$; for nE indices $K=3n+1$ at $0 \leq n \leq \{(J-1)/3\}$, or $K=3(n-[(J-1)/3])-1$ at $n \geq 1+\{(J-1)/3\}$. The symbol $\{B\}$ above denotes the integer part of the number B.

able to assign ro-vibrational transitions to 57 (for CH_3D) and 40 (for CHD_3) previously unknown bands. Transitions with values of the quantum number $J \leq 8$ to 12 for the strong bands and $J \leq 5$ to 6 for the weak bands were assigned in the spectra recorded at a temperature of about 80 K.

As in our previous analysis of the CH_2D_2 low temperature ro-vibrational spectra [32], a line

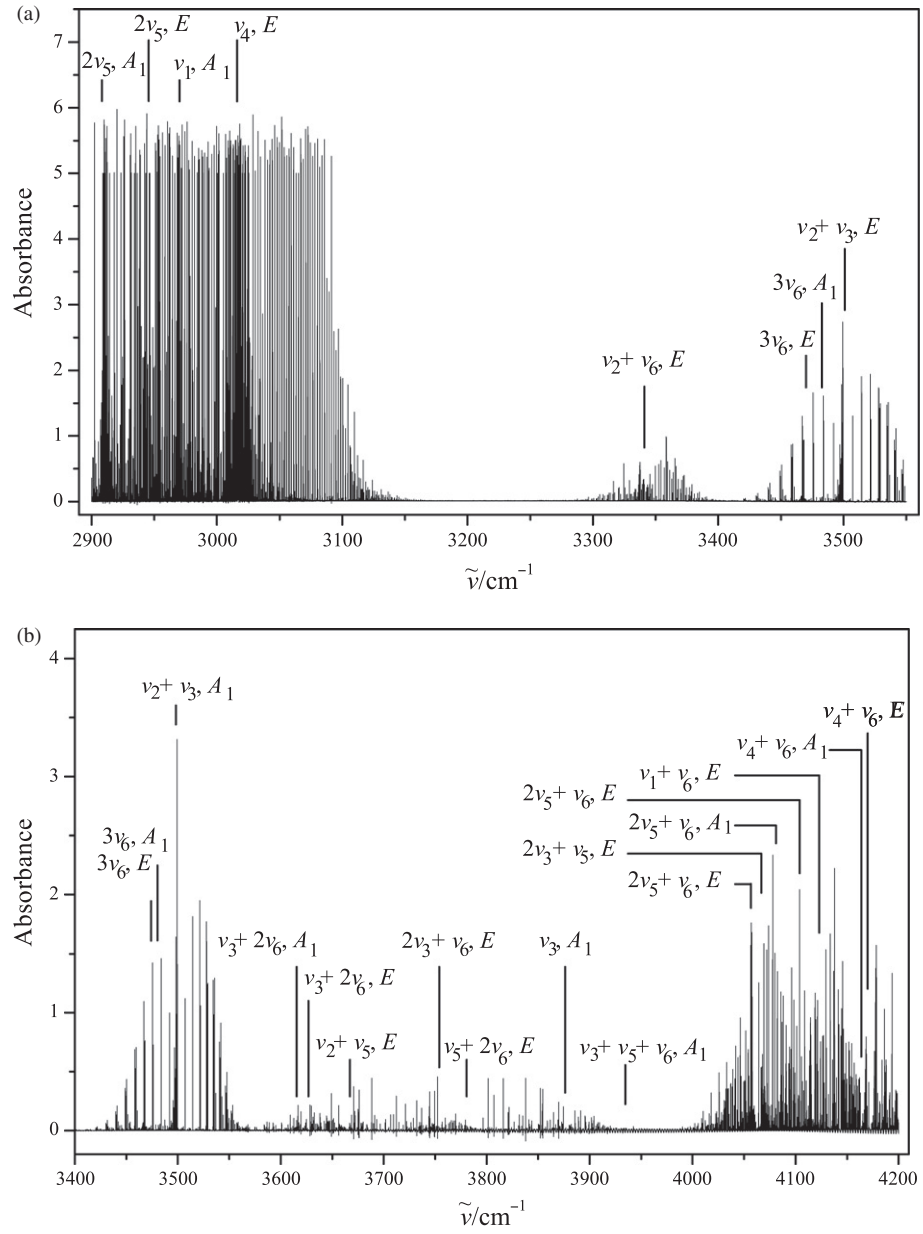


Figure 3. Survey spectrum as decadic absorbance $\lg(I_0/I)$ of CH_3D in the region of 2900–6500 cm^{-1}. Experimental conditions are presented in Table 1.

assignment in the low temperature spectra was much easier than the assignment of 'room temperature' spectra because of the smaller number of lines in the cold spectra. As an illustration, Figure 5 presents a small part of the spectrum of CH_3D recorded at 80 K in the region of 4128.50 to 4129.75 cm^{-1} (upper trace). For comparison, a spectrum in the same region previously recorded with our BOMEM FTIR spectrometer at room temperature is shown in the lower trace of Figure 5. The great improvement in the new data is clearly visible. On the basis of our new experimental data, more than 5700 transitions were assigned to 57 newly identified bands of CH_3D, and more than 4400 transitions were assigned to 40 newly identified bands of CHD_3. The rotational assignment was confirmed with the help of the Ground State Combination Differences (GSCD) method, and the ground state energies were taken from [62] for CH_3D and [63] for CHD_3 (Table 9). Because of numerous and strong resonance interactions, an effective Hamiltonian of the form defined by Equations (1)–(11) was used for the calculation and preliminary prediction of line positions for both molecules.

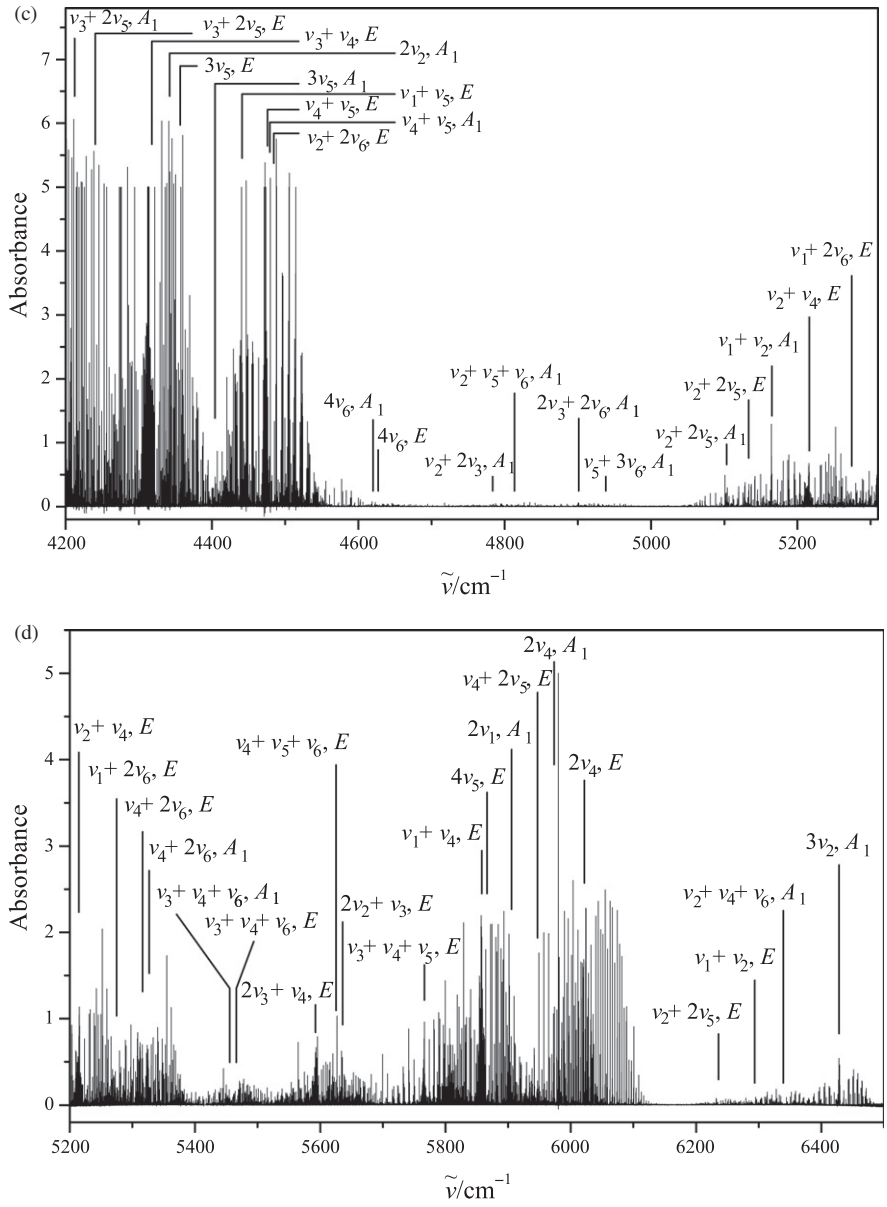


Figure 3. Continued.

To make a vibrational assignment, some additional criteria were used. Firstly, preliminary estimates of the band centres were made on the basis of the methane intramolecular potential functions determined earlier from analysis of 94 experimental band centres of CH_2D_2 (see [32] and references cited therein). The second criterion for the vibrational symmetry assignment arose from the analysis of pronounced sets of P transitions in the experimental spectra. One of them is the set of transitions of the type

$$\langle v\gamma_v, J\ K, e| \leftarrow \langle v_{\text{ground}}, J' = J+1\ K' = 1, e|, \qquad (20)$$

where notations of the upper and lower ro-vibrational states correspond to Equation (12); $K=1$ for the A_1-, and $K=0$ for the E-type vibrational bands. In this case, if the set of transitions with $J+1=\ldots,6,5,4,\ldots$, Equation (20), is limited by the value $J+1=2$, one can expect that a corresponding set of transitions belongs to a band of the A_1 symmetry. When the set of transitions is limited by the value $J+1=1$, one can be sure that a corresponding set of transitions belongs to the $\Delta K=-1$ subband of an E-type vibrational band.

Similarly, if a set of transitions $J+1=\ldots,6,5,4,\ldots$ with

$$\langle v\gamma_v, J\ K, a_2/a_1| \leftarrow \langle v_{\text{ground}}, J' = J+1\ K' = 3, a_1/a_2|, \qquad (21)$$

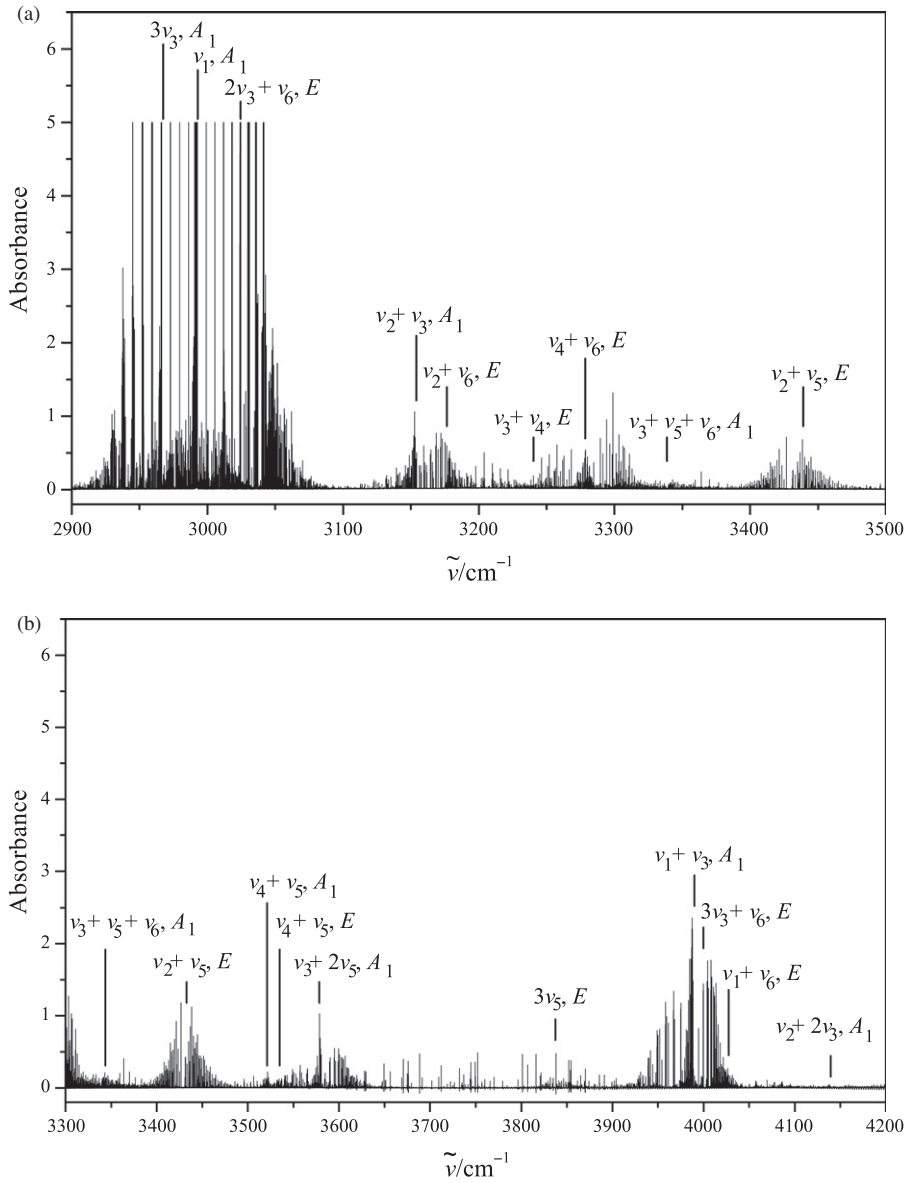


Figure 4. Survey spectrum as decadic absorbance $\lg(I_0/I)$ of CHD_3 in the region of 2900–6500 cm^{-1}. Experimental conditions are presented in Table 1.

is limited by the value $J+1=3$, 4, or 2, one can expect that a corresponding set of transitions belongs to a vibrational band of the A_1 symmetry, or to a $\Delta K=+1$, or $\Delta K=-1$ subband of an E-type vibrational band, respectively. As an additional criterion, the set of transitions

$$\langle v\gamma_v, J\ K, a_2/a_1| \leftarrow \langle v_{ground}, J'=J+1\ K'=0, a_1/a_2|, \tag{22}$$

can be used as well. This assignment procedure is illustrated by Figures 6 and 7. Tables 10 and 11 provide examples of numerical results in the procedure. It is thus important to stress that the band centres of practically all bands were found from an experimental transition assigned in the spectrum. The total list of experimental band centres is presented in column 5 of Table 12 for CH_3D.

The same assignment procedure was used also for the analysis of the experimental spectrum of CHD_3. The list of band centres for the bands analysed is presented in column 5 of Table 13.

5. Results of the vibrational analysis

As a first step in the theoretical analysis of high-resolution spectra of the C_{3v} symmetric isotopomers of

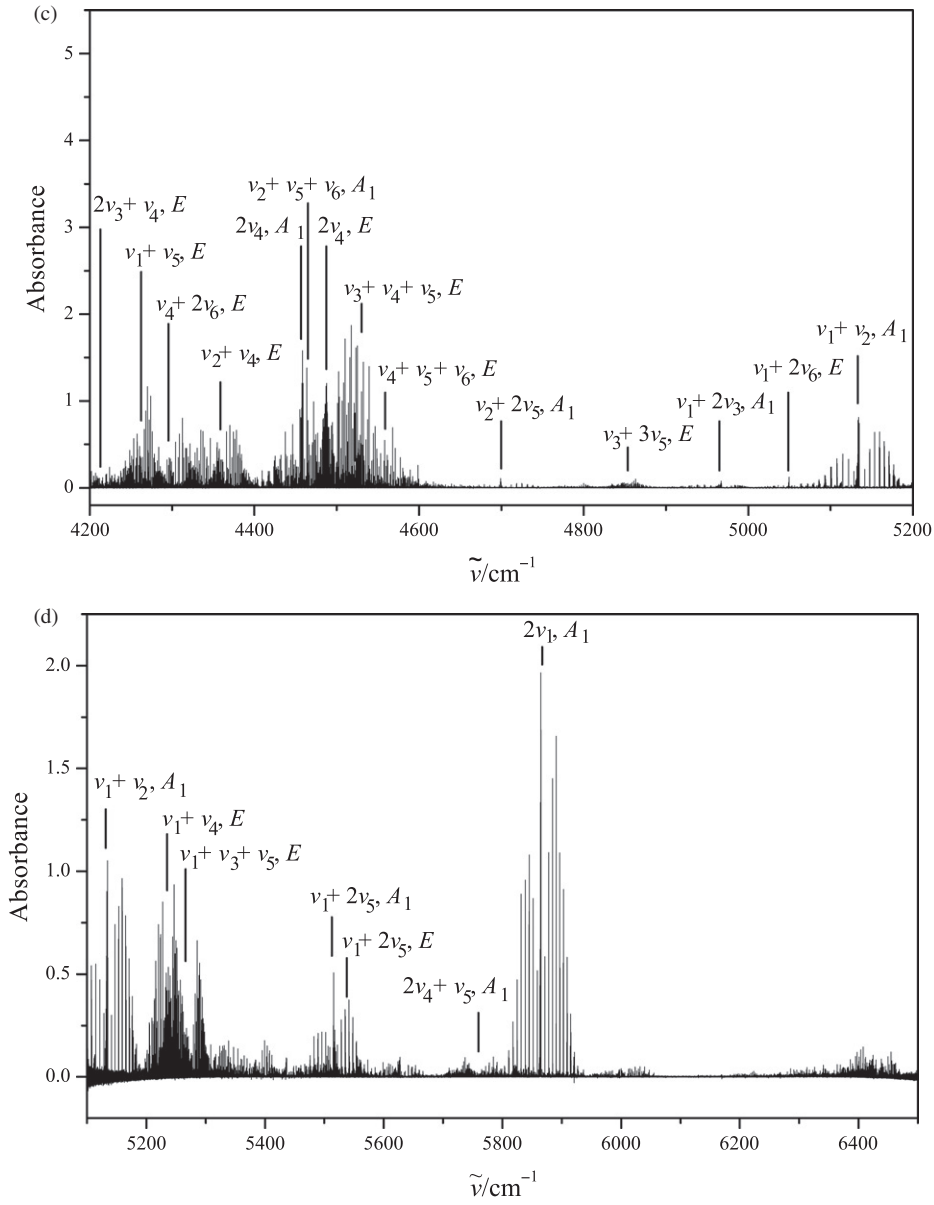


Figure 4. Continued.

methane, we present here a pure vibrational analysis of all band centres of CH_3D and CHD_3 as known now up to about 9000 cm^{-1}. The analysis was carried out with the Hamiltonian model of Section 3.2 which takes into account both the anharmonicity of vibrations, and some types of pure vibrational resonance interactions:

$$H^{\mathrm{vib.}} = \sum_{vl\gamma_v,\,\tilde{v}\tilde{l}\gamma_v} |vl\gamma_v\rangle\langle\tilde{v}\tilde{l}\gamma_v| H_{vl\gamma_v\,\tilde{v}\tilde{l}\gamma_v}. \tag{23}$$

Here the summation includes all vibrational states studied.

As mentioned in Section 4, the use of the symmetrised wave functions is suitable in the theoretical study of symmetric top molecules. Following this strategy, we used symmetrised vibrational functions of the type

$$|v_1\ v_2\ v_3\rangle|[(v_4\ l_4\ \gamma_4)\otimes(v_5\ l_5\ \gamma_5)]^{\gamma_{45}}\otimes(v_6\ l_6\ \gamma_6)\rangle^{\gamma}, \tag{24}$$

in the construction of the elements $H_{vl\gamma\,\tilde{v}\tilde{l}\gamma}$, Equation (23) where γ_λ denotes the symmetry of the elementary vibrational functions $|v_\lambda\ l_\lambda\rangle$, and γ_{45} denotes a symmetry of that part of the full vibrational wave function, which depends on the doubly degenerate coordinates q_{4s} and q_{5s} $(s=1,2)$.

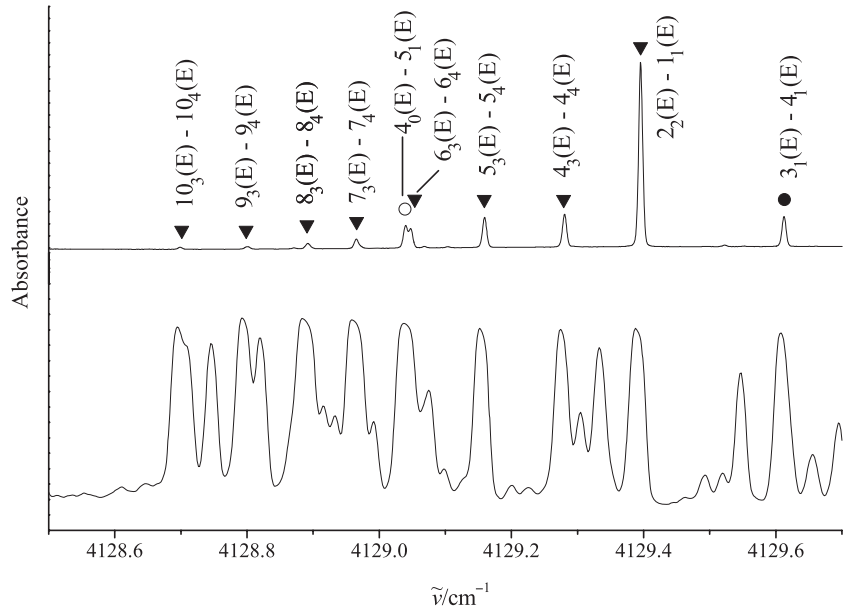


Figure 5. Small portion of the spectrum of the CH_3D molecule. Upper trace: Bruker IFS 125 Zürich prototype (ZP 2001) spectrum at 80 K. Lines belonging to the $\nu_1+\nu_6$, $\nu_4+\nu_6(A_1)$, and $\nu_4+\nu_6(E)$ bands are marked by dark triangles, dark circles, and open circles, respectively. Lower trace: Bomem DA002 spectrum at 293 K (conditions commonly used in [20]).

Table 9. Ground state parameters of the CH_3D and CHD_3 isotopomers of methane (in cm^{-1}).[a]

Parameter	CH_3D [62]	CHD_3 [63]
1	2	3
$A(C)$	3.880193378	2.6289695
B	5.25082109	3.2791847
$D_J/10^4$	0.5262994	0.49494
$D_{JK}/10^4$	1.264339	−0.38315
$D_K/10^4$	−0.7896593	0.13391
$H_J/10^8$	0.143479	0.2127
$H_{JK}/10^8$	1.214490	−0.3298
$H_{KJ}/10^8$	−0.67214	0.1874
$H_K/10^8$	−0.16436	−0.0178
$L_J/10^{12}$	–	−0.134
$L_{JJK}/10^{12}$	−0.1836	0.171
$L_{JK}/10^{12}$	–	–
$L_{KKJ}/10^{12}$	1.490	–
$L_K/10^{12}$	–	–
$\tilde{\epsilon}/10^5$	0.32	−0.289
$\tilde{h}_3/10^{10}$	0.32503	1.0191

Note: [a]These parameters were determined from ground state combination differences. Direct measurements of the far infrared spectrum exist as well [4] (pressure broadened).

In our present analysis we used two types of matrix elements in Equation (23):

(a) *diagonal elements* $H_{vl\gamma vl\gamma}$. It is possible to show that all diagonal elements $H_{vl\gamma vl\gamma}$ have the form

$$H_{vl\gamma vl\gamma}=\sum_{\lambda}\omega_\lambda\left(v_\lambda+\frac{d_\lambda}{2}\right)+\sum_{\lambda,\mu\geq\lambda}x_{\lambda\mu}\left(v_\lambda+\frac{d_\lambda}{2}\right)\left(v_\mu+\frac{d_\mu}{2}\right)+\sum_{\lambda,\mu\geq\lambda,\,\nu\geq\mu}y_{\lambda\mu\nu}\left(v_\lambda+\frac{d_\lambda}{2}\right)\left(v_\mu+\frac{d_\mu}{2}\right)\left(v_\nu+\frac{d_\nu}{2}\right)+\sum_{\lambda}g_{\lambda\lambda}l_\lambda^2+\sum_{\lambda,\mu>\lambda}g_{\lambda\mu}l_\lambda l_\mu, \tag{25}$$

where $d_\lambda=1$ for the nondegenerate modes $q_\lambda=1,2,3$, and $d_\lambda=2$ for the doubly degenerate vibrational modes $q_\lambda=4,5,6$.

(b) '*resonance interaction*' *elements of the type* $H_{vl\gamma\tilde{v}\tilde{l}\gamma}$ $(vl\neq\tilde{v}\tilde{l})$. Because of numerous perturbations even in 'pure vibrational' spectra of both molecules, a correct analysis has to take into account resonance interactions between the corresponding interacting vibrational states. In order to decide which type of vibrational states should be connected by resonance interactions, we firstly made calculations of the absolute values of ratios

$$\frac{\langle v\gamma|k_{\lambda\mu\nu}\{(q_\lambda\otimes q_\mu)\otimes q_\nu\}|v'\gamma\rangle}{(E_v-E_{v'})} \tag{26}$$

and

$$\frac{\langle v\gamma|k_{\lambda\mu\nu\xi}\{(q_\lambda\otimes q_\mu)\otimes(q_\nu\otimes q_\xi)\}|v'\gamma\rangle}{(E_v-E_{v'})}. \tag{27}$$

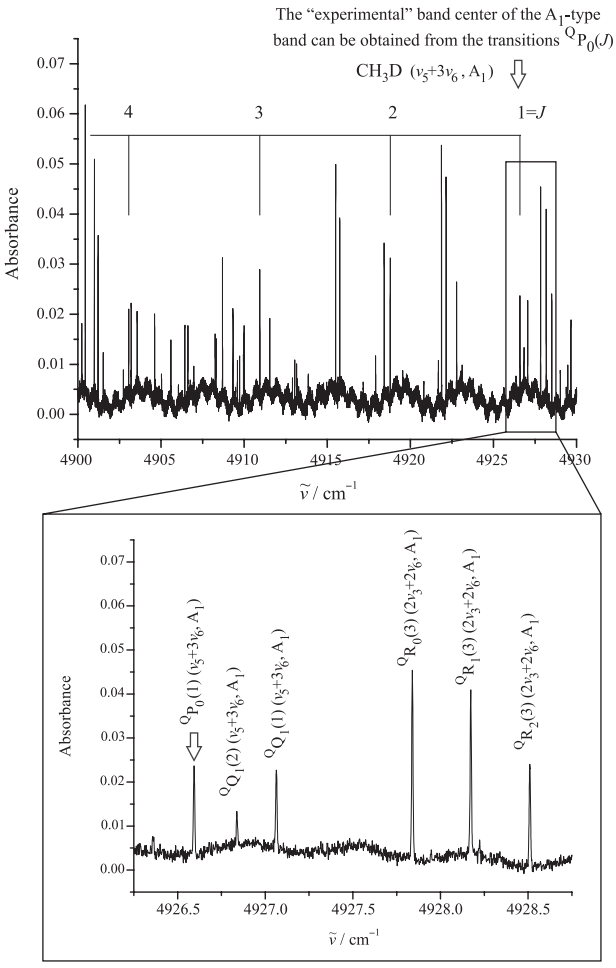


Figure 6. Set of transitions, ${}^{Q}P_0(J)$, for the A_1-type band, $\nu_5+3\nu_6$, of the CH_3D isotopomer. The first line of the progression, which corresponds to the transition ${}^{Q}P_0(1)$ with $J^{\text{upper}}=0$, can be recognised beyond doubt. The lower part of the Figure 6 shows in more detail the section of the spectrum close to the transition ${}^{Q}P_0(1)$. Assigned lines of some other bands also indicated. See also Figure 8.

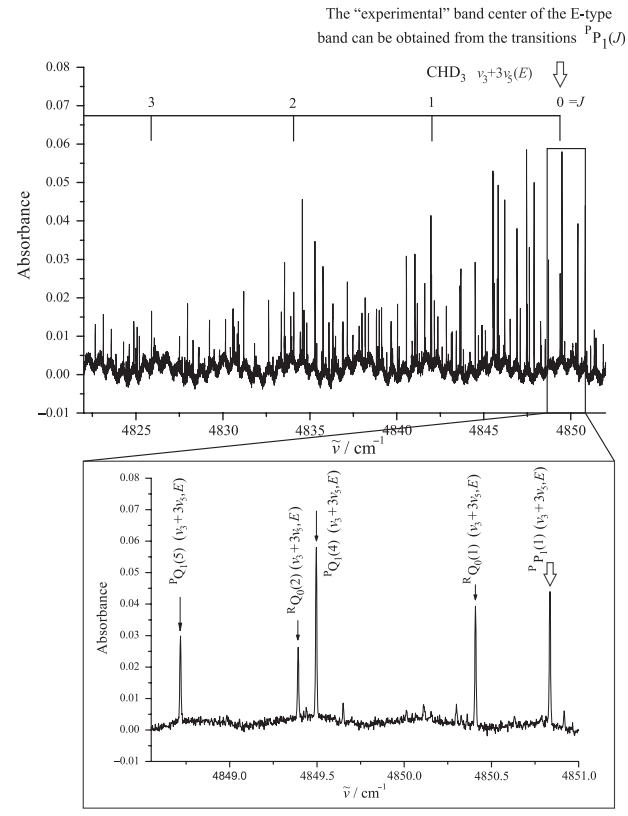


Figure 7. Analogous set of transitions, ${}^{Q}P_0(J)$, for the E-type band, $\nu_3+3\nu_5$ of the CHD_3 isotopomer. The first line of the progression, which corresponds to the transition ${}^{P}P_1(1)$ with $J^{\text{upper}}=0$, again can be recognised beyond doubt (see also the lower part of the Figure 7 and caption to Figure 6). See also Figure 9.

The latter have been calculated with the methane potential function estimated on the basis of highly accurate experimental CH_2D_2 data in [32].

Both the harmonic frequencies ω_λ, and the parameters $k_{\lambda\ldots\nu}$ (effective anharmonic coupling constants in normal mode notations) are quite different for CH_3D and CHD_3. Therefore the vibrational resonance interactions are also quite different for these molecules. As the analysis shows, for our present investigation the resonance interactions are important, as follows:

$$(1)\quad H_{vl\gamma,\tilde{v}\tilde{l}\gamma}=\frac{k_{i\lambda\lambda}}{2(2^{1/2})}\left\{\frac{2v_i\pm1+1}{4}\right\}^{1/2}(q_\lambda^+q_\lambda^-+q_\lambda^-q_\lambda^+), \tag{28}$$

if $|vl\gamma\rangle=(\ldots,v_i,\ldots,v_\lambda l_\lambda\gamma_\lambda,\ldots)$ and $|\tilde{v}\tilde{l}\gamma\rangle=(\ldots,v_i\pm1,\ldots,v_\lambda\mp2l_\lambda\gamma_\lambda,\ldots)$. In this case, we took into account $v_i=v_1$ and $v_\lambda=v_5$ for CH_3D and CHD_3.

$$(2)\quad H_{vl\gamma,\tilde{v}\tilde{l}\gamma}=\frac{F_{ii,\lambda\lambda}}{2^{1/2}}\left\{\frac{v_i\pm1+1}{2}\right\}^{1/2}\left\{\frac{v_i\pm1}{2}\right\}^{1/2}\times(q_\lambda^+q_\lambda^-+q_\lambda^-q_\lambda^+), \tag{29}$$

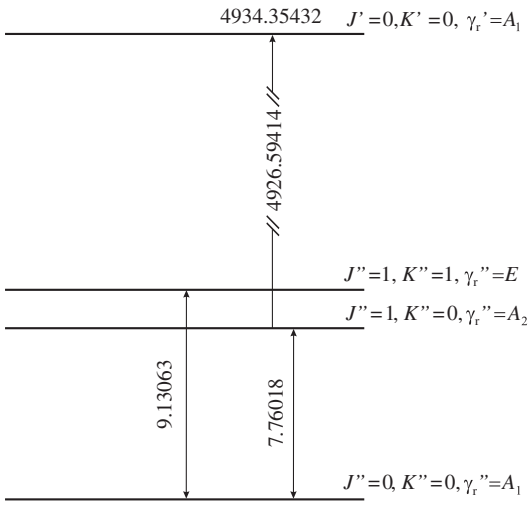
if $|vl\gamma\rangle=(\ldots,v_i,\ldots,v_\lambda l_\lambda\gamma_\lambda,\ldots)$ and $|\tilde{v}\tilde{l}\gamma\rangle=(\ldots,v_i\pm2,\ldots,v_\lambda\mp2l_\lambda\gamma_\lambda,\ldots)$. For CH_3D one should take $v_i=v_1$ and $v_\lambda=v_4$; and for CHD_3 one should take $v_i=v_3$ and $v_\lambda=v_6$. For the CHD_3 isotopomer one has:

$$(3)\quad H_{vl\gamma,\tilde{v}\tilde{l}\gamma}=H_{\tilde{v}\tilde{l}\gamma,\,vl\gamma}=\frac{k_{345}}{4}(v_3+1)^{1/2}(q_4^+q_5^-+q_4^-q_5^+). \tag{30}$$

Here $\tilde{v}_1=v_1$, $\tilde{v}_2=v_2$, $\tilde{v}_3=v_3+1$, $\tilde{v}_4=v_4-1$, $\tilde{v}_5=v_5+1$, $\tilde{v}_6=v_6$.

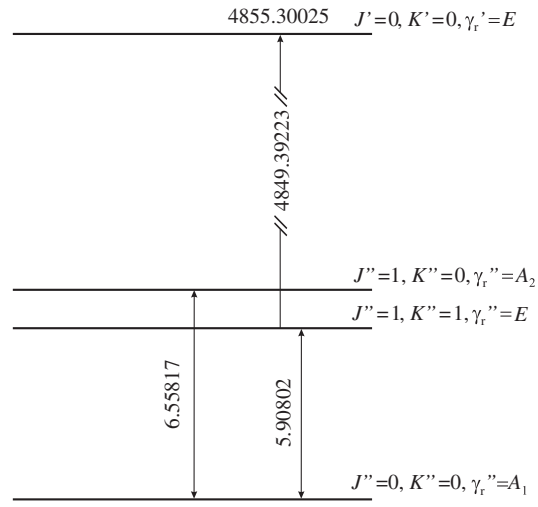
For the CH_3D isotopomer one has:

$$(4)\quad H_{vl\gamma,\tilde{v}\tilde{l}\gamma}=H_{\tilde{v}\tilde{l}\gamma,\,vl\gamma}=\frac{F_{3356}}{4(2^{1/2})}\{v_3(v_3-1)\}^{1/2}\times(q_5^+q_6^-+q_5^-q_6^+) \tag{31}$$



CH_3D "parallel" $\nu_5+3\nu_6$, (A_1) band

Figure 8. Level scheme relating to Figure 6.



CHD_3 "perpendicular" $3\nu_5+\nu_6$, (E) band

Figure 9. Level scheme relating to Figure 7.

Table 10. Line positions and levels for the transitions $[J'=0](upper\ vibr.\ st.) \leftarrow [J''=1](gr.\ vibr.\ st.)$ for some absorption bands of CH_3D (in cm^{-1}).

Band		Transition	J'' K'' γ_r''	$E''_{rot.}/hc$	$E'_{vib.}/hc$
$\nu_3+\nu_3+\nu_3$	(A_1)	3927.4877	1 0 a_2	7.7602	3935.2479
$2\nu_5+\nu_6$	$(1E)$	4049.5611	1 1 e	9.1306	4058.6917
$2\nu_3+\nu_5$	(E)	4058.7280	1 1 e	9.1306	4067.8586
$2\nu_5+\nu_6$	(A_1)	4073.1815	1 0 a_2	7.7602	4080.9417
$2\nu_5+\nu_6$	$(2E)$	4093.3113	1 1 e	9.1306	4102.4419
$\nu_1+\nu_6$	(E)	4113.4594	1 1 e	9.1306	4122.5901
$\nu_4+\nu_6$	(A_1)	4155.7331	1 0 a_2	7.7602	4163.4933
$\nu_4+\nu_6$	(E)	4161.2319	1 1 e	9.1306	4170.3625
$\nu_3+2\nu_5$	(A_1)	4207.5285	1 0 a_2	7.7602	4215.2887
$\nu_3+2\nu_5$	(E)	4232.6136	1 1 e	9.1306	4241.7442

Table 11. Line positions and levels for the transitions $[J'=0](upper\ vibr.\ st.) \leftarrow [J''=1](gr.\ vibr.\ st.)$ for some absorption bands of CHD_3 (in cm^{-1}).

Band		Transition	J'' K'' γ_r''	$E''_{rot.}/hc$	$E'_{vib.}/hc$
$2\nu_3+\nu_4$	(E)	4206.4244	1 1 e	5.9080	4212.3324
$\nu_1+\nu_5$	(E)	4255.7536	1 1 e	5.9080	4261.6616
$\nu_2+\nu_4$	(E)	4350.6155	1 1 e	5.9080	4356.5235
$2\nu_4$	(A_1)	4451.2228	1 0 a_2	6.5582	4457.7810
$\nu_2+\nu_5+\nu_6$	(A_1)	4456.4283	1 0 a_2	6.5582	4462.9865
$2\nu_4$	(E)	4480.4003	1 1 e	5.9080	4486.3083
$\nu_3+\nu_4+\nu_5$	(E)	4523.1538	1 1 e	5.9080	4529.0618
$\nu_4+\nu_5+\nu_6$	$(1E)$	4552.0213	1 1 e	5.9080	4557.9293
$\nu_2+2\nu_5$	(A_1)	4692.3241	1 0 a_2	6.5582	4698.8823
$\nu_3+3\nu_5$	(E)	4849.3922	1 1 e	5.9080	4855.3003

Table 12. Values of the experimental band centres of CH_3D (in cm^{-1}).[a]

Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.	Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.
1	2	3	4	5	6	1	2	3	4	5	6
ν_6, E	1163.29	1160.89	1160.74	1161.103	[54]	$\nu_2+\nu_3+\nu_6$, E	4637.57	4639.30	4639.33		
ν_3, A_1	1309.77	1307.34	1307.48	1306.848	[54]	$4\nu_6$, $2E$	4664.03	4643.18	4643.49		
ν_5, E	1471.99	1472.14	1472.16	1472.022	[54]	$\nu_3+3\nu_6$, E	4796.64	4769.91	4769.92		
ν_2, A_1	2194.60	2199.34	2199.08	2200.041	[25]	$\nu_3+3\nu_6$, A_1	4787.06	4781.90	4782.04	4781.529	*tw*
$2\nu_6$, A_1	2325.81	2316.62	2316.37	2316.273	[25]	$\nu_2+2\nu_3$, A_1	4801.80	4782.83	4782.83		
$2\nu_6$, E	2328.39	2322.61	2322.44	2323.289	[25]	$\nu_2+\nu_5+\nu_6$, E	4795.16	4801.06	4801.10		
$\nu_3+\nu_6$, E	2471.97	2465.14	2465.14	2465.458	[25]	$\nu_2+\nu_5+\nu_6$, A_1	4805.27	4811.54	4811.54	4811.172	*tw*
$2\nu_3$, A_1	2605.94	2598.43	2598.57	2597.681	[25]	$2\nu_3+2\nu_6$, A_1	4927.39	4901.65	4901.65	4901.422	*tw*
$\nu_5+\nu_6$, E	2626.16	2623.17	2623.13	2623.433	[25]	$2\nu_3+2\nu_6$, E	4929.97	4907.66	4907.72		
$\nu_5+\nu_6$, A_1	2636.27	2633.43	2633.37	2633.155	[25]	$\nu_5+3\nu_6$, $1E$	4939.93	4924.69	4924.76		
$\nu_3+\nu_5$, E	2779.73	2776.61	2776.73	2776.287	[25]	$\nu_5+3\nu_6$, $2E$	4944.88	4926.39	4926.63		
$2\nu_5$, A_1	2938.18	2910.14	2910.01	2910.120	[25]	$\nu_5+3\nu_6$, A_1	4954.99	4935.08	4935.11	4934.354	*tw*
$2\nu_5$, E	2941.01	2940.22	2940.25	2940.098	[25]	$\nu_5+3\nu_6$, $3E$	4970.26	4955.49	4955.70		
ν_1, A_1	2939.47	2969.61	2969.49	2969.512	[25]	$\nu_2+\nu_3+\nu_5$, E	4964.26	4964.94	4964.98		
ν_4, E	3012.02	3015.80	3015.90	3016.713	[25]	$3\nu_3+\nu_6$, E	5048.52	5027.63	5027.40		
$\nu_2+\nu_6$, E	3335.62	3342.42	3342.24	3342.573	*tw*	$\nu_3+\nu_5+2\nu_6$, A_1	5087.69	5073.33	5073.48		
$3\nu_6$, E	3490.14	3471.84	3471.66	3471.465	*tw*	$\nu_3+\nu_5+2\nu_6$, $1E$	5095.23	5077.52	5077.57		
$3\nu_6$, A_1	3495.30	3483.83	3483.79	3482.240	*tw*	$\nu_3+\nu_5+2\nu_6$, $2E$	5107.92	5093.52	5093.61		
$\nu_2+\nu_3$, A_1	3497.63	3499.31	3499.25	3499.718	*tw*	$\nu_2+2\nu_5$, A_1	5127.41	5103.61	5103.53	5103.572	*tw*
$\nu_3+2\nu_6$, A_1	3633.40	3617.78	3617.71	3616.793	*tw*	$\nu_2+2\nu_5$, E	5128.94	5132.28	5132.29	5132.103	*tw*
$\nu_3+2\nu_6$, E	3635.98	3623.78	3623.77	3625.011	*tw*	$4\nu_3$, A_1	5157.46	5135.13	5134.70		
$\nu_2+\nu_5$, E	3663.26	3667.83	3667.72	3668.078	*tw*	$\nu_1+\nu_2$, A_1	5130.90	5164.61	5164.53	5165.046	*tw*
$2\nu_3+\nu_6$, E	3767.05	3752.70	3752.74	3753.889	*tw*	$2\nu_5+2\nu_6$, $1A_1$	5249.01	5206.46	5206.55		
$\nu_5+2\nu_6$, A_1	3782.14	3775.03	3775.05			$2\nu_3+\nu_5+\nu_6$, E	5225.85	5206.50	5206.68		
$\nu_5+2\nu_6$, $1E$	3789.67	3778.97	3778.91	3779.769	*tw*	$\nu_2+\nu_4$, E	5232.90	5207.26	5207.25		
$\nu_5+2\nu_6$, $2E$	3802.36	3794.54	3794.53			$2\nu_5+2\nu_6$, $1E$	5208.26	5216.66	5216.66	5215.206	*tw*
$3\nu_3$, A_1	3888.50	3874.44	3874.39	3874.741	*tw*	$2\nu_3+\nu_5+\nu_6$, A_1	5235.96	5221.92	5221.83		
$\nu_3+\nu_5+\nu_6$, E	3932.81	3924.55	3924.62			$2\nu_5+2\nu_6$, $2E$	5250.55	5223.41	5223.60		
$\nu_3+\nu_5+\nu_6$, A_1	3942.92	3935.47	3935.48	3935.248	*tw*	$2\nu_5+2\nu_6$, $3E$	5251.59	5237.32	5237.40		
$2\nu_5+\nu_6$, $1E$	4094.62	4059.64	4059.68	4058.692	*tw*	$2\nu_5+2\nu_6$, $2A_1$	5273.35	5262.33	5262.47		
$2\nu_3+\nu_5$, E	4073.87	4066.77	4066.73	4067.859	*tw*	$\nu_1+2\nu_6$, A_1	5252.76	5269.72	5269.69		
$2\nu_5+\nu_6$, A_1	4086.05	4081.40	4081.44	4080.942	*tw*	$\nu_1+2\nu_6$, E	5255.34	5275.64	5275.68	5276.520	*tw*
$2\nu_5+\nu_6$, $2E$	4106.27	4101.00	4101.02	4102.442	*tw*	$\nu_4+2\nu_6$, $1E$	5322.46	5313.31	5313.41		
$\nu_1+\nu_6$, E	4095.86	4122.20	4122.10	4122.590	*tw*	$\nu_4+2\nu_6$, $2E$	5325.50	5313.66	5313.67	5314.220	*tw*
$\nu_4+\nu_6$, A_1	4167.85	4164.13	4164.18	4163.493	*tw*	$\nu_4+2\nu_6$, A_1	5324.58	5325.99	5326.05	5325.677	*tw*
$\nu_4+\nu_6$, E	4167.39	4170.47	4170.50	4170.363	*tw*	$3\nu_3+\nu_5$, E	5354.40	5336.62	5336.54		
$\nu_3+2\nu_5$, A_1	4245.18	4215.16	4214.98	4215.289	*tw*	$\nu_3+2\nu_5+\nu_6$, $1E$	5399.24	5364.60	5364.43		
$\nu_3+2\nu_5$, E	4246.71	4241.83	4241.92	4241.744	*tw*	$\nu_3+2\nu_5+\nu_6$, A_1	5390.66	5379.92	5380.03		
$\nu_1+\nu_3$, A_1	4246.97	4279.17	4278.54			$\nu_3+2\nu_5+\nu_6$, $2E$	5410.89	5400.18	5400.24		
$\nu_3+\nu_4$, E	4312.35	4312.78	4312.86	4313.422	*tw*	$\nu_1+\nu_3+\nu_6$, E	5403.56	5428.93	5428.32		
$2\nu_2$, A_1	4326.87	4342.50	4342.27	4344.123	*tw*	$\nu_3+\nu_4+\nu_6$, A_1	5467.09	5458.03	5458.07	5456.630	*tw*
$3\nu_5$, E	4403.97	4356.14	4356.27	4356.890	*tw*	$\nu_3+\nu_4+\nu_6$, E	5466.63	5464.37	5464.39	5464.627	*tw*
$3\nu_5$, A_1	4407.04	4404.27	4404.27	4404.366	*tw*	$2\nu_2+\nu_6$, E	5445.62	5467.76	5467.84		
$\nu_1+\nu_5$, E	4391.15	4440.42	4440.71	4439.733	*tw*	$3\nu_5+\nu_6$, $1E$	5542.96	5497.43	5497.71		
$\nu_4+\nu_5$, E	4467.68	4472.68	4472.63	4472.657	*tw*	$2\nu_3+2\nu_5$, A_1	5537.28	5498.22	5498.28		
$\nu_2+2\nu_6$, A_1	4475.88	4480.34	4480.28			$3\nu_5+\nu_6$, A_1	5560.11	5512.94	5512.82		
$\nu_2+2\nu_6$, E	4478.46	4486.33	4486.34	4486.893	*tw*	$2\nu_3+2\nu_5$, E	5538.82	5527.10	5527.11		
$\nu_4+\nu_5$, A_1	4471.12	4486.84	4486.76	4484.820	*tw*	$3\nu_5+\nu_6$, $2E$	5549.99	5535.59	5535.69		
$4\nu_6$, A_1	4653.71	4619.20	4619.24	4618.447	*tw*	$3\nu_5+\nu_6$, $3E$	5573.29	5564.92	5564.85		
$4\nu_6$, $1E$	4656.29	4625.20	4625.31	4626.909	*tw*	$\nu_1+\nu_5+\nu_6$, E	5539.71	5583.15	5583.55		
$\nu_1+2\nu_3$, A_1	5542.16	5572.34	5571.13			$\nu_3+\nu_5+3\nu_6$, $2E$	6249.40	6221.60	6221.98		
$2\nu_3+\nu_4$, E	5599.08	5593.53	5593.45	5593.699	*tw*	$\nu_3+\nu_5+3\nu_6$, A_1	6259.52	6231.56	6231.65		
$\nu_1+\nu_5+\nu_6$, A_1	5549.82	5594.30	5594.51			$\nu_2+2\nu_5+\nu_6$, $1E$	6260.30	6236.08	6236.32	6236.184	*tw*
$\nu_4+\nu_5+\nu_6$, A_1	5613.93	5617.51	5617.45			$\nu_2+2\nu_3+\nu_5$, E	6251.80	6246.67	6246.70		
$\nu_2+3\nu_6$, E	5617.95	5617.74	5617.98			$\nu_3+\nu_5+3\nu_6$, $3E$	6274.79	6251.66	6251.96		

(*continued*)

Table 12. Continued.

Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.	Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.
1	2	3	4	5	6	1	2	3	4	5	6
$\nu_4+\nu_5+\nu_6$, $1E$	5617.83	5621.09	5621.04			$\nu_2+2\nu_5+\nu_6$, A_1	6251.81	6255.65	6255.90		
$\nu_4+\nu_5+\nu_6$, $2E$	5624.50	5625.33	5625.26	5627.609	*tw*	$\nu_2+2\nu_5+\nu_6$, $2E$	6272.03	6275.45	6275.65		
$\nu_2+3\nu_6$, A_1	5623.11	5629.73	5630.11			$4\nu_3+\nu_6$, E	6316.52	6282.61	6282.14		
$2\nu_2+\nu_3$, A_1	5623.16	5635.10	5635.13	5635.975	*tw*	$\nu_1+\nu_2+\nu_6$, E	6266.31	6299.47	6299.64	6298.488	*tw*
$\nu_4+\nu_5+\nu_6$, $3E$	5627.48	5641.37	5641.27			$\nu_2+\nu_4+\nu_6$, A_1	6341.83	6337.79	6337.95	6337.064	*tw*
$\nu_3+3\nu_5$, E	5707.64	5658.39	5658.40			$\nu_2+\nu_4+\nu_6$, E	6341.47	6344.13	6344.26		
$\nu_3+3\nu_5$, A_1	5710.71	5703.00	5703.03			$2\nu_3+\nu_5+2\nu_6$, $1E$	6387.26	6346.99	6347.41		
$\nu_1+\nu_3+\nu_5$, E	5697.91	5747.02	5746.79			$2\nu_3+\nu_5+2\nu_6$, A_1	6379.73	6352.08	6352.39		
$5\nu_6$, $1E$	5819.09	5763.38	5763.88			$2\nu_5+3\nu_6$, $1E$	6381.60	6364.91	6365.40		
$\nu_3+\nu_4+\nu_5$, E	5765.98	5766.80	5766.68	5767.069	*tw*	$2\nu_5+3\nu_6$, $2E$	6405.24	6365.90	6365.83		
$\nu_2+\nu_3+2\nu_6$, A_1	5776.73	5774.13	5774.30			$2\nu_5+3\nu_6$, $1A_1$	6396.67	6367.40	6367.76		
$5\nu_6$, A_1	5824.25	5775.37	5776.00			$2\nu_5+3\nu_6$, $2A_1$	6410.40	6373.88	6374.11		
$4\nu_5$, A_1	5863.95	5775.85	5775.10			$2\nu_3+\nu_5+2\nu_6$, $2E$	6399.95	6375.02	6375.12		
$\nu_2+\nu_3+2\nu_6$, E	5779.31	5780.12	5780.36			$5\nu_3$, A_1	6412.97	6380.48	6379.50		
$\nu_3+\nu_4+\nu_5$, A_1	5769.42	5780.96	5780.81			$2\nu_5+3\nu_6$, $3E$	6416.89	6390.36	6390.74		
$5\nu_6$, $2E$	5834.57	5799.35	5800.26			$\nu_2+\nu_3+2\nu_5$, A_1	6424.49	6400.94	6400.88		
$4\nu_5$, $1E$	5841.15	5800.65	5801.04			$\nu_1+3\nu_6$, E	6411.55	6417.14	6417.34		
$2\nu_2+\nu_5$, E	5792.20	5807.34	5807.39			$2\nu_5+3\nu_6$, $4E$	6442.28	6423.10	6423.52		
$\nu_1+2\nu_5$, A_1	5839.62	5829.74	5822.83			$\nu_2+\nu_3+2\nu_5$, $2E$	6428.03	6426.52	6426.64		
$\nu_1+\nu_4$, E	5877.43	5855.01	5854.93	5855.063	*tw*	$\nu_1+3\nu_6$, A_1	6416.71	6428.61	6428.96		
$\nu_1+2\nu_5$, E	5865.48	5864.26	5864.22	5864.066	*tw*	$3\nu_2$, A_1	6396.80	6429.44	6429.58	6428.364	*tw*
$2\nu_1$, A_1	5841.96	5903.96	5903.74	5904.157	*tw*	$\nu_4+3\nu_6$, A_1	6479.38	6456.32	6456.49		
$4\nu_5$, $2E$	5870.09	5904.62	5905.27			$\nu_4+3\nu_6$, $1E$	6478.92	6461.98	6462.30		
$\nu_3+4\nu_6$, A_1	5959.12	5914.19	5914.43			$\nu_4+3\nu_6$, $2E$	6483.62	6462.67	6462.81		
$\nu_2+2\nu_3+\nu_6$, E	5925.90	5919.16	5919.30			$\nu_1+\nu_2+\nu_3$, A_1	6433.09	6467.13	6467.58		
$\nu_3+4\nu_6$, $1E$	5961.70	5920.19	5920.49			$3\nu_3+\nu_5+\nu_6$, E	6505.40	6477.36	6477.31		
$\nu_4+2\nu_5$, A_1	5920.36	5925.52	5925.28			$\nu_4+3\nu_6$, $3E$	6485.00	6481.00	6481.26		
$\nu_2+\nu_5+2\nu_6$, A_1	5928.87	5935.11	5935.44			$3\nu_3+\nu_5+\nu_6$, A_1	6515.51	6487.03	6486.98		
$\nu_3+4\nu_6$, $2E$	5969.44	5938.17	5938.68			$\nu_2+\nu_3+\nu_4$, E	6501.98	6496.87	6496.90		
$\nu_2+\nu_5+2\nu_6$, $1E$	5936.40	5939.23	5939.46			$\nu_3+2\nu_5+2\nu_6$, $1A_1$	6552.60	6509.74	6509.58		
$\nu_4+2\nu_5$, $1E$	5922.27	5940.46	5940.61	5940.240	*tw*	$\nu_3+2\nu_5+2\nu_6$, $1E$	6536.49	6514.18	6514.18		
$\nu_4+2\nu_5$, $2E$	5927.25	5953.85	5953.54			$\nu_3+2\nu_5+2\nu_6$, $2E$	6554.13	6518.84	6519.11		
$\nu_2+\nu_5+2\nu_6$, $2E$	5949.10	5954.77	5955.06			$\nu_3+2\nu_5+2\nu_6$, $3E$	6555.18	6533.45	6533.56		
$2\nu_4$, A_1	5935.55	5980.41	5980.42	5980.416	*tw*	$\nu_2+3\nu_5$, E	6588.67	6545.98	6546.27		
$2\nu_4$, E	5986.09	6022.14	6022.08	6022.214	*tw*	$\nu_3+2\nu_5+2\nu_6$, $2A_1$	6576.94	6559.06	6559.21		
$2\nu_3+3\nu_6$, E	6089.62	6047.35	6047.62			$\nu_1+\nu_3+2\nu_6$, A_1	6559.46	6573.62	6573.10		
$\nu_2+3\nu_3$, A_1	6063.04	6051.50	6051.36			$\nu_1+\nu_3+2\nu_6$, E	6562.04	6579.53	6579.08		
$2\nu_3+3\nu_6$, A_1	6094.78	6061.00	6061.35			$2\nu_2+2\nu_6$, A_1	6563.76	6587.87	6588.30		
$\nu_5+4\nu_6$, $1A_1$	6101.93	6069.67	6069.99			$\nu_2+3\nu_5$, A_1	6591.74	6592.69	6592.79		
$\nu_5+4\nu_6$, $1E$	6099.56	6075.89	6076.09			$2\nu_2+2\nu_6$, E	6566.34	6593.86	6593.76		
$\nu_5+4\nu_6$, $2E$	6109.47	6075.94	6076.56			$4\nu_3+\nu_5$, E	6621.46	6594.24	6594.36		
$\nu_5+4\nu_6$, $3E$	6122.16	6085.99	6086.48			$\nu_3+\nu_4+2\nu_6$, $1E$	6620.68	6604.12	6604.23		
$\nu_2+\nu_3+\nu_5+\nu_6$, E	6095.18	6095.08	6095.28			$\nu_3+\nu_4+2\nu_6$, $2E$	6623.72	6604.47	6604.48		
$\nu_2+\nu_3+\nu_5+\nu_6$, A_1	6105.30	6106.19	6106.32			$\nu_3+\nu_4+2\nu_6$, A_1	6622.80	6616.80	6616.86		
$\nu_5+4\nu_6$, $2A_1$	6140.01	6114.58	6115.21			$\nu_1+\nu_2+\nu_5$, E	6580.67	6631.77	6632.23		
$3\nu_3+2\nu_6$, A_1	6207.88	6170.88	6170.75			$2\nu_3+2\nu_5+\nu_6$, $1E$	6690.34	6636.08	6636.49		
$3\nu_3+2\nu_6$, E	6210.46	6177.08	6177.01			$2\nu_3+2\nu_5+\nu_6$, A_1	6681.76	6636.80	6637.41		
$\nu_3+\nu_5+3\nu_6$, $1E$	6244.45	6220.01	6220.21			$3\nu_5+2\nu_6$, $1E$	6680.73	6650.99	6651.19		
$\nu_2+\nu_4+\nu_5$, E	6660.69	6660.50	6660.46			$4\nu_5+\nu_6$, $3E$	7022.66	6985.72	6985.86		
$3\nu_5+2\nu_6$, $1A_1$	6697.88	6664.24	6664.26			$\nu_1+\nu_4+\nu_6$, A_1	7027.73	6995.48	6995.56		
$3\nu_5+2\nu_6$, $2E$	6705.41	6665.11	6665.18			$\nu_1+\nu_4+\nu_6$, E	7027.27	7001.80	7001.86		
$3\nu_5+2\nu_6$, $3E$	6718.10	6667.74	6667.76			$4\nu_5+\nu_6$, $2A_1$	7037.38	7024.77	7024.85		
$\nu_2+\nu_4+\nu_5$, A_1	6664.13	6674.67	6674.59			$\nu_1+2\nu_3+\nu_5$, E	6991.18	7032.76	7032.24		
$2\nu_3+2\nu_5+\nu_6$, $2E$	6701.99	6681.82	6681.84			$\nu_1+2\nu_5+\nu_6$, A_1	6980.65	7037.53	7038.38		
$3\nu_5+2\nu_6$, $2A_1$	6708.48	6691.49	6691.69			$2\nu_3+\nu_4+\nu_5$, E	7050.77	7041.40	7041.23		

(*continued*)

Table 12. Continued.

Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.	Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.
1	2	3	4	5	6	1	2	3	4	5	6
$\nu_1+2\nu_3+\nu_6$, E	6697.76	6715.55	6714.73			$\nu_1+2\nu_5+\nu_6$, $1E$	6989.23	7047.67	7047.65		
$3\nu_5+2\nu_6$, $4E$	6741.40	6726.03	6726.30			$\nu_2+2\nu_3+2\nu_6$, A_1	7064.12	7050.15	7050.49		
$\nu_1+\nu_5+2\nu_6$, A_1	6690.14	6727.18	6727.79			$\nu_3+5\nu_6$, $1E$	7123.47	7055.28	7055.99		
$\nu_1+\nu_5+2\nu_6$, $1E$	6697.67	6732.00	6732.41			$\nu_2+2\nu_3+2\nu_6$, E	7066.70	7055.93	7056.36		
$2\nu_3+\nu_4+\nu_6$, A_1	6752.83	6732.82	6732.84			$2\nu_3+\nu_4+\nu_5$, A_1	7054.22	7056.74	7056.48		
$2\nu_3+\nu_4+\nu_6$, E	6752.37	6739.97	6739.93			$\nu_4+2\nu_5+\nu_6$, $1E$	7057.54	7060.49	7060.33		
$\nu_2+4\nu_6$, A_1	6759.34	6747.30	6747.98			$\nu_1+2\nu_5+\nu_6$, $2E$	7000.87	7061.02	7061.35		
$\nu_1+\nu_5+2\nu_6$, $2E$	6710.36	6749.24	6749.49			$\nu_3+5\nu_6$, A_1	7128.63	7067.27	7068.12		
$\nu_2+4\nu_6$, $1E$	6761.92	6753.30	6754.04			$\nu_2+\nu_5+3\nu_6$, $1E$	7064.49	7067.50	7068.05		
$2\nu_2+\nu_3+\nu_6$, E	6741.00	6757.28	6757.62			$\nu_2+\nu_5+3\nu_6$, $2E$	7069.44	7068.66	7069.43		
$\nu_4+\nu_5+2\nu_6$, $1E$	6762.04	6760.91	6760.90			$\nu_4+2\nu_5+\nu_6$, $2E$	7064.88	7076.66	7076.38		
$\nu_4+\nu_5+2\nu_6$, $2E$	6766.40	6763.16	6763.23			$\nu_3+4\nu_5$, A_1	7144.43	7077.40	7076.66		
$\nu_4+\nu_5+2\nu_6$, $3E$	6770.03	6764.65	6764.72			$\nu_2+\nu_5+3\nu_6$, A_1	7079.56	7077.84	7078.35		
$\nu_2+4\nu_6$, $2E$	6769.66	6771.28	6772.23			$\nu_4+2\nu_5+\nu_6$, $1A_1$	7070.02	7079.38	7079.61		
$\nu_4+\nu_5+2\nu_6$, $1A_1$	6773.48	6772.12	6772.12			$\nu_4+2\nu_5+\nu_6$, $3E$	7069.56	7082.48	7082.26		
$3\nu_3+2\nu_5$, A_1	6815.89	6772.21	6771.88			$\nu_4+2\nu_5+\nu_6$, $4E$	7078.22	7085.60	7085.81		
$\nu_4+\nu_5+2\nu_6$, $2A_1$	6783.19	6775.21	6775.14			$\nu_3+5\nu_6$, $2E$	7138.95	7091.25	7092.37		
$3\nu_3+2\nu_5$, E	6817.42	6791.00	6791.11			$2\nu_2+\nu_3+\nu_5$, E	7086.63	7097.09	7097.34		
$\nu_4+\nu_5+2\nu_6$, $4E$	6785.71	6798.30	6798.24			$\nu_2+\nu_5+3\nu_6$, $3E$	7094.83	7097.93	7097.53		
$\nu_3+3\nu_5+\nu_6$, $1E$	6845.60	6802.44	6802.25			$\nu_3+4\nu_5$, $1E$	7167.19	7099.99	7100.20		
$\nu_3+3\nu_5+\nu_6$, A_1	6862.76	6810.87	6810.74			$\nu_4+2\nu_5+\nu_6$, $2A_1$	7084.65	7110.02	7109.69		
$\nu_3+3\nu_5+\nu_6$, $2E$	6852.64	6831.24	6831.37			$2\nu_4+\nu_6$, $1E$	7083.52	7124.34	7124.51		
$\nu_1+3\nu_3$, A_1	6823.88	6852.03	6849.83			$\nu_3+2\nu_4$, A_1	7149.89	7132.12	7131.50		
$3\nu_3+\nu_4$, E	6872.33	6859.21	6858.78			$\nu_1+\nu_3+\nu_4$, $1E$	7176.88	7156.01	7155.27		
$\nu_3+3\nu_5+\nu_6$, $3E$	6875.94	6861.54	6861.59			$2\nu_4+\nu_6$, $2E$	7134.53	7157.93	7157.89		
$\nu_1+\nu_3+\nu_5+\nu_6$, E	6845.47	6886.88	6886.76			$\nu_3+4\nu_5$, $2E$	7171.80	7160.13	7160.06		
$6\nu_6$, $1A_1$	6983.74	6897.01	6898.21			$2\nu_4+\nu_6$, A_1	7133.61	7170.61	7170.53		
$\nu_1+\nu_3+\nu_5+\nu_6$, A_1	6855.58	6898.60	6898.30			$\nu_2+3\nu_3+\nu_6$, E	7200.80	7184.50	7184.52		
$6\nu_6$, $1E$	6986.32	6903.10	6904.28			$2\nu_3+4\nu_6$, A_1	7251.01	7190.03	7190.52		
$\nu_2+\nu_3+3\nu_6$, E	6917.82	6908.46	6908.93			$2\nu_3+4\nu_6$, $1E$	7253.59	7195.16	7195.80		
$\nu_3+\nu_4+\nu_5+\nu_6$, A_1	6911.21	6908.53	6908.43			$5\nu_5$, $1E$	7321.00	7199.91	7199.88		
$2\nu_2+2\nu_3$, A_1	6906.04	6910.91	6911.09			$\nu_1+\nu_3+2\nu_5$, A_1	7165.66	7204.53	7204.06		
$\nu_3+\nu_4+\nu_5+\nu_6$, $1E$	6915.11	6912.41	6912.30			$\nu_1+\nu_3+2\nu_5$, E	7145.97	7208.40	7208.51		
$4\nu_5+\nu_6$, $1E$	6996.93	6915.22	6915.09			$\nu_5+5\nu_6$, $1E$	7260.77	7206.11	7207.19		
$\nu_3+\nu_4+\nu_5+\nu_6$, $2E$	6921.78	6916.36	6916.24			$\nu_5+5\nu_6$, $2E$	7265.73	7207.94	7208.69		
$\nu_2+\nu_3+3\nu_6$, A_1	6922.98	6920.45	6921.06			$\nu_3+\nu_4+2\nu_5$, A_1	7216.71	7216.77	7216.43		
$6\nu_6$, $2E$	6994.06	6920.99	6922.46			$2\nu_3+4\nu_6$, $2E$	7261.33	7217.83	7218.35		
$2\nu_2+\nu_5+\nu_6$, E	6901.98	6922.76	6923.19			$\nu_5+5\nu_6$, $1A_1$	7260.98	7218.13	7218.85		
$4\nu_5+\nu_6$, $1A_1$	7002.43	6932.22	6932.82			$\nu_5+5\nu_6$, $2A_1$	7275.84	7222.20	7223.55		
$\nu_3+\nu_4+\nu_5+\nu_6$, $3E$	6924.77	6932.72	6932.56			$\nu_2+\nu_3+\nu_5+2\nu_6$, A_1	7227.81	7226.05	7226.55		
$2\nu_2+\nu_5+\nu_6$, A_1	6912.09	6933.58	6933.93			$\nu_2+\nu_3+\nu_5+2\nu_6$, $1E$	7235.34	7230.34	7230.74		
$2\nu_3+3\nu_5$, E	6997.80	6940.78	6940.64			$\nu_3+\nu_4+2\nu_5$, $1E$	7218.61	7233.30	7233.25		
$6\nu_6$, $2A_1$	7006.96	6950.97	6952.78			$\nu_5+5\nu_6$, $3E$	7291.11	7237.35	7238.36		
$4\nu_5+\nu_6$, $2E$	7011.01	6956.58	6956.46			$2\nu_2+2\nu_5$, A_1	7253.16	7240.76	7241.03		
$2\nu_1+\nu_6$, E	6994.12	6973.88	6967.38			$5\nu_5$, A_1	7324.07	7242.41	7243.04		
$2\nu_3+3\nu_5$, A_1	7000.87	6984.90	6984.83			$\nu_3+\nu_4+2\nu_5$, $2E$	7223.59	7245.10	7244.68		
$\nu_2+\nu_3+\nu_5+2\nu_6$, $2E$	7248.03	7246.40	7246.83			$2\nu_3+\nu_5+3\nu_6$, $3E$	7565.68	7530.35	7530.67		
$2\nu_2+2\nu_5$, E	7254.70	7268.16	7268.44			$\nu_2+\nu_3+2\nu_5+\nu_6$, $1E$	7558.29	7532.84	7532.97		
$\nu_5+5\nu_6$, $4E$	7311.54	7270.48	7271.78			$2\nu_5+4\nu_6$, $3A_1$	7585.02	7545.40	7546.08		
$2\nu_1+\nu_5$, E	7276.02	7278.79	7272.77			$\nu_2+\nu_3+2\nu_5+\nu_6$, A_1	7549.72	7546.80	7547.17		
$2\nu_1+\nu_3$, A_1	7226.52	7284.26	7283.59			$\nu_1+4\nu_6$, A_1	7569.51	7556.01	7556.61		
$\nu_1+\nu_4+\nu_5$, E	7314.15	7292.20	7292.25			$\nu_1+4\nu_6$, $1E$	7572.09	7561.89	7562.57		
$\nu_1+2\nu_2$, A_1	7261.46	7303.55	7303.82			$\nu_2+\nu_3+2\nu_5+\nu_6$, $2E$	7569.94	7567.26	7567.55		
$\nu_2+4\nu_3$, A_1	7325.30	7304.82	7304.36			$\nu_1+4\nu_6$, $2E$	7579.83	7579.77	7580.65		
$\nu_1+\nu_4+\nu_5$, A_1	7317.59	7306.37	7306.37			$2\nu_5+4\nu_6$, $5E$	7612.98	7581.91	7582.83		

(*continued*)

Table 12. Continued.

Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.	Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.
1	2	3	4	5	6	1	2	3	4	5	6
$\nu_3+2\nu_4$, E	7277.07	7308.76	7308.52			$\nu_4+4\nu_6$, $1E$	7635.04	7597.14	7597.67		
$3\nu_3+3\nu_6$, E	7368.94	7315.85	7315.90			$\nu_4+4\nu_6$, $2E$	7638.08	7597.49	7597.93		
$5\nu_5$, $2E$	7330.21	7320.21	7320.09			$\nu_1+\nu_2+\nu_3+\nu_6$, E	7567.42	7599.14	7598.85		
$3\nu_3+3\nu_6$, A_1	7374.10	7330.45	7330.51			$\nu_4+4\nu_6$, $1A_1$	7637.16	7608.79	7609.54		
$2\nu_2+\nu_4$, E	7342.32	7342.53	7342.72			$\nu_4+4\nu_6$, $2A_1$	7646.28	7609.82	7610.31		
$\nu_1+3\nu_5$, E	7285.17	7359.80	7359.05			$6\nu_3$, A_1	7654.76	7610.51	7608.78		
$\nu_3+\nu_5+4\nu_6$, $1A_1$	7405.34	7360.99	7361.52			$3\nu_3+\nu_5+2\nu_6$, A_1	7658.11	7618.98	7619.10		
$\nu_1+3\nu_5$, A_1	7288.24	7363.48	7364.47			$3\nu_3+\nu_5+2\nu_6$, $1E$	7665.64	7622.82	7622.85		
$\nu_3+\nu_5+4\nu_6$, $1E$	7402.97	7364.46	7364.94			$\nu_2+\nu_3+\nu_4+\nu_6$, A_1	7634.46	7624.32	7624.52		
$\nu_2+2\nu_5+2\nu_6$, $1A_1$	7416.85	7364.49	7365.05			$\nu_2+\nu_3+\nu_4+\nu_6$, E	7633.99	7630.66	7630.84		
$\nu_2+2\nu_3+\nu_5+\nu_6$, E	7381.52	7367.24	7367.79			$\nu_4+4\nu_6$, $3E$	7644.44	7634.15	7634.82		
$\nu_3+\nu_5+4\nu_6$, $2E$	7412.87	7368.02	7368.84			$3\nu_3+\nu_5+2\nu_6$, $2E$	7678.34	7638.54	7638.64		
$\nu_4+3\nu_5$, $1E$	7370.12	7374.31	7373.87			$\nu_3+2\nu_5+3\nu_6$, $1E$	7684.07	7654.03	7654.04		
$\nu_2+2\nu_5+2\nu_6$, $1E$	7376.40	7376.39	7376.72			$\nu_3+2\nu_5+3\nu_6$, $2E$	7707.71	7657.25	7657.84		
$\nu_2+2\nu_5+2\nu_6$, $2E$	7394.05	7379.85	7380.46			$\nu_3+2\nu_5+3\nu_6$, $1A_1$	7699.13	7662.02	7662.44		
$\nu_3+\nu_5+4\nu_6$, $3E$	7425.56	7380.62	7381.11			$\nu_3+2\nu_5+3\nu_6$, $2A_1$	7712.86	7667.36	7667.59		
$\nu_2+2\nu_3+\nu_5+\nu_6$, A_1	7391.63	7384.62	7383.32			$\nu_2+3\nu_5+\nu_6$, $1E$	7705.40	7669.44	7670.09		
$\nu_4+3\nu_5$, $2E$	7370.48	7389.54	7389.90			$\nu_2+2\nu_3+2\nu_5$, A_1	7711.89	7673.24	7673.73		
$\nu_2+2\nu_5+2\nu_6$, $3E$	7395.09	7394.15	7394.61			$\nu_3+2\nu_5+3\nu_6$, $3E$	7719.36	7686.00	7686.29		
$\nu_4+3\nu_5$, A_1	7373.93	7403.71	7404.02			$\nu_2+3\nu_5+\nu_6$, A_1	7722.55	7688.05	7688.05		
$\nu_3+\nu_5+4\nu_6$, $2A_1$	7443.42	7405.46	7406.31			$\nu_2+2\nu_3+2\nu_5$, E	7713.42	7704.12	7704.24		
$\nu_4+3\nu_5$, $3E$	7380.44	7416.81	7416.24			$\nu_2+3\nu_5+\nu_6$, $2E$	7712.44	7706.20	7706.62		
$\nu_2+2\nu_5+2\nu_6$, $2A_1$	7392.51	7419.07	7419.61			$\nu_3+2\nu_5+3\nu_6$, $4E$	7744.74	7716.73	7718.28		
$4\nu_3+2\nu_6$, A_1	7474.69	7424.74	7424.30			$\nu_1+\nu_3+3\nu_6$, E	7717.10	7718.26	7716.86		
$\nu_1+\nu_2+2\nu_6$, A_1	7401.08	7429.26	7429.73			$\nu_1+\nu_3+3\nu_6$, A_1	7722.26	7729.64	7729.50		
$4\nu_3+2\nu_6$, E	7477.27	7431.00	7430.62			$4\nu_3+\nu_5+\nu_6$, E	7771.27	7731.58	7731.17		
$\nu_1+\nu_2+2\nu_6$, E	7403.66	7435.18	7435.72			$\nu_2+3\nu_5+\nu_6$, $3E$	7735.73	7735.80	7736.16		
$2\nu_4+\nu_5$, $1E$	7378.38	7441.28	7441.74			$4\nu_3+\nu_5+\nu_6$, A_1	7781.38	7741.91	7741.47		
$2\nu_4+\nu_5$, A_1	7425.48	7463.77	7463.37			$\nu_3+\nu_4+3\nu_6$, A_1	7776.47	7744.04	7744.23		
$\nu_2+\nu_4+2\nu_6$, $1E$	7474.27	7469.15	7469.59			$\nu_3+\nu_4+3\nu_6$, $1E$	7776.01	7749.70	7750.04		
$\nu_2+\nu_4+2\nu_6$, $2E$	7477.31	7469.50	7469.84			$\nu_3+\nu_4+3\nu_6$, $2E$	7780.71	7750.38	7750.55		
$\nu_2+\nu_4+2\nu_6$, A_1	7476.39	7481.83	7482.23			$\nu_1+\nu_2+2\nu_3$, A_1	7721.57	7752.36	7751.48		
$2\nu_5+4\nu_6$, $1A_1$	7532.09	7489.43	7490.18			$\nu_1+\nu_2+\nu_5+\nu_6$, E	7706.96	7756.75	7757.54		
$2\nu_3+\nu_5+3\nu_6$, $1E$	7535.35	7491.82	7492.48			$\nu_3+\nu_4+3\nu_6$, $3E$	7782.09	7768.72	7768.99		
$2\nu_4+\nu_5$, $2E$	7432.37	7492.10	7491.62			$\nu_1+\nu_2+\nu_5+\nu_6$, A_1	7717.07	7768.73	7769.15		
$2\nu_3+\nu_5+3\nu_6$, $2E$	7540.30	7495.73	7496.41			$\nu_2+2\nu_3+\nu_4$, E	7782.00	7770.02	7769.96		
$2\nu_5+4\nu_6$, $1E$	7544.57	7502.12	7502.60			$2\nu_3+2\nu_5+2\nu_6$, $1E$	7826.44	7777.67	7778.47		
$2\nu_5+4\nu_6$, $2A_1$	7560.68	7504.56	7505.56			$3\nu_5+3\nu_6$, $1E$	7845.45	7780.20	7781.15		
$2\nu_5+4\nu_6$, $2E$	7562.21	7507.77	7508.49			$2\nu_3+2\nu_5+2\nu_6$, $1A_1$	7842.55	7780.54	7781.05		
$\nu_2+3\nu_3+\nu_5$, E	7525.62	7509.70	7509.69			$\nu_2+\nu_4+\nu_5+\nu_6$, A_1	7784.68	7787.52	7787.70		
$2\nu_3+\nu_5+3\nu_6$, A_1	7550.41	7511.62	7511.75			$\nu_2+\nu_4+\nu_5+\nu_6$, $1E$	7788.58	7791.28	7791.44		
$2\nu_5+4\nu_6$, $3E$	7563.26	7518.46	7519.20			$3\nu_5+3\nu_6$, $2E$	7847.54	7793.47	7793.72		
$2\nu_5+4\nu_6$, $4E$	7571.00	7521.02	7521.59			$\nu_2+\nu_4+\nu_5+\nu_6$, $2E$	7795.25	7795.34	7795.50		
$5\nu_3+\nu_6$, E	7570.82	7524.58	7523.59			$2\nu_3+2\nu_5+2\nu_6$, $2E$	7844.08	7798.12	7798.43		
$3\nu_5+3\nu_6$, $1A_1$	7820.28	7799.38	7800.09			$\nu_3+\nu_4+\nu_5+2\nu_6$, $1E$	8058.19	8049.14	8049.09		
$3\nu_5+3\nu_6$, $2A_1$	7862.60	7799.82	7799.84			$\nu_3+\nu_4+\nu_5+2\nu_6$, $2E$	8062.55	8051.11	8051.14		
$\nu_2+\nu_4+\nu_5+\nu_6$, $3E$	7798.24	7811.05	7811.19			$\nu_3+\nu_4+\nu_5+2\nu_6$, $3E$	8066.18	8052.59	8052.62		
$2\nu_3+2\nu_5+2\nu_6$, $3E$	7845.13	7811.55	7811.79			$4\nu_5+2\nu_6$, $1A_1$	8125.54	8054.29	8054.33		
$3\nu_5+3\nu_6$, $3E$	7852.49	7815.13	7815.58			$4\nu_3+2\nu_5$, E	8082.35	8054.63	8053.79		
$3\nu_5+3\nu_6$, $4E$	7875.79	7817.99	7818.44			$\nu_3+\nu_4+\nu_5+2\nu_6$, $1A_1$	8069.62	8058.46	8058.48		
$5\nu_3+\nu_5$, E	7874.82	7836.54	7835.47			$4\nu_5+2\nu_6$, $1E$	8141.16	8060.28	8060.39		
$2\nu_3+2\nu_5+2\nu_6$, $2A_1$	7866.89	7837.79	7837.91			$\nu_3+\nu_4+\nu_5+2\nu_6$, $2A_1$	8079.33	8063.26	8063.15		
$\nu_2+\nu_3+3\nu_5$, E	7885.63	7840.63	7840.85			$4\nu_5+2\nu_6$, $2E$	8158.80	8064.97	8065.90		
$3\nu_5+3\nu_6$, $5E$	7877.88	7846.36	7846.82			$4\nu_5+2\nu_6$, $3E$	8159.85	8077.70	8078.58		
$\nu_1+2\nu_3+2\nu_6$, A_1	7852.50	7858.66	7857.90			$\nu_3+\nu_4+\nu_5+2\nu_6$, $4E$	8081.86	8085.18	8085.13		

(*continued*)

Table 12. Continued.

Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.	Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.
1	2	3	4	5	6	1	2	3	4	5	6
$\nu_1+\nu_5+3\nu_6$, $1E$	7842.32	7862.88	7862.75			$\nu_1+\nu_2+2\nu_5$, A_1	8025.80	8090.96	8091.01		
$\nu_1+\nu_5+3\nu_6$, $2E$	7847.28	7869.80	7870.83			$\nu_1+\nu_2+2\nu_5$, E	8027.34	8092.37	8093.31		
$\nu_1+2\nu_3+2\nu_6$, E	7855.08	7871.22	7871.24			$2\nu_3+3\nu_5+\nu_6$, $1E$	8134.61	8101.25	8101.86		
$2\nu_3+\nu_4+2\nu_6$, $1E$	7905.26	7878.40	7878.40			$4\nu_5+2\nu_6$, $2A_1$	8157.27	8102.42	8103.38		
$2\nu_3+\nu_4+2\nu_6$, $2E$	7908.30	7878.63	7878.55			$4\nu_5+2\nu_6$, $3A_1$	8181.61	8108.02	8108.46		
$\nu_1+\nu_5+3\nu_6$, A_1	7857.39	7880.58	7881.01			$4\nu_3+\nu_4$, E	8131.88	8109.55	8108.59		
$\nu_2+\nu_3+3\nu_5$, A_1	7888.71	7884.06	7884.22			$\nu_2+\nu_4+2\nu_5$, A_1	8110.05	8109.70	8109.60		
$3\nu_5+3\nu_6$, $3A_1$	7911.28	7886.61	7887.23			$2\nu_3+3\nu_5+\nu_6$, A_1	8151.77	8110.61	8111.22		
$2\nu_3+\nu_4+2\nu_6$, A_1	7907.38	7889.88	7889.91			$2\nu_3+3\nu_5+\nu_6$, $2E$	8141.65	8111.55	8111.53		
$\nu_1+\nu_5+3\nu_6$, $3E$	7872.66	7899.55	7900.43			$2\nu_1+2\nu_6$, A_1	8145.43	8111.67	8104.82		
$\nu_4+\nu_5+3\nu_6$, $1A_1$	7917.33	7900.95	7901.09			$2\nu_1+2\nu_6$, E	8148.01	8117.67	8110.87		
$\nu_4+\nu_5+3\nu_6$, $2A_1$	7945.70	7903.46	7903.83			$\nu_1+4\nu_3$, A_1	8091.89	8119.83	8116.26		
$\nu_4+\nu_5+3\nu_6$, $1E$	7911.92	7903.66	7903.86			$\nu_2+\nu_4+2\nu_5$, $1E$	8111.96	8125.21	8125.50		
$\nu_4+\nu_5+3\nu_6$, $2E$	7921.24	7907.17	7907.39			$\nu_1+\nu_4+2\nu_6$, $1E$	8176.73	8136.78	8137.11		
$\nu_4+\nu_5+3\nu_6$, $3E$	7927.91	7908.31	7908.66			$\nu_1+\nu_4+2\nu_6$, $2E$	8179.77	8137.13	8137.38		
$3\nu_3+2\nu_5+\nu_6$, $1E$	7967.78	7913.41	7913.21			$\nu_2+\nu_4+2\nu_5$, $2E$	8116.93	8138.03	8137.84		
$\nu_4+\nu_5+3\nu_6$, $4E$	7930.89	7918.56	7918.93			$4\nu_5+2\nu_6$, $4E$	8163.41	8139.47	8139.87		
$\nu_4+\nu_5+3\nu_6$, $5E$	7943.64	7922.87	7923.08			$2\nu_3+3\nu_5+\nu_6$, $3E$	8164.95	8139.64	8139.64		
$3\nu_3+2\nu_5+\nu_6$, A_1	7959.20	7923.05	7923.24			$\nu_1+\nu_4+2\nu_6$, A_1	8178.84	8149.41	8149.70		
$\nu_1+\nu_2+\nu_3+\nu_5$, E	7880.72	7931.24	7931.23			$\nu_1+2\nu_3+\nu_5+\nu_6$, E	8137.56	8154.27	8152.73		
$3\nu_3+2\nu_5+\nu_6$, $2E$	7979.42	7938.34	7938.60			$\nu_1+2\nu_3+\nu_5+\nu_6$, A_1	8147.67	8163.63	8162.10		
$\nu_3+3\nu_5+2\nu_6$, $1A_1$	7999.40	7941.01	7941.10			$\nu_2+2\nu_4$, A_1	8133.54	8168.88	8169.24		
$\nu_2+\nu_3+\nu_4+\nu_5$, E	7952.29	7947.25	7947.20			$\nu_1+2\nu_5+2\nu_6$, $1E$	8121.90	8171.09	8172.27		
$\nu_4+\nu_5+3\nu_6$, $3A_1$	7916.74	7951.35	7951.64			$2\nu_3+\nu_4+\nu_5+\nu_6$, A_1	8194.85	8182.30	8182.08		
$\nu_3+3\nu_5+2\nu_6$, $1E$	7982.25	7951.41	7951.23			$4\nu_5+2\nu_6$, $5E$	8206.44	8182.91	8183.41		
$\nu_3+3\nu_5+2\nu_6$, $2E$	8006.93	7959.44	7959.53			$\nu_1+2\nu_5+2\nu_6$, $1A_1$	8138.01	8183.12	8183.24		
$\nu_3+3\nu_5+2\nu_6$, $3E$	8019.63	7960.30	7960.67			$\nu_1+2\nu_5+2\nu_6$, $2E$	8139.54	8183.82	8184.94		
$\nu_2+\nu_3+\nu_4+\nu_5$, A_1	7955.72	7961.42	7961.33			$2\nu_3+\nu_4+\nu_5+\nu_6$, $1E$	8198.75	8186.31	8186.06		
$\nu_2+4\nu_5$, A_1	8045.33	7963.00	7962.72			$\nu_1+2\nu_5+2\nu_6$, $3E$	8140.59	8189.11	8189.30		
$\nu_3+3\nu_5+2\nu_6$, $2A_1$	8010.01	7985.00	7985.19			$2\nu_3+\nu_4+\nu_5+\nu_6$, $2E$	8205.42	8190.41	8190.16		
$\nu_2+4\nu_5$, $1E$	8046.86	7986.82	7987.48			$\nu_4+2\nu_5+2\nu_6$, $1E$	8196.48	8196.29	8196.34		
$\nu_1+3\nu_3+\nu_6$, E	7978.29	7994.80	7992.76			$\nu_4+2\nu_5+2\nu_6$, $1A_1$	8204.29	8204.16	8204.10		
$3\nu_3+\nu_4+\nu_6$, A_1	8024.89	7997.54	7997.13			$3\nu_3+3\nu_5$, E	8274.30	8205.33	8205.24		
$3\nu_3+\nu_4+\nu_6$, E	8024.43	8003.95	8003.51			$\nu_2+2\nu_4$, E	8184.09	8205.72	8205.70		
$2\nu_1+\nu_2$, A_1	8032.96	8018.11	8011.18			$2\nu_3+\nu_4+\nu_5+\nu_6$, $3E$	8208.40	8206.53	8206.27		
$\nu_3+3\nu_5+2\nu_6$, $4E$	8042.92	8020.46	8020.66			$\nu_1+2\nu_5+2\nu_6$, $2A_1$	8162.35	8208.54	8209.74		
$\nu_1+\nu_3+\nu_5+2\nu_6$, A_1	7994.75	8027.56	8027.69			$\nu_4+2\nu_5+2\nu_6$, $2A_1$	8214.59	8211.94	8211.95		
$\nu_1+\nu_3+\nu_5+2\nu_6$, $1E$	8002.28	8032.18	8032.15			$\nu_4+2\nu_5+2\nu_6$, $2E$	8216.49	8218.94	8219.38		
$4\nu_3+2\nu_5$, A_1	8080.81	8034.21	8033.11			$\nu_4+2\nu_5+2\nu_6$, $3E$	8219.53	8219.65	8219.94		
$\nu_1+\nu_2+\nu_4$, E	8071.93	8042.95	8043.14			$\nu_3+4\nu_5+\nu_6$, $1E$	8297.51	8221.82	8221.14		
$\nu_1+\nu_3+\nu_5+2\nu_6$, $2E$	8014.97	8048.38	8048.34			$\nu_4+2\nu_5+2\nu_6$, $4E$	8221.47	8223.04	8223.06		
$\nu_2+4\nu_5$, $2E$	8051.47	8049.04	8049.21			$\nu_3+4\nu_5+\nu_6$, $1A_1$	8303.01	8227.19	8227.65		
$\nu_4+2\nu_5+2\nu_6$, $3A_1$	8218.61	8231.30	8231.72			$\nu_4+3\nu_5+\nu_6$, $1E$	8498.13	8499.42	8499.15		
$\nu_4+2\nu_5+2\nu_6$, $5E$	8237.85	8231.82	8231.72			$\nu_1+3\nu_5+\nu_6$, A_1	8435.71	8502.45	8501.81		
$\nu_3+4\nu_5+\nu_6$, $2E$	8311.59	8250.95	8251.09			$2\nu_3+\nu_4+2\nu_5$, $1E$	8501.30	8509.12	8508.80		
$3\nu_3+3\nu_5$, A_1	8277.37	8252.78	8252.41			$\nu_1+3\nu_5+\nu_6$, $3E$	8448.89	8517.14	8518.12		
$2\nu_4+2\nu_6$, $1A_1$	8230.68	8263.10	8263.50			$2\nu_3+\nu_4+2\nu_5$, $2E$	8506.28	8519.24	8519.68		
$\nu_4+2\nu_5+2\nu_6$, $6E$	8243.82	8263.20	8263.14			$\nu_4+3\nu_5+\nu_6$, $1A_1$	8508.61	8522.48	8522.23		
$2\nu_4+2\nu_6$, $1E$	8233.26	8269.10	8269.56			$\nu_4+3\nu_5+\nu_6$, $2A_1$	8508.91	8525.22	8525.66		
$\nu_3+2\nu_4+\nu_6$, $1E$	8373.36	8272.50	8264.39			$\nu_4+3\nu_5+\nu_6$, $2E$	8512.51	8529.09	8529.53		
$\nu_3+4\nu_5+\nu_6$, $3E$	8323.24	8278.51	8278.63			$\nu_4+3\nu_5+\nu_6$, $3E$	8519.18	8533.36	8533.77		
$\nu_1+\nu_3+\nu_4+\nu_6$, A_1	8326.02	8293.08	8292.51			$\nu_4+3\nu_5+\nu_6$, $3A_1$	8528.92	8535.58	8535.20		
$2\nu_4+2\nu_6$, $2A_1$	8284.72	8294.56	8294.66			$\nu_3+5\nu_5$, A_1	8623.71	8538.81	8539.21		
$\nu_1+\nu_3+\nu_4+\nu_6$, E	8325.56	8298.75	8298.18			$\nu_4+3\nu_5+\nu_6$, $4E$	8522.16	8548.93	8549.38		
$2\nu_4+2\nu_6$, $2E$	8281.22	8301.24	8301.24			$\nu_4+3\nu_5+\nu_6$, $5E$	8538.79	8570.93	8570.51		

(*continued*)

Table 12. Continued.

Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.	Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.
1	2	3	4	5	6	1	2	3	4	5	6
$3\nu_3+\nu_4+\nu_5$, E	8321.90	8307.69	8306.98			$2\nu_1+2\nu_3$, A_1	8444.13	8571.84	8570.30		
$\nu_1+3\nu_3+\nu_5$, E	8270.76	8312.25	8310.50			$2\nu_4+\nu_5+\nu_6$, $1E$	8517.18	8575.41	8576.13		
$\nu_3+4\nu_5+\nu_6$, $2A_1$	8337.96	8315.95	8316.11			$\nu_3+2\nu_4+\nu_5$, $1E$	8667.27	8578.98	8571.51		
$2\nu_4+2\nu_6$, $3E$	8282.88	8319.92	8319.94			$2\nu_3+2\nu_4$, E	8554.39	8579.03	8578.48		
$3\nu_3+\nu_4+\nu_5$, A_1	8325.34	8321.40	8320.67			$6\nu_5$, $1A_1$	8728.28	8585.24	8573.74		
$5\nu_5+\nu_6$, $1E$	8451.85	8331.50	8331.90			$2\nu_4+\nu_5+\nu_6$, $1A_1$	8527.29	8587.22	8587.50		
$\nu_1+\nu_3+2\nu_5+\nu_6$, A_1	8284.32	8338.41	8338.72			$\nu_1+\nu_3+\nu_4+\nu_5$, E	8611.50	8589.29	8588.68		
$5\nu_5+\nu_6$, $1A_1$	8447.89	8340.97	8341.33			$2\nu_4+\nu_5+\nu_6$, $2E$	8563.82	8599.83	8598.78		
$\nu_1+\nu_3+2\nu_5+\nu_6$, $1E$	8292.89	8344.87	8344.53			$2\nu_4+\nu_5+\nu_6$, $3E$	8574.86	8602.39	8602.05		
$\nu_3+\nu_4+2\nu_5+\nu_6$, $1E$	8352.75	8348.65	8348.41			$\nu_1+\nu_3+\nu_4+\nu_5$, A_1	8614.94	8603.46	8602.80		
$\nu_1+\nu_3+2\nu_5+\nu_6$, $2E$	8304.54	8359.49	8359.59			$\nu_1+2\nu_4$, A_1	8773.49	8609.67	8608.92		
$\nu_3+\nu_4+2\nu_5+\nu_6$, $2E$	8630.09	8362.67	8362.38			$\nu_3+5\nu_5$, $2E$	8629.85	8613.22	8613.03		
$5\nu_5+\nu_6$, $2E$	8458.90	8364.15	8365.07			$2\nu_4+\nu_5+\nu_6$, $2A_1$	8571.63	8618.04	8617.66		
$\nu_3+\nu_4+2\nu_5+\nu_6$, $1A_1$	8365.22	8369.45	8369.48			$6\nu_5$, $1E$	8775.03	8622.95	8623.57		
$\nu_3+\nu_4+2\nu_5+\nu_6$, $3E$	8364.76	8370.64	8370.34			$2\nu_1+\nu_4$, E	8708.56	8634.08	8624.00		
$\nu_3+\nu_4+2\nu_5+\nu_6$, $4E$	8373.43	8375.66	8375.67			$2\nu_4+\nu_5+\nu_6$, $4E$	8580.82	8640.34	8639.91		
$2\nu_3+4\nu_5$, $1E$	8455.26	8379.42	8379.66			$\nu_1+\nu_3+3\nu_5$, E	8587.89	8655.44	8654.55		
$5\nu_5+\nu_6$, $3E$	8482.19	8396.70	8397.20			$\nu_3+\nu_4+3\nu_5$, $1E$	8664.38	8662.69	8662.11		
$\nu_3+\nu_4+2\nu_5+\nu_6$, $2A_1$	8379.85	8396.98	8396.61			$\nu_1+\nu_3+3\nu_5$, A_1	8590.96	8664.47	8664.87		
$2\nu_3+4\nu_5$, A_1	8453.72	8401.33	8402.30			$\nu_3+\nu_4+3\nu_5$, $2E$	8664.75	8680.59	8680.64		
$2\nu_3+2\nu_4$, A_1	8503.84	8405.58	8396.48			$6\nu_5$, $2E$	8779.63	8680.93	8681.77		
$2\nu_1+\nu_5+\nu_6$, E	8418.97	8412.50	8406.73			$\nu_3+\nu_4+3\nu_5$, A_1	8668.19	8694.75	8694.76		
$2\nu_1+\nu_5+\nu_6$, A_1	8429.08	8423.09	8416.92			$\nu_3+\nu_4+3\nu_5$, $3E$	8674.71	8705.19	8704.48		
$2\nu_1+\nu_3+\nu_6$, E	8300.87	8425.50	8425.00			$2\nu_1+2\nu_5$, A_1	8705.47	8714.27	8710.43		
$\nu_1+\nu_4+\nu_5+\nu_6$, A_1	8454.80	8428.90	8429.14			$2\nu_1+2\nu_5$, E	8707.01	8722.82	8717.73		
$\nu_1+\nu_4+\nu_5+\nu_6$, $1E$	8458.70	8430.18	8430.23			$\nu_1+\nu_4+2\nu_5$, A_1	8747.83	8725.70	8725.82		
$5\nu_5+\nu_6$, $2A_1$	8469.01	8431.82	8431.96			$\nu_1+\nu_4+2\nu_5$, $1E$	8749.73	8729.92	8728.78		
$\nu_1+\nu_4+\nu_5+\nu_6$, $2E$	8465.37	8436.74	8436.96			$2\nu_1+\nu_3+\nu_5$, E	8581.83	8743.35	8743.13		
$2\nu_3+4\nu_5$, $2E$	8459.87	8438.78	8438.60			$\nu_3+2\nu_4+\nu_5$, A_1	8714.37	8747.53	8746.91		
$\nu_3+2\nu_4+\nu_6$, $2E$	8424.36	8441.47	8441.26			$\nu_1+\nu_4+2\nu_5$, $2E$	8754.71	8754.03	8754.07		
$\nu_1+2\nu_3+\nu_4$, E	8462.66	8441.50	8440.42			$\nu_1+2\nu_4$, E	8778.82	8767.16	8767.51		
$\nu_1+\nu_4+\nu_5+\nu_6$, $3E$	8468.35	8454.00	8453.97			$6\nu_5$, $2A_1$	8787.31	8772.11	8771.89		
$\nu_3+2\nu_4+\nu_6$, A_1	8423.44	8454.15	8453.90			$\nu_3+2\nu_4+\nu_5$, $2E$	8721.26	8775.86	8775.16		
$\nu_1+2\nu_3+2\nu_5$, A_1	8435.59	8462.07	8459.48			$\nu_1+4\nu_5$, A_1	8726.14	8805.58	8803.34		
$5\nu_5+\nu_6$, $4E$	8498.45	8480.52	8480.61			$\nu_1+4\nu_5$, $1E$	8727.68	8810.43	8809.10		
$\nu_1+3\nu_5+\nu_6$, $1E$	8418.55	8486.59	8487.84			$\nu_1+4\nu_5$, $2E$	8732.29	8817.49	8818.78		
$\nu_1+3\nu_5+\nu_6$, $2E$	8425.59	8489.73	8489.20			$\nu_4+4\nu_5$, $1E$	8817.59	8819.06	8818.38		
$2\nu_3+\nu_4+2\nu_5$, A_1	8499.40	8490.85	8490.34			$\nu_4+4\nu_5$, $1A_1$	8815.68	8834.26	8834.79		
$\nu_1+2\nu_3+2\nu_5$, E	8437.12	8497.13	8496.72			$\nu_4+4\nu_5$, $2E$	8816.85	8841.59	8841.04		
$\nu_3+5\nu_5$, $1E$	8620.63	8498.89	8498.70			$3\nu_1$, A_1	8711.48	8857.31	8857.17		
$\nu_4+4\nu_5$, $3E$	8822.57	8862.59	8863.04			$2\nu_4+2\nu_5$, $3E$	8867.19	8925.06	8924.61		
$3\nu_4$, E	8821.20	8872.55	8870.97			$2\nu_4+2\nu_5$, $1A_1$	8816.65	8929.69	8929.86		
$\nu_4+4\nu_5$, $2A_1$	8830.62	8875.72	8874.88			$2\nu_4+2\nu_5$, $2A_1$	8875.61	8958.02	8957.09		
$2\nu_4+2\nu_5$, $1E$	8818.18	8897.20	8898.13			$3\nu_4$, A_1	8922.29	9019.01	9018.53		
$2\nu_4+2\nu_5$, $2E$	8861.84	8901.36	8900.60								

Note: [a]Values presented in column 2 were calculated with the parameters from Tables I (cc-pVQZ) and VI of [64]. Band centres presented in columns 3 and 4 were calculated with the parameters from Tables 14 and 15 of the present paper. Experimental values of the band centres are given in column 5.

if $\tilde{v}_1 = v_1$, $\tilde{v}_2 = v_2$, $\tilde{v}_3 = v_3 - 2$, $\tilde{v}_4 = v_4$, $\tilde{v}_5 = v_5 + 1$, $\tilde{v}_6 = v_6 + 1$ (for CHD_3).

For the CHD_3 isotopomer one has:

$$(5)\quad H_{vl\gamma,\tilde{v}\tilde{l}\gamma} = H_{\tilde{v}\tilde{l}\gamma,vl\gamma} = \frac{F_{1333}}{4}\left\{v_1(v_3+1)(v_3+2)(v_3+3)\right\}^{1/2} \tag{32}$$

if $\tilde{v}_1 = v_1 - 1$, $\tilde{v}_2 = v_2$, $\tilde{v}_3 = v_3 + 3$, $\tilde{v}_4 = v_4$, $\tilde{v}_5 = v_5$, $\tilde{v}_6 = v_6$. In Equations (28)–(31) $q_\lambda^+ = (q_{\lambda 1} + iq_{\lambda 2})$ and $q_\lambda^- = (q_{\lambda 1} - iq_{\lambda 2})$ are the 'creation' and 'annihilation' operators for doubly degenerate vibrational modes q_λ, which increase and decrease the value of the quantum

Table 13. Values of the experimental band centres of CHD_3 (in cm^{-1}).[a]

Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.	Band	Centre [64]	Centre calc., I	Centre calc., II	exp.	Ref.
1	2	3	4	5	6	1	2	3	4	5	6
ν_3, A_1	1006.10	1004.39	1004.42	1004.548	[55]	$\nu_2+2\nu_3$, A_1	4172.90	4140.72	4140.70	4139.233	*tw*
ν_6, E	1036.91	1035.45	1035.52	1035.920	[55]	$\nu_2+\nu_3+\nu_6$, E	4208.76	4188.41	4187.84		
ν_5, E	1292.77	1292.12	1292.26	1292.500	[55]	$\nu_2+2\nu_6$, A_1	4209.37	4200.37	4199.83		
$2\nu_3$, A_1	1997.74	1991.23	1991.47	1991.084	[56]	$\nu_2+2\nu_6$, E	4222.38	4205.82	4205.43		
$\nu_3+\nu_6$, E	2044.64	2043.41	2043.20	2041.441	[56]	$2\nu_3+\nu_4$, E	4232.88	4212.28	4212.28	4212.332	*tw*
$2\nu_6$, A_1	2056.31	2059.87	2059.77	2058.9	[56]	$\nu_1+\nu_5$, E	4258.52	4261.91	4262.35	4261.662	*tw*
$2\nu_6$, E	2069.31	2066.28	2066.32	2066.3	[56]	$\nu_3+\nu_4+\nu_6$, A_1	4280.56	4269.94	4269.87		
ν_2, A_1	2143.71	2144.30	2144.41	2142.583	[56]	$\nu_3+\nu_4+\nu_6$, E	4279.11	4274.10	4274.37		
ν_4, E	2252.04	2251.58	2251.30	2250.828	[56]	$3\nu_3+\nu_5$, E	4264.60	4274.37	4275.11		
$\nu_3+\nu_5$, E	2297.84	2301.02	2301.08	2301.165	[56]	$2\nu_2$, A_1	4269.78	4290.38	4291.79		
$\nu_5+\nu_6$, A_1	2328.81	2326.71	2327.12			$\nu_4+2\nu_6$, $1E$	4291.55	4293.48	4293.54	4294.337	*tw*
$\nu_5+\nu_6$, E	2330.65	2338.40	2338.27			$\nu_4+2\nu_6$, $2E$	4306.01	4296.01	4295.51		
$2\nu_5$, A_1	2565.53	2564.63	2564.72	2564.676	[83]	$\nu_4+2\nu_6$, A_1	4303.09	4301.56	4301.78		
$2\nu_5$, E	2587.14	2585.58	2585.60	2586.043	[83]	$2\nu_3+\nu_5+\nu_6$, A_1	4327.77	4324.90	4325.27		
$3\nu_3$, A_1	2974.91	2965.28	2965.65	2966.055	*tw*	$2\nu_3+\nu_5+\nu_6$, E	4329.61	4334.84	4334.68		
ν_1, A_1	2986.85	2992.73	2992.85	2992.786	*tw*	$\nu_2+\nu_4$, E	4358.41	4356.34	4356.39	4356.524	*tw*
$2\nu_3+\nu_6$, E	3037.92	3024.37	3024.47	3025.400	*tw*	$\nu_3+\nu_5+2\nu_6$, $1E$	4365.07	4369.43	4369.10		
$3\nu_6$, E	3071.21	3069.31	3069.39			$\nu_3+\nu_5+2\nu_6$, $2E$	4357.54	4378.37	4377.24		
$\nu_3+2\nu_6$, A_1	3065.68	3076.09	3075.25			$\nu_5+3\nu_6$, $1E$	4363.23	4382.03	4382.66		
$\nu_3+2\nu_6$, E	3078.69	3077.80	3077.24			$\nu_5+3\nu_6$, A_1	4368.70	4383.07	4382.67		
$3\nu_6$, A_1	3097.22	3092.49	3092.38			$\nu_3+\nu_5+2\nu_6$, A_1	4372.38	4392.26	4390.86		
$\nu_2+\nu_3$, A_1	3165.54	3151.77	3151.71	3154.341	*tw*	$\nu_5+3\nu_6$, $2E$	4392.92	4394.66	4393.72		
$\nu_2+\nu_6$, E	3185.29	3177.37	3177.28	3178.224	*tw*	$\nu_5+3\nu_6$, $3E$	4387.40	4417.11	4416.09		
$\nu_3+\nu_4$, E	3249.69	3240.48	3240.56	3239.943	*tw*	$\nu_2+\nu_3+\nu_5$, E	4453.27	4439.72	4439.34		
$\nu_4+\nu_6$, A_1	3281.28	3276.44	3276.12			$2\nu_4$, A_1	4450.38	4457.55	4457.63	4457.781	*tw*
$\nu_4+\nu_6$, E	3279.82	3279.50	3279.53	3279.044	*tw*	$\nu_2+\nu_5+\nu_6$, A_1	4473.18	4463.45	4463.54	4462.987	*tw*
$2\nu_3+\nu_5$, E	3288.45	3294.01	3294.60			$\nu_2+\nu_5+\nu_6$, E	4475.03	4475.14	4474.69		
$\nu_3+\nu_5+\nu_6$, A_1	3335.52	3337.39	3337.29	3338.729	*tw*	$2\nu_4$, E	4483.39	4486.02	4486.30	4486.308	*tw*
$\nu_3+\nu_5+\nu_6$, E	3337.36	3348.33	3347.70			$\nu_3+\nu_4+\nu_5$, A_1	4534.30	4511.81	4511.14		
$\nu_5+2\nu_6$, $1E$	3349.19	3356.52	3356.91			$\nu_3+\nu_4+\nu_5$, E	4534.18	4529.92	4529.86	4529.062	*tw*
$\nu_5+2\nu_6$, $2E$	3360.35	3361.30	3361.20			$\nu_4+\nu_5+\nu_6$, $1E$	4565.93	4555.42	4555.81		
$\nu_5+2\nu_6$, A_1	3364.04	3380.07	3379.55			$\nu_4+\nu_5+\nu_6$, $2E$	4564.59	4558.56	4558.60	4557.929	*tw*
$\nu_2+\nu_5$, E	3432.47	3431.23	3431.33	3430.959	*tw*	$\nu_4+\nu_5+\nu_6$, $3E$	4567.89	4569.51	4570.22		
$\nu_4+\nu_5$, A_1	3537.68	3523.29	3523.09	3523.509	*tw*	$\nu_4+\nu_5+\nu_6$, A_1	4566.31	4573.71	4573.54		
$\nu_4+\nu_5$, E	3537.56	3533.86	3533.63	3533.031	*tw*	$2\nu_3+2\nu_5$, A_1	4559.15	4576.98	4577.94		
$\nu_3+2\nu_5$, A_1	3569.57	3578.83	3579.08	3578.927	*tw*	$2\nu_3+2\nu_5$, E	4580.76	4592.93	4593.39		
$\nu_3+2\nu_5$, E	3591.18	3596.56	3596.41			$\nu_3+2\nu_5+\nu_6$, $1E$	4608.22	4623.53	4623.09		
$2\nu_5+\nu_6$, $1E$	3602.55	3610.05	3610.07			$\nu_3+2\nu_5+\nu_6$, $2E$	4627.99	4631.36	4631.17		
$2\nu_5+\nu_6$, $2E$	3622.32	3619.31	3619.80			$2\nu_5+2\nu_6$, $1A_1$	4622.06	4643.27	4642.97		
$2\nu_5+\nu_6$, A_1	3626.00	3642.70	3642.09			$2\nu_5+2\nu_6$, $2A_1$	4652.66	4648.42	4649.27		
$3\nu_5$, E	3839.89	3838.48	3838.26	3838.040	*tw*	$2\nu_5+2\nu_6$, $1E$	4635.06	4650.86	4650.69		
$3\nu_5$, A_1	3883.11	3880.39	3880.01			$\nu_3+2\nu_5+\nu_6$, A_1	4631.68	4653.61	4652.32		
$4\nu_3$, A_1	3937.63	3926.37	3926.84			$2\nu_5+2\nu_6$, $2E$	4643.67	4664.16	4663.78		
$\nu_1+\nu_3$, A_1	3983.22	3988.59	3988.56	3988.646	*tw*	$2\nu_5+2\nu_6$, $3E$	4660.36	4695.20	4693.85		
$3\nu_3+\nu_6$, E	4016.73	3998.34	3998.31	3997.988	*tw*	$\nu_2+2\nu_5$, A_1	4701.21	4698.56	4698.45	4698.882	*tw*
$\nu_1+\nu_6$, E	4023.45	4027.14	4027.06	4027.331	*tw*	$\nu_2+2\nu_5$, E	4722.82	4719.51	4719.33		
$2\nu_3+2\nu_6$, A_1	4060.60	4039.58	4039.58			$\nu_4+2\nu_5$, $1E$	4803.18	4788.90	4788.49		
$2\nu_3+2\nu_6$, E	4073.60	4046.71	4046.76			$\nu_4+2\nu_5$, $2E$	4824.92	4816.35	4817.85		
$\nu_3+3\nu_6$, E	4082.23	4107.55	4105.88			$\nu_4+2\nu_5$, A_1	4824.68	4818.58	4818.14		
$\nu_3+3\nu_6$, A_1	4108.23	4107.57	4106.55			$\nu_3+3\nu_5$, E	4842.90	4855.65	4855.79	4855.300	*tw*
$4\nu_6$, A_1	4068.62	4109.06	4107.39			$5\nu_3$, A_1	4855.89	4874.60	4875.15		
$4\nu_6$, $1E$	4081.62	4109.53	4108.20			$3\nu_5+\nu_6$, A_1	4876.04	4883.04	4882.94		
$4\nu_6$, $2E$	4120.63	4114.07	4113.72			$\nu_3+3\nu_5$, A_1	4886.12	4892.33	4891.71		
$3\nu_5+\nu_6$, $1E$	4877.88	4894.74	4894.09			$2\nu_3+\nu_5+2\nu_6$, $2E$	5351.42	5370.98	5369.95		
$3\nu_5+\nu_6$, $2E$	4917.42	4913.25	4913.55			$\nu_2+\nu_4+\nu_6$, A_1	5392.31	5377.64	5377.32		

(*continued*)

Table 13. Continued.

Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.	Band	Centre [64]	Centre calc., I	Centre calc., II	exp.	Ref.
1	2	3	4	5	6	1	2	3	4	5	6
$3\nu_5+\nu_6$, $3E$	4922.95	4948.34	4946.98			$\nu_5+4\nu_6$, $1E$	5372.77	5379.68	5379.99		
$4\nu_3+\nu_6$, E	4981.09	4956.30	4956.32			$\nu_2+\nu_4+\nu_6$, E	5390.85	5380.24	5380.28		
$\nu_1+2\nu_3$, A_1	4965.13	4968.23	4968.15	4968.171	*tw*	$\nu_3+\nu_5+3\nu_6$, $1E$	5375.06	5394.41	5392.64		
$3\nu_3+2\nu_6$, A_1	5041.05	5019.48	5018.80			$\nu_3+\nu_5+3\nu_6$, $2E$	5402.91	5397.93	5397.30		
$3\nu_3+2\nu_6$, E	5054.06	5023.31	5022.82			$\nu_5+4\nu_6$, $1A_1$	5376.46	5402.75	5403.33		
$\nu_1+\nu_3+\nu_6$, E	5021.46	5025.59	5025.15			$\nu_3+\nu_5+3\nu_6$, A_1	5373.21	5407.19	5405.35		
$5\nu_6$, $1E$	5061.52	5045.67	5045.28			$\nu_5+4\nu_6$, $2E$	5417.31	5415.30	5413.33		
$\nu_1+2\nu_6$, A_1	5042.55	5049.64	5049.15			$\nu_5+4\nu_6$, $2A_1$	5409.94	5428.65	5426.52		
$\nu_1+2\nu_6$, E	5055.55	5056.88	5056.49			$\nu_2+2\nu_3+\nu_5$, E	5459.60	5431.31	5430.88		
$5\nu_6$, A_1	5087.53	5059.04	5058.93			$\nu_3+\nu_5+3\nu_6$, $3E$	5397.38	5432.10	5429.83		
$4\nu_5$, A_1	5094.23	5092.73	5092.00			$\nu_3+2\nu_4$, A_1	5439.58	5435.12	5436.24		
$4\nu_5$, $1E$	5115.84	5113.68	5112.87			$\nu_5+4\nu_6$, $3E$	5361.61	5449.54	5447.91		
$\nu_2+3\nu_3$, A_1	5160.81	5117.20	5117.16			$\nu_3+2\nu_4$, E	5472.59	5458.73	5459.38		
$5\nu_6$, $2E$	5139.55	5131.04	5130.32			$2\nu_4+\nu_6$, $1E$	5470.48	5473.10	5473.29		
$\nu_3+4\nu_6$, $1E$	5133.28	5132.72	5131.14			$\nu_2+\nu_3+\nu_5+\nu_6$, A_1	5495.62	5474.89	5474.15		
$\nu_1+\nu_2$, A_1	5128.37	5135.02	5134.96	5135.054	*tw*	$\nu_2+\nu_3+\nu_5+\nu_6$, E	5497.46	5486.29	5485.01		
$2\nu_3+3\nu_6$, A_1	5104.79	5135.91	5133.71			$3\nu_3+2\nu_5$, A_1	5534.27	5486.88	5486.53		
$\nu_3+4\nu_6$, $2E$	5094.27	5137.93	5135.25			$\nu_2+\nu_5+2\nu_6$, $1E$	5498.24	5491.04	5491.03		
$2\nu_3+3\nu_6$, E	5078.78	5139.44	5136.50			$\nu_2+\nu_5+2\nu_6$, $2E$	5509.40	5496.29	5495.58		
$\nu_3+4\nu_6$, A_1	5081.27	5139.82	5136.77			$2\nu_4+\nu_6$, A_1	5502.03	5507.24	5508.19		
$\nu_2+2\nu_3+\nu_6$, E	5217.76	5169.36	5168.96			$2\nu_3+\nu_4+\nu_5$, E	5516.34	5510.37	5511.18		
$3\nu_3+\nu_4$, E	5201.61	5171.24	5171.49			$2\nu_4+\nu_6$, $2E$	5504.95	5512.50	5513.48		
$4\nu_5$, $2E$	5180.68	5176.53	5175.49			$\nu_2+\nu_5+2\nu_6$, A_1	5513.08	5514.43	5513.32		
$\nu_2+\nu_3+2\nu_6$, A_1	5234.47	5219.78	5218.32			$\nu_1+2\nu_5$, A_1	5510.16	5514.98	5515.04	5515.603	*tw*
$\nu_2+\nu_3+2\nu_6$, E	5247.48	5220.42	5219.24			$\nu_1+2\nu_5$, E	5531.78	5535.82	5535.84	5535.919	*tw*
$\nu_2+3\nu_6$, E	5228.95	5224.17	5222.86			$\nu_3+\nu_4+\nu_5+\nu_6$, $1E$	5562.85	5548.17	5547.73		
$\nu_2+3\nu_6$, A_1	5254.96	5229.65	5228.85			$2\nu_3+\nu_4+\nu_5$, A_1	5516.46	5560.22	5561.73		
$\nu_1+\nu_4$, E	5241.08	5235.78	5235.59	5237.638	*tw*	$\nu_3+\nu_4+\nu_5+\nu_6$, $2E$	5564.19	5566.44	5567.60		
$2\nu_3+\nu_4+\nu_6$, A_1	5265.39	5237.99	5238.24			$\nu_3+\nu_4+\nu_5+\nu_6$, $3E$	5566.15	5566.69	5567.90		
$4\nu_3+\nu_5$, E	5226.29	5241.08	5241.99			$\nu_3+\nu_4+\nu_5+\nu_6$, A_1	5564.57	5570.77	5570.44		
$2\nu_3+\nu_4+\nu_6$, E	5263.93	5246.81	5247.83			$2\nu_2+\nu_5$, E	5554.52	5572.13	5573.37		
$\nu_1+\nu_3+\nu_5$, E	5253.85	5273.96	5273.74	5273.275	*tw*	$3\nu_3+2\nu_5$, E	5555.88	5574.67	5575.52		
$3\nu_3+\nu_5+\nu_6$, A_1	5305.55	5292.60	5292.59			$\nu_4+\nu_5+2\nu_6$, $1A_1$	5577.30	5577.89	5578.02		
$\nu_3+\nu_4+2\nu_6$, $1E$	5292.47	5295.66	5295.30			$\nu_4+\nu_5+2\nu_6$, $2A_1$	5589.80	5578.31	5578.62		
$\nu_3+\nu_4+2\nu_6$, $2E$	5306.94	5296.03	5295.84			$\nu_4+\nu_5+2\nu_6$, $1E$	5577.18	5578.53	5579.67		
$\nu_1+\nu_5+\nu_6$, A_1	5294.25	5299.48	5299.20			$\nu_4+\nu_5+2\nu_6$, $2E$	5593.60	5587.97	5588.34		
$2\nu_2+\nu_3$, A_1	5307.33	5300.93	5301.98			$\nu_4+\nu_5+2\nu_6$, $3E$	5587.00	5598.19	5598.08		
$\nu_3+\nu_4+2\nu_6$, A_1	5304.02	5301.16	5301.45			$\nu_4+\nu_5+2\nu_6$, $4E$	5590.56	5601.38	5600.65		
$\nu_4+3\nu_6$, $1E$	5326.25	5301.60	5300.90			$2\nu_3+2\nu_5+\nu_6$, $1E$	5599.44	5601.98	5600.17		
$\nu_1+\nu_5+\nu_6$, E	5296.09	5309.02	5308.67			$2\nu_3+2\nu_5+\nu_6$, $2E$	5619.36	5616.02	5616.21		
$\nu_4+3\nu_6$, $2E$	5297.32	5310.63	5309.83			$\nu_2+\nu_4+\nu_5$, A_1	5640.28	5626.53	5626.87		
$\nu_4+3\nu_6$, A_1	5298.78	5311.96	5312.36			$\nu_2+\nu_4+\nu_5$, E	5640.16	5635.09	5635.23		
$\nu_4+3\nu_6$, $3E$	5321.87	5318.47	5318.74			$2\nu_3+2\nu_5+\nu_6$, A_1	5623.04	5643.60	5642.76		
$2\nu_2+\nu_6$, E	5316.03	5321.07	5322.02			$\nu_3+2\nu_5+2\nu_6$, $1A_1$	5629.57	5661.76	5660.33		
$3\nu_3+\nu_5+\nu_6$, E	5307.40	5337.07	5336.46			$\nu_3+2\nu_5+2\nu_6$, $2A_1$	5660.50	5662.30	5662.00		
$2\nu_3+\nu_5+2\nu_6$, $1E$	5362.58	5350.49	5350.40			$\nu_3+2\nu_5+2\nu_6$, $1E$	5642.57	5665.30	5664.14		
$\nu_2+\nu_3+\nu_4$, E	5371.78	5352.16	5352.79			$2\nu_5+3\nu_6$, $1E$	5637.31	5672.90	5674.01		
$2\nu_3+\nu_5+2\nu_6$, A_1	5366.27	5367.75	5367.03			$2\nu_5+3\nu_6$, $2E$	5657.09	5674.65	5673.73		
$\nu_3+2\nu_5+2\nu_6$, $2E$	5651.18	5681.43	5679.76			$\nu_2+4\nu_3$, A_1	6144.39	6081.26	6081.12		
$2\nu_5+3\nu_6$, $3E$	5679.41	5682.34	5681.89			$\nu_1+3\nu_6$, A_1	6042.31	6082.04	6081.24		
$2\nu_5+3\nu_6$, $1A_1$	5660.77	5687.04	5686.57			$\nu_4+3\nu_5$, $2E$	6113.62	6096.94	6098.44		
$2\nu_5+3\nu_6$, $2A_1$	5663.32	5707.04	5705.49			$\nu_4+3\nu_5$, $3E$	6113.98	6105.31	6104.39		
$\nu_2+\nu_3+2\nu_5$, A_1	5721.18	5708.68	5707.97			$\nu_3+4\nu_5$, A_1	6096.39	6113.21	6113.16		
$\nu_3+2\nu_5+2\nu_6$, $3E$	5667.87	5712.28	5710.19			$4\nu_3+\nu_4$, E	6155.99	6116.92	6117.03		
$2\nu_4+\nu_5$, $1E$	5728.99	5725.11	5725.55			$\nu_3+4\nu_5$, $1E$	6118.00	6133.03	6132.89		

(*continued*)

Table 13. Continued.

Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.	Band	Centre [64]	Centre calc., I	Centre calc., II	exp.	Ref.
1	2	3	4	5	6	1	2	3	4	5	6
$\nu_2+\nu_3+2\nu_5$, E	5742.79	5728.41	5727.48			$\nu_1+\nu_2+\nu_3$, A_1	6140.59	6133.64	6133.28		
$\nu_2+2\nu_5+\nu_6$, $1E$	5743.15	5741.61	5741.15			$6\nu_6$, $2A_1$	6037.24	6143.39	6142.19		
$2\nu_5+3\nu_6$, $4E$	5690.46	5743.08	5740.88			$\nu_2+3\nu_3+\nu_6$, E	6212.48	6146.68	6145.95		
$\nu_2+2\nu_5+\nu_6$, $2E$	5762.92	5750.86	5750.88			$4\nu_5+\nu_6$, $1E$	6131.58	6148.13	6147.17		
$2\nu_4+\nu_5$, $2E$	5762.13	5755.03	5756.65			$\nu_3+5\nu_6$, $1E$	6076.07	6153.25	6150.99		
$2\nu_4+\nu_5$, A_1	5761.77	5758.66	5758.85	5759.766	*tw*	$4\nu_5+\nu_6$, $2E$	6151.35	6157.38	6156.89		
$\nu_2+2\nu_5+\nu_6$, A_1	5766.61	5774.25	5773.17			$2\nu_3+4\nu_6$, $1E$	6092.68	6160.77	6157.64		
$2\nu_3+3\nu_5$, E	5831.59	5785.21	5784.81			$\nu_3+5\nu_6$, A_1	6102.08	6166.74	6162.92		
$6\nu_3$, A_1	6037.24	5809.93	5810.54			$\nu_1+\nu_2+\nu_6$, E	6169.81	6166.81	6166.31		
$\nu_3+\nu_4+2\nu_5$, $1E$	5798.96	5813.36	5815.51			$2\nu_3+4\nu_6$, $2E$	6131.69	6170.88	6166.57		
$\nu_3+\nu_4+2\nu_5$, A_1	5820.45	5817.23	5816.81			$\nu_3+5\nu_6$, $2E$	6154.10	6173.42	6168.82		
$\nu_4+2\nu_5+\nu_6$, $1A_1$	5832.76	5824.59	5824.45			$2\nu_3+4\nu_6$, A_1	6079.67	6174.23	6169.52		
$\nu_4+2\nu_5+\nu_6$, $1E$	5831.30	5830.47	5830.58			$\nu_2+4\nu_6$, A_1	6231.35	6179.48	6178.64		
$\nu_4+2\nu_5+\nu_6$, $2A_1$	5851.19	5842.59	5844.59			$4\nu_5+\nu_6$, $1A_1$	6155.03	6180.77	6179.18		
$\nu_4+2\nu_5+\nu_6$, $2E$	5852.41	5842.79	5842.89			$\nu_2+4\nu_6$, $1E$	6244.35	6186.69	6185.92		
$\nu_3+\nu_4+2\nu_5$, $2E$	5820.69	5857.15	5858.10			$\nu_3+4\nu_5$, $2E$	6182.84	6188.79	6187.41		
$\nu_4+2\nu_5+\nu_6$, $3E$	5854.64	5860.31	5860.95			$5\nu_3+\nu_5$, E	6173.59	6192.40	6195.34		
$2\nu_1$, A_1	5855.27	5865.64	5865.81	5865.004	*tw*	$3\nu_3+\nu_4+\nu_6$, A_1	6235.92	6197.14	6197.28		
$\nu_4+2\nu_5+\nu_6$, $4E$	5856.33	5869.87	5869.24			$3\nu_3+\nu_4+\nu_6$, E	6234.46	6202.61	6203.16		
$2\nu_3+3\nu_5$, A_1	5874.81	5890.57	5890.57			$4\nu_5+\nu_6$, $2A_1$	6214.34	6208.54	6208.37		
$\nu_3+3\nu_5+\nu_6$, A_1	5880.87	5898.56	5898.05			$\nu_1+2\nu_3+\nu_5$, E	6234.80	6214.22	6212.82		
$5\nu_3+\nu_6$, E	5931.06	5902.55	5902.47			$\nu_2+\nu_3+3\nu_6$, A_1	6281.97	6247.81	6245.90		
$\nu_3+3\nu_5+\nu_6$, $1E$	5922.25	5910.04	5909.01			$\nu_2+4\nu_6$, $2E$	6283.36	6248.86	6247.54		
$3\nu_5+2\nu_6$, $1E$	5907.92	5922.99	5922.90			$\nu_4+4\nu_6$, $1E$	6287.36	6248.94	6249.40		
$\nu_3+3\nu_5+\nu_6$, $2E$	5927.78	5925.91	5925.35			$\nu_2+2\nu_3+2\nu_6$, E	6258.34	6250.04	6247.74		
$3\nu_5+2\nu_6$, $2E$	5947.46	5926.62	5925.86			$\nu_2+\nu_3+3\nu_6$, E	6255.96	6250.32	6247.75		
$\nu_1+3\nu_3$, A_1	5932.60	5935.89	5935.64			$\nu_2+2\nu_3+2\nu_6$, A_1	6245.34	6251.14	6248.51		
$3\nu_5+2\nu_6$, $3E$	5958.51	5941.50	5942.36			$\nu_4+4\nu_6$, $2E$	6301.82	6251.94	6252.00		
$3\nu_5+2\nu_6$, $1A_1$	5911.61	5946.38	5945.19			$4\nu_5+\nu_6$, $3E$	6221.71	6255.32	6252.95		
$\nu_3+3\nu_5+\nu_6$, $3E$	5882.71	5959.61	5957.40			$\nu_4+4\nu_6$, $1A_1$	6298.90	6258.94	6259.77		
$3\nu_5+2\nu_6$, $2A_1$	5939.98	5968.44	5969.02			$4\nu_3+\nu_5+\nu_6$, A_1	6268.99	6262.97	6265.88		
$\nu_2+3\nu_5$, E	5971.79	5967.23	5967.38			$\nu_1+\nu_3+\nu_4$, E	6229.12	6264.07	6264.36		
$6\nu_6$, $1A_1$	6154.27	5968.93	5968.55			$\nu_1+\nu_4+\nu_6$, A_1	6270.17	6266.37	6262.72		
$6\nu_6$, $1E$	6050.24	5974.63	5974.34			$\nu_1+\nu_4+\nu_6$, E	6268.71	6269.20	6267.96		
$\nu_1+2\nu_3+\nu_6$, E	6005.08	6001.50	6000.98			$4\nu_3+\nu_5+\nu_6$, E	6270.84	6273.09	6273.21		
$\nu_2+3\nu_5$, A_1	6015.02	6009.12	6008.40			$2\nu_2+2\nu_3$, A_1	6330.66	6291.62	6292.53		
$3\nu_5+2\nu_6$, $4E$	5896.76	6011.67	6009.23			$\nu_1+\nu_3+\nu_5+\nu_6$, A_1	6291.34	6305.18	6304.62		
$3\nu_3+3\nu_6$, E	6005.69	6035.15	6033.64			$3\nu_3+\nu_5+2\nu_6$, $1E$	6331.01	6309.09	6307.77		
$4\nu_3+2\nu_6$, A_1	6007.17	6039.98	6038.92			$3\nu_3+\nu_5+2\nu_6$, $2E$	6342.17	6311.85	6310.25		
$\nu_4+3\nu_5$, A_1	6070.63	6040.50	6039.41			$\nu_3+\nu_4+3\nu_6$, $1E$	6300.14	6312.49	6311.58		
$3\nu_3+3\nu_6$, A_1	6087.05	6040.55	6039.53			$\nu_1+\nu_3+\nu_5+\nu_6$, E	6293.18	6314.70	6313.75		
$4\nu_3+2\nu_6$, E	6020.17	6045.02	6044.16			$\nu_3+\nu_4+3\nu_6$, $2E$	6324.69	6315.08	6314.60		
$\nu_4+3\nu_5$, $1E$	6070.51	6054.83	6053.98			$\nu_3+\nu_4+3\nu_6$, A_1	6301.60	6315.72	6314.88		
$\nu_1+\nu_3+2\nu_6$, A_1	6083.32	6058.84	6057.29			$\nu_3+\nu_4+3\nu_6$, $3E$	6329.07	6319.68	6319.19		
$\nu_1+\nu_3+2\nu_6$, E	6055.32	6061.40	6060.12			$2\nu_3+\nu_4+2\nu_6$, A_1	6290.69	6319.95	6318.93		
$6\nu_6$, $2E$	6089.25	6063.64	6063.21			$\nu_4+4\nu_6$, $2A_1$	6342.29	6320.40	6319.16		
$\nu_1+3\nu_6$, E	6057.31	6070.59	6069.44			$\nu_1+\nu_5+2\nu_6$, $1E$	6314.48	6325.72	6325.78		
$\nu_2+2\nu_3+\nu_4$, E	6370.92	6329.10	6330.15			$3\nu_3+\nu_4+\nu_5$, E	6484.19	6509.62	6510.48		
$\nu_1+\nu_5+2\nu_6$, $2E$	6325.64	6329.46	6329.01			$\nu_2+\nu_5+3\nu_6$, $1E$	6519.10	6514.00	6513.79		
$\nu_4+4\nu_6$, $3E$	6336.46	6332.80	6333.21			$\nu_2+\nu_3+\nu_5+2\nu_6$, $2E$	6533.73	6515.30	6513.26		
$2\nu_3+\nu_4+2\nu_6$, $1E$	6279.14	6333.29	6333.31			$\nu_2+2\nu_4$, A_1	6519.70	6519.92	6520.35		
$2\nu_2+\nu_3+\nu_6$, E	6355.50	6335.18	6335.46			$2\nu_4+2\nu_6$, $2E$	6506.38	6520.67	6522.07		
$2\nu_3+\nu_4+2\nu_6$, $2E$	6293.61	6339.14	6338.82			$\nu_1+\nu_4+\nu_5$, A_1	6505.76	6526.55	6528.44		
$2\nu_2+2\nu_6$, A_1	6345.11	6343.03	6343.24			$\nu_2+\nu_3+\nu_5+2\nu_6$, A_1	6537.42	6528.57	6526.28		
$3\nu_3+\nu_5+2\nu_6$, A_1	6345.85	6345.48	6344.89			$\nu_2+\nu_5+3\nu_6$, $2E$	6541.42	6528.71	6526.83		

(*continued*)

Table 13. Continued.

Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.	Band	Centre [64]	Centre calc., I	Centre calc., II	exp.	Ref.
1	2	3	4	5	6	1	2	3	4	5	6
$2\nu_2+2\nu_6$, E	6358.11	6347.14	6347.52			$2\nu_3+\nu_4+\nu_5+\nu_6$, $1E$	6546.84	6537.26	6539.59		
$5\nu_5$, $1E$	6350.39	6348.32	6346.81			$\nu_1+\nu_4+\nu_5$, E	6505.64	6540.93	6542.52		
$\nu_1+\nu_5+2\nu_6$, A_1	6329.32	6352.33	6351.20			$\nu_2+\nu_5+3\nu_6$, $3E$	6546.95	6549.09	6547.22		
$\nu_5+5\nu_6$, $1A_1$	6353.95	6356.73	6356.60			$2\nu_3+\nu_4+\nu_5+\nu_6$, $2E$	6548.18	6551.01	6553.16		
$\nu_5+5\nu_6$, $1E$	6355.79	6358.96	6359.34			$\nu_2+2\nu_4$, E	6552.70	6552.20	6553.19		
$\nu_5+5\nu_6$, $2E$	6378.12	6367.16	6366.50			$2\nu_4+2\nu_6$, $3E$	6516.47	6554.45	6555.17		
$\nu_2+\nu_3+\nu_4+\nu_6$, E	6406.13	6380.54	6380.96			$2\nu_3+\nu_4+\nu_5+\nu_6$, $3E$	6550.15	6555.31	6557.81		
$\nu_5+5\nu_6$, $3E$	6383.64	6381.79	6381.27			$\nu_1+2\nu_5+\nu_6$, $1E$	6547.02	6558.10	6557.61		
$\nu_2+\nu_3+\nu_4+\nu_6$, A_1	6407.59	6384.90	6385.57			$\nu_1+2\nu_5+\nu_6$, $2E$	6566.79	6567.36	6567.34		
$5\nu_5$, A_1	6393.61	6390.22	6388.55			$2\nu_3+\nu_4+\nu_5+\nu_6$, A_1	6548.57	6567.47	6569.92		
$\nu_2+\nu_4+2\nu_6$, $1E$	6407.57	6390.37	6389.82			$\nu_3+\nu_4+\nu_5+2\nu_6$, $1E$	6577.32	6576.79	6576.93		
$\nu_2+\nu_4+2\nu_6$, $2E$	6422.03	6394.16	6393.36			$\nu_3+\nu_4+\nu_5+2\nu_6$, $1A_1$	6577.44	6577.53	6577.19		
$2\nu_3+2\nu_4$, A_1	6414.52	6394.17	6395.50			$\nu_3+\nu_4+\nu_5+2\nu_6$, $2A_1$	6589.94	6577.60	6576.73		
$\nu_1+\nu_2+\nu_5$, E	6396.18	6398.53	6398.58			$3\nu_3+2\nu_5+\nu_6$, $1E$	6576.35	6580.58	6576.73		
$\nu_2+\nu_4+2\nu_6$, A_1	6419.12	6399.19	6399.11			$2\nu_2+\nu_3+\nu_5$, E	6591.31	6582.38	6582.87		
$\nu_2+3\nu_3+\nu_5$, E	6451.65	6413.39	6412.95			$3\nu_3+2\nu_5+\nu_6$, $2E$	6596.12	6589.84	6586.00		
$2\nu_3+2\nu_4$, E	6447.53	6415.16	6415.76			$\nu_3+\nu_4+\nu_5+2\nu_6$, $2E$	6587.14	6590.36	6589.82		
$\nu_5+5\nu_6$, $4E$	6428.29	6418.86	6419.28			$\nu_1+2\nu_5+\nu_6$, A_1	6570.48	6590.74	6589.63		
$\nu_3+\nu_5+4\nu_6$, $1A_1$	6388.33	6421.66	6420.63			$\nu_4+\nu_5+3\nu_6$, $1E$	6582.50	6592.12	6592.20		
$2\nu_3+\nu_5+3\nu_6$, $1E$	6370.79	6429.08	6425.03			$\nu_4+\nu_5+3\nu_6$, $1A_1$	6584.22	6595.20	6596.78		
$\nu_3+\nu_5+4\nu_6$, $1E$	6373.49	6434.87	6432.14			$\nu_4+\nu_5+3\nu_6$, $2E$	6583.84	6595.85	6596.65		
$3\nu_2$, A_1	6378.53	6438.24	6442.15			$\nu_3+\nu_4+\nu_5+2\nu_6$, $3E$	6590.71	6597.42	6597.51		
$2\nu_3+\nu_5+3\nu_6$, A_1	6368.94	6441.57	6438.33			$\nu_4+\nu_5+3\nu_6$, $3E$	6585.80	6600.72	6601.07		
$\nu_3+\nu_5+4\nu_6$, $2E$	6384.65	6447.02	6443.35			$2\nu_2+\nu_5+\nu_6$, A_1	6600.22	6601.96	6602.94		
$2\nu_4+2\nu_6$, $1A_1$	6473.38	6448.45	6448.71			$\nu_4+\nu_5+3\nu_6$, $4E$	6609.46	6605.42	6605.48		
$2\nu_3+\nu_5+3\nu_6$, $2E$	6393.11	6452.93	6449.15			$\nu_3+\nu_4+\nu_5+2\nu_6$, $4E$	6593.74	6607.53	6606.87		
$\nu_3+\nu_5+4\nu_6$, $2A_1$	6421.82	6457.61	6453.77			$3\nu_3+2\nu_5+\nu_6$, A_1	6599.81	6613.23	6608.29		
$\nu_3+2\nu_4+\nu_6$, $1E$	6461.57	6459.96	6461.88			$2\nu_2+\nu_5+\nu_6$, E	6602.06	6613.65	6614.09		
$2\nu_2+\nu_4$, E	6447.44	6460.69	6462.15			$\nu_4+\nu_5+3\nu_6$, $2A_1$	6605.21	6614.84	6614.95		
$\nu_2+2\nu_3+\nu_5+\nu_6$, A_1	6503.81	6467.31	6465.24			$\nu_2+\nu_3+\nu_4+\nu_5$, A_1	6652.63	6620.41	6620.45		
$\nu_3+\nu_5+4\nu_6$, $3E$	6429.19	6467.58	6464.36			$\nu_4+\nu_5+3\nu_6$, $3A_1$	6615.11	6623.16	6622.25		
$\nu_2+2\nu_3+\nu_5+\nu_6$, E	6505.65	6471.18	6469.93			$\nu_2+\nu_3+\nu_4+\nu_5$, E	6652.51	6632.11	6632.31		
$5\nu_5$, $2E$	6480.06	6474.02	6472.04			$\nu_4+\nu_5+3\nu_6$, $5E$	6610.61	6635.70	6635.21		
$4\nu_3+2\nu_5$, E	6516.65	6474.62	6476.08			$2\nu_3+2\nu_5+2\nu_6$, $1A_1$	6622.43	6641.53	6641.29		
$\nu_5+5\nu_6$, $2A_1$	6437.50	6477.37	6475.00			$2\nu_3+2\nu_5+2\nu_6$, $2A_1$	6653.36	6644.61	6644.96		
$4\nu_3+2\nu_5$, A_1	6495.04	6477.59	6477.96			$3\nu_4$, E	6628.31	6646.47	6647.83		
$2\nu_3+\nu_5+3\nu_6$, $3E$	6398.64	6479.76	6476.10			$2\nu_3+2\nu_5+2\nu_6$, $1E$	6635.43	6648.12	6647.75		
$2\nu_4+2\nu_6$, $1E$	6486.38	6482.95	6483.10			$\nu_2+\nu_4+\nu_5+\nu_6$, $1E$	6671.91	6652.77	6653.41		
$3\nu_3+\nu_4+\nu_5$, A_1	6484.31	6484.05	6487.37			$\nu_2+\nu_4+\nu_5+\nu_6$, $2E$	6673.25	6655.95	6655.98		
$\nu_1+\nu_3+2\nu_5$, A_1	6504.58	6484.55	6483.04			$2\nu_3+2\nu_5+2\nu_6$, $2E$	6644.04	6659.81	6659.16		
$\nu_3+2\nu_4+\nu_6$, $2E$	6496.03	6485.51	6487.36			$\nu_2+\nu_4+\nu_5+\nu_6$, $3E$	6675.21	6664.08	6664.39		
$\nu_3+2\nu_4+\nu_6$, A_1	6493.12	6492.43	6494.91			$\nu_2+\nu_4+\nu_5+\nu_6$, A_1	6673.63	6666.53	6666.83		
$\nu_1+\nu_3+2\nu_5$, E	6526.19	6498.94	6497.35			$\nu_3+2\nu_5+3\nu_6$, $1E$	6646.28	6680.43	6678.75		
$\nu_2+\nu_5+3\nu_6$, A_1	6517.26	6502.52	6501.94			$2\nu_3+2\nu_5+2\nu_6$, $3E$	6660.73	6687.95	6686.06		
$\nu_2+\nu_3+\nu_5+2\nu_6$, $1E$	6522.57	6505.59	6504.41			$\nu_3+2\nu_5+3\nu_6$, $2E$	6666.05	6689.00	6687.66		
$2\nu_4+2\nu_6$, $2A_1$	6522.30	6509.50	6509.47			$\nu_3+2\nu_5+3\nu_6$, $3E$	6688.37	6689.09	6688.63		
$2\nu_5+4\nu_6$, $1E$	6647.89	6692.77	6694.03			$\nu_4+2\nu_5+2\nu_6$, $2A_1$	6864.69	6884.17	6884.52		
$\nu_3+2\nu_4+\nu_5$, $1E$	6717.17	6701.18	6700.98			$\nu_2+\nu_4+2\nu_5$, $1E$	6901.81	6887.83	6888.08		
$3\nu_4$, A_1	6694.32	6702.84	6704.33			$\nu_1+4\nu_3$, A_1	6885.60	6893.79	6893.16		
$2\nu_5+4\nu_6$, $1A_1$	6634.88	6702.87	6700.55			$2\nu_1+\nu_6$, E	6891.63	6899.53	6899.19		
$\nu_2+2\nu_3+2\nu_5$, A_1	6726.49	6703.06	6702.34			$\nu_4+2\nu_5+2\nu_6$, $3A_1$	6883.07	6900.65	6900.29		
$\nu_3+2\nu_5+3\nu_6$, $1A_1$	6669.73	6703.35	6701.42			$2\nu_3+3\nu_5+\nu_6$, $1E$	6872.91	6905.94	6905.58		
$2\nu_5+4\nu_6$, $2A_1$	6665.81	6703.36	6702.41			$\nu_2+\nu_4+2\nu_5$, $2E$	6923.54	6908.36	6909.72		
$2\nu_5+4\nu_6$, $2E$	6656.49	6705.95	6704.02			$\nu_4+2\nu_5+2\nu_6$, $6E$	6879.92	6914.94	6913.95		
$\nu_3+2\nu_5+3\nu_6$, $2A_1$	6672.28	6711.81	6709.37			$\nu_2+\nu_4+2\nu_5$, A_1	6923.30	6915.61	6915.56		

(*continued*)

Table 13. Continued.

Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.	Band	Centre [64]	Centre calc., I	Centre calc., II	exp.	Ref.
1	2	3	4	5	6	1	2	3	4	5	6
$2\nu_5+4\nu_6$, $3E$	6673.18	6718.60	6717.73			$2\nu_3+3\nu_5+\nu_6$, $2E$	6912.45	6919.79	6919.61		
$\nu_2+2\nu_3+2\nu_5$, E	6748.11	6721.60	6720.48			$\nu_3+3\nu_5+2\nu_6$, $1E$	6903.05	6925.78	6923.35		
$2\nu_5+4\nu_6$, $4E$	6686.90	6723.27	6720.82			$\nu_3+3\nu_5+2\nu_6$, $2E$	6914.21	6945.87	6943.90		
$\nu_3+2\nu_4+\nu_5$, $2E$	6750.30	6733.31	6736.10			$3\nu_5+3\nu_6$, $1A_1$	6910.96	6946.82	6946.28		
$\nu_3+2\nu_4+\nu_5$, A_1	6750.06	6742.46	6743.06			$2\nu_3+3\nu_5+\nu_6$, $3E$	6917.97	6951.84	6949.98		
$2\nu_4+\nu_5+\nu_6$, $1A_1$	6748.29	6744.21	6745.67			$\nu_3+3\nu_5+2\nu_6$, $3E$	6953.75	6955.61	6955.09		
$2\nu_5+4\nu_6$, $5E$	6701.14	6749.63	6746.50			$3\nu_5+3\nu_6$, $1E$	6912.80	6958.31	6958.13		
$2\nu_4+\nu_5+\nu_6$, $1E$	6750.13	6753.28	6753.89			$\nu_3+3\nu_5+2\nu_6$, $1A_1$	6917.90	6961.68	6959.45		
$\nu_2+\nu_3+2\nu_5+\nu_6$, $1E$	6764.56	6753.63	6752.12			$3\nu_5+3\nu_6$, $2A_1$	6972.82	6965.12	6966.44		
$\nu_3+2\nu_5+3\nu_6$, $4E$	6699.42	6757.69	6753.92			$3\nu_5+3\nu_6$, $2E$	6935.13	6967.79	6966.09		
$\nu_2+\nu_3+2\nu_5+\nu_6$, $2E$	6784.33	6762.30	6761.16			$2\nu_4+2\nu_5$, $1A_1$	6987.41	6972.22	6972.40		
$\nu_1+3\nu_5$, E	6763.55	6763.48	6763.52			$\nu_2+\nu_3+3\nu_5$, E	6990.54	6978.32	6977.05		
$3\nu_3+3\nu_5$, E	6061.04	6770.39	6770.04			$\nu_3+3\nu_5+2\nu_6$, $2A_1$	6946.28	6985.47	6983.01		
$\nu_2+2\nu_5+2\nu_6$, $1A_1$	6767.39	6772.86	6771.79			$3\nu_5+3\nu_6$, $3E$	6940.65	6986.12	6985.35		
$2\nu_4+\nu_5+\nu_6$, $2E$	6779.96	6773.93	6774.52			$2\nu_4+2\nu_5$, $1E$	7009.02	6990.02	6989.91		
$2\nu_4+\nu_5+\nu_6$, $3E$	6781.56	6775.44	6778.06			$\nu_1+3\nu_3+\nu_6$, E	6974.17	6990.56	6988.89		
$\nu_2+2\nu_5+2\nu_6$, $2A_1$	6798.32	6777.59	6777.71			$3\nu_5+3\nu_6$, $4E$	6952.34	6993.40	6991.56		
$\nu_2+2\nu_5+2\nu_6$, $1E$	6780.39	6780.03	6779.12			$\nu_2+3\nu_5+\nu_6$, A_1	7012.67	7009.41	7008.69		
$2\nu_4+\nu_5+\nu_6$, $2A_1$	6784.71	6781.02	6782.66			$2\nu_4+2\nu_5$, $2E$	7020.42	7015.75	7018.17		
$\nu_2+\nu_3+2\nu_5+\nu_6$, A_1	6788.02	6785.19	6782.95			$\nu_2+\nu_3+3\nu_5$, A_1	7033.76	7018.01	7016.28		
$2\nu_5+4\nu_6$, $3A_1$	6715.88	6786.34	6783.18			$2\nu_4+2\nu_5$, $2A_1$	7042.27	7020.52	7021.45		
$2\nu_4+\nu_5+\nu_6$, $4E$	6782.63	6792.72	6793.49			$3\nu_5+3\nu_6$, $5E$	6957.87	7021.09	7018.68		
$\nu_2+2\nu_5+2\nu_6$, $2E$	6789.00	6793.76	6792.62			$\nu_2+3\nu_5+\nu_6$, $1E$	7014.51	7021.11	7019.83		
$2\nu_3+\nu_4+2\nu_5$, $1E$	6780.10	6795.65	6798.91			$\nu_3+3\nu_5+2\nu_6$, $4E$	6964.81	7023.86	7020.03		
$3\nu_3+3\nu_5$, A_1	6848.91	6801.11	6801.54			$2\nu_4+2\nu_5$, $3E$	7041.79	7034.86	7034.74		
$\nu_1+3\nu_5$, A_1	6806.78	6810.73	6810.31			$\nu_1+2\nu_3+2\nu_6$, A_1	7027.50	7037.37	7035.16		
$\nu_2+2\nu_5+2\nu_6$, $3E$	6805.69	6824.37	6822.28			$\nu_2+3\nu_5+\nu_6$, $2E$	7054.05	7039.62	7039.29		
$\nu_3+\nu_4+2\nu_5+\nu_6$, $1E$	6828.54	6827.11	6826.32			$2\nu_3+4\nu_5$, A_1	7083.92	7045.05	7046.54		
$2\nu_2+2\nu_5$, A_1	6819.55	6834.27	6835.16			$\nu_1+2\nu_3+2\nu_6$, E	7040.50	7050.12	7048.15		
$\nu_3+\nu_4+2\nu_5+\nu_6$, $2E$	6849.64	6841.83	6841.44			$2\nu_3+4\nu_5$, $1E$	7105.53	7054.85	7054.00		
$\nu_3+\nu_4+2\nu_5+\nu_6$, $1A_1$	6829.99	6842.68	6844.76			$\nu_1+4\nu_6$, A_1	7054.46	7056.26	7055.31		
$2\nu_3+\nu_4+2\nu_5$, $2E$	6801.83	6842.89	6844.37			$\nu_1+\nu_3+3\nu_6$, E	7058.60	7066.29	7064.46		
$2\nu_1+\nu_3$, A_1	6841.94	6848.20	6848.33	6848.112	*tw*	$\nu_1+4\nu_6$, $1E$	7067.46	7067.71	7066.68		
$\nu_3+\nu_4+2\nu_5+\nu_6$, $2A_1$	6848.43	6851.55	6853.83			$3\nu_5+3\nu_6$, $3A_1$	6989.40	7070.39	7066.74		
$\nu_4+2\nu_5+2\nu_6$, $1E$	6843.19	6855.01	6855.47			$\nu_2+3\nu_5+\nu_6$, $3E$	7059.58	7074.70	7072.72		
$2\nu_2+2\nu_5$, E	6841.16	6855.22	6856.03			$\nu_4+3\nu_5+\nu_6$, $1E$	7097.70	7085.32	7084.81		
$\nu_3+\nu_4+2\nu_5+\nu_6$, $3E$	6851.87	6857.24	6858.09			$\nu_1+\nu_3+3\nu_6$, A_1	7084.61	7088.99	7087.06		
$\nu_4+2\nu_5+2\nu_6$, $2E$	6864.93	6861.63	6862.10			$\nu_4+3\nu_5+\nu_6$, $2E$	7099.04	7090.53	7090.10		
$\nu_4+2\nu_5+2\nu_6$, $3E$	6857.66	6863.12	6865.98			$\nu_3+\nu_4+3\nu_5$, $1E$	7065.08	7093.47	7095.46		
$\nu_4+2\nu_5+2\nu_6$, $1A_1$	6854.74	6864.55	6865.01			$\nu_1+4\nu_6$, $2E$	7106.47	7101.76	7100.43		
$\nu_4+2\nu_5+2\nu_6$, $4E$	6872.79	6868.05	6868.80			$\nu_3+\nu_4+3\nu_5$, $2E$	7108.18	7105.12	7104.12		
$\nu_3+\nu_4+2\nu_5+\nu_6$, $4E$	6853.57	6868.19	6868.94			$\nu_4+3\nu_5+\nu_6$, $1A_1$	7099.42	7107.12	7106.53		
$2\nu_3+3\nu_5+\nu_6$, A_1	6871.07	6869.12	6864.91			$\nu_4+3\nu_5+\nu_6$, $3E$	7101.00	7108.05	7109.54		
$2\nu_3+\nu_4+2\nu_5$, A_1	6801.59	6873.35	6873.73			$2\nu_1+\nu_5$, E	7105.89	7115.98	7116.07	7115.499	*tw*
$\nu_4+2\nu_5+2\nu_6$, $5E$	6875.46	6873.73	6874.88			$\nu_1+\nu_2+2\nu_3$, A_1	7138.23	7116.19	7115.54		
$\nu_3+\nu_4+3\nu_5$, A_1	7065.20	7118.46	7119.50			$\nu_1+\nu_3+\nu_5+2\nu_6$, A_1	7327.94	7354.58	7352.70		
$\nu_4+3\nu_5+\nu_6$, $4E$	7139.20	7122.32	7124.79			$\nu_1+\nu_5+3\nu_6$, $2E$	7352.43	7358.34	7357.22		
$\nu_4+3\nu_5+\nu_6$, $2A_1$	7140.30	7128.89	7128.78			$\nu_3+5\nu_5$, $1E$	7351.34	7371.21	7370.73		
$\nu_3+\nu_4+3\nu_5$, $3E$	7108.54	7136.54	7137.21			$\nu_3+5\nu_5$, A_1	7394.57	7378.78	7379.81		
$\nu_4+3\nu_5+\nu_6$, $3A_1$	7146.19	7152.67	7153.00			$\nu_1+\nu_5+3\nu_6$, $3E$	7357.95	7386.49	7384.59		
$\nu_3+4\nu_5+\nu_6$, $1E$	7135.21	7165.91	7164.76			$\nu_4+4\nu_5$, $3E$	7403.97	7393.84	7392.18		
$\nu_1+\nu_2+\nu_3+\nu_6$, E	7183.55	7167.53	7166.51			$5\nu_5+\nu_6$, $1A_1$	7386.70	7402.86	7401.31		
$\nu_4+3\nu_5+\nu_6$, $5E$	7144.37	7167.82	7166.43			$\nu_1+\nu_2+\nu_3+\nu_5$, E	7407.25	7404.72	7403.96		
$\nu_3+4\nu_5+\nu_6$, $2E$	7154.98	7174.20	7173.40			$\nu_4+4\nu_5$, $2A_1$	7404.45	7411.60	7411.11		
$\nu_1+3\nu_3+\nu_5$, E	7201.22	7176.84	7175.17			$5\nu_5+\nu_6$, $1E$	7388.54	7414.55	7412.46		

(*continued*)

Table 13. Continued.

Band	Centre [64]	Centre calc., I	Centre calc., II	Centre exp.	Ref.	Band	Centre [64]	Centre calc., I	Centre calc., II	exp.	Ref.
1	2	3	4	5	6	1	2	3	4	5	6
$\nu_1+\nu_2+2\nu_6$, A_1	7193.63	7185.66	7184.59			$\nu_1+\nu_2+\nu_5+\nu_6$, A_1	7436.64	7429.54	7429.26		
$2\nu_3+4\nu_5$, $2E$	7170.37	7187.99	7187.20			$5\nu_5+\nu_6$, $2E$	7428.08	7433.06	7431.91		
$4\nu_5+2\nu_6$, $1A_1$	7151.26	7190.46	7189.06			$\nu_1+\nu_2+\nu_5+\nu_6$, E	7438.48	7440.93	7440.08		
$\nu_1+\nu_2+2\nu_6$, E	7206.64	7193.98	7192.92			$\nu_1+\nu_4+\nu_5+\nu_6$, $1E$	7532.41	7460.96	7458.89		
$4\nu_5+2\nu_6$, $2A_1$	7182.19	7196.46	7196.19			$\nu_1+\nu_4+\nu_5+\nu_6$, $2E$	7533.75	7465.63	7465.06		
$\nu_3+4\nu_5+\nu_6$, $1A_1$	7158.66	7197.44	7195.62			$5\nu_5+\nu_6$, $3E$	7433.61	7468.15	7465.35		
$4\nu_5+2\nu_6$, $1E$	7172.87	7198.90	7197.60			$\nu_1+2\nu_3+2\nu_5$, A_1	7484.43	7472.42	7468.78		
$4\nu_5+2\nu_6$, $2E$	7164.26	7211.38	7209.90			$\nu_3+5\nu_5$, $2E$	7481.02	7486.13	7483.73		
$\nu_2+4\nu_5$, A_1	7222.16	7216.29	7215.05			$\nu_1+2\nu_4$, A_1	7441.81	7488.55	7492.32		
$\nu_3+4\nu_5+\nu_6$, $2A_1$	7217.97	7221.27	7220.10			$\nu_1+2\nu_4$, E	7474.82	7496.95	7501.02		
$4\nu_5+2\nu_6$, $3E$	7189.56	7235.92	7236.52			$5\nu_5+\nu_6$, $4E$	7512.69	7505.17	7504.26		
$\nu_2+4\nu_5$, $1E$	7243.77	7237.24	7235.92			$\nu_1+2\nu_3+2\nu_5$, E	7506.04	7505.48	7501.02		
$\nu_1+2\nu_3+\nu_4$, E	7202.58	7238.42	7239.25			$\nu_1+\nu_3+\nu_4+\nu_5$, A_1	7492.66	7532.61	7533.10		
$4\nu_5+2\nu_6$, $4E$	7237.70	7243.25	7240.76			$\nu_1+\nu_4+\nu_5+\nu_6$, A_1	7534.14	7541.73	7539.77		
$\nu_1+\nu_3+\nu_4+\nu_6$, E	7258.27	7246.82	7246.89			$\nu_1+\nu_4+\nu_5+\nu_6$, $3E$	7535.71	7541.96	7541.38		
$\nu_1+2\nu_3+\nu_5+\nu_6$, A_1	7273.86	7248.07	7247.39			$\nu_1+\nu_3+\nu_4+\nu_5$, E	7492.54	7547.30	7547.59		
$\nu_3+4\nu_5+\nu_6$, $3E$	7225.34	7266.52	7263.13			$5\nu_5+\nu_6$, $2A_1$	7521.90	7563.64	7559.98		
$\nu_1+2\nu_2$, A_1	7252.46	7269.59	7270.48			$\nu_1+\nu_3+2\nu_5+\nu_6$, $1E$	7542.97	7575.40	7574.57		
$4\nu_5+2\nu_6$, $5E$	7243.34	7274.15	7272.43			$\nu_1+\nu_3+2\nu_5+\nu_6$, $2E$	7562.74	7581.64	7580.85		
$\nu_1+\nu_4+2\nu_6$, $1E$	7280.18	7282.42	7280.62			$6\nu_5$, $1A_1$	7586.36	7584.30	7581.81		
$\nu_1+\nu_4+2\nu_6$, $2E$	7294.64	7285.96	7283.83			$\nu_1+2\nu_5+2\nu_6$, $1A_1$	7566.28	7600.38	7598.02		
$\nu_4+4\nu_5$, $1E$	7317.76	7289.68	7287.84			$\nu_1+2\nu_5+2\nu_6$, $2A_1$	7597.21	7600.94	7598.56		
$\nu_1+\nu_3+\nu_4+\nu_6$, A_1	7259.73	7291.92	7291.64			$\nu_1+\nu_3+2\nu_5+\nu_6$, A_1	7566.43	7602.23	7600.10		
$\nu_1+\nu_4+2\nu_6$, A_1	7291.73	7292.61	7291.06			$\nu_1+2\nu_5+2\nu_6$, $1E$	7579.28	7603.06	7600.49		
$\nu_1+2\nu_3+\nu_5+\nu_6$, E	7275.70	7299.61	7299.04			$6\nu_5$, $1E$	7607.97	7605.25	7602.36		
$\nu_2+4\nu_5$, $2E$	7308.61	7300.09	7298.54			$\nu_1+2\nu_5+2\nu_6$, $2E$	7587.89	7614.68	7613.22		
$\nu_4+4\nu_5$, $1A_1$	7339.25	7322.33	7320.78			$\nu_1+2\nu_5+2\nu_6$, $3E$	7604.58	7643.77	7641.86		
$\nu_4+4\nu_5$, $2E$	7339.49	7326.12	7327.90			$\nu_1+\nu_2+2\nu_5$, A_1	7643.85	7645.81	7645.49		
$4\nu_5+2\nu_6$, $3A_1$	7258.08	7329.49	7325.67			$\nu_1+\nu_2+2\nu_5$, E	7665.47	7666.60	7666.19		
$\nu_1+\nu_3+\nu_5+2\nu_6$, $1E$	7313.10	7330.56	7329.12			$6\nu_5$, $2E$	7672.80	7668.10	7665.30		
$\nu_1+\nu_3+\nu_5+2\nu_6$, $2E$	7324.26	7340.95	7339.25			$\nu_1+\nu_3+3\nu_5$, E	7756.84	7676.29	7671.87		
$\nu_1+\nu_2+\nu_4$, E	7345.46	7346.55	7345.20			$\nu_1+\nu_4+2\nu_5$, A_1	7771.69	7762.08	7759.88		
$\nu_1+\nu_5+3\nu_6$, $1E$	7330.10	7347.43	7347.07			$\nu_1+\nu_4+2\nu_5$, $1E$	7750.20	7768.93	7769.11		
$\nu_1+\nu_5+3\nu_6$, A_1	7328.26	7348.64	7347.71			$6\nu_5$, $2A_1$	7780.86	7772.85	7769.67		
$\nu_1+3\nu_5+\nu_6$, A_1	7799.45	7795.04	7794.42			$2\nu_1+\nu_2$, A_1	7994.72	8004.98	8004.79		
$\nu_1+\nu_4+2\nu_5$, $2E$	7771.93	7802.74	7802.26			$\nu_1+4\nu_5$, $1E$	8018.44	8021.56	8019.35		
$2\nu_1+2\nu_3$, A_1	7814.12	7823.21	7822.89			$\nu_1+4\nu_5$, $2E$	8083.28	8083.67	8082.56		
$\nu_1+3\nu_5+\nu_6$, $1E$	7801.29	7823.40	7822.38			$2\nu_1+\nu_3+\nu_5$, E	8091.50	8088.39	8087.11		
$\nu_1+\nu_3+3\nu_5$, A_1	7800.06	7835.76	7834.29			$2\nu_1+\nu_4$, E	8111.80	8137.87	8136.45		
$\nu_1+3\nu_5+\nu_6$, $2E$	7840.83	7841.85	7841.72			$2\nu_1+\nu_5+\nu_6$, A_1	8141.36	8149.64	8149.39		
$\nu_1+3\nu_5+\nu_6$, $3E$	7846.35	7876.74	7874.98			$2\nu_1+\nu_5+\nu_6$, E	8143.21	8161.44	8159.37		
$2\nu_1+\nu_3+\nu_6$, E	7879.91	7880.87	7880.44			$2\nu_1+2\nu_5$, A_1	8336.47	8347.05	8346.88	8346.919	*tw*
$2\nu_1+2\nu_6$, A_1	7910.47	7921.17	7920.15			$2\nu_1+2\nu_5$, E	8358.08	8368.65	8367.05		
$2\nu_1+2\nu_6$, E	7923.48	7928.59	7927.66			$3\nu_1$, A_1	8605.28	8622.89	8622.78	8623.349	*tw*
$\nu_1+4\nu_5$, A_1	7996.83	7999.40	7999.17								

Note: [a]See footnote to Table 12.

numbers l_λ:

$$q_\lambda^+|v_\lambda\ l_\lambda\rangle = \left\{\frac{v-l}{2}\right\}^{1/2}|v_\lambda-1\ l_\lambda+1\rangle - \left\{\frac{v+l+2}{2}\right\}^{1/2}|v_\lambda+1\ l_\lambda+1\rangle \quad (33)$$

and

$$q_\lambda^-|v_\lambda\ l_\lambda\rangle = -\left\{\frac{v+l}{2}\right\}^{1/2}|v_\lambda-1\ l_\lambda-1\rangle - \left\{\frac{v-l+2}{2}\right\}^{1/2}|v_\lambda+1\ l_\lambda-1\rangle \quad (34)$$

Table 14. F_{ij} parameters of the methane molecule.

Parameter	Present work, I	Present work, II	[64]	[32]
F_{11}/aJ Å^{-2}	5.47384[a]	5.47384[a]	5.47384	5.47384[a]
F_{22}/aJ	0.574225(638)	0.574203(613)	0.57770	0.578602
F_{33}/aJ Å^{-2}	5.374354(744)	5.400781(731)	5.37696	5.387874
F_{34}/aJ Å^{-1}	−0.16080 (983)	−0.21057[a]	−0.21057	−0.21057[a]
F_{44}/aJ	0.531674(539)	0.532938(506)	0.53225	0.533740
N[b]	124	124		
n[b]	64	63		
d_{rms}/cm^{-1}	0.73	0.75		

Notes:[a]Constrained to the value from [64].
[b]N is the number of experimental band centres; n is the number of fitted parameters.

As a result of our analysis of experimental band centres a set of 64 parameters was obtained which are presented in column 2 of Table 14 and columns 2 and 5 of Table 15. Values in parenthesis are 1σ statistical confidence intervals. Columns 4 and 5 of Table 14 give, for comparison, the values of quadratic F_{ij} parameters obtained from *ab initio* calculations, [64], and from the fit of experimental band centres of the CH_2D_2 molecule, [32], respectively. One finds reasonable agreement between all sets of parameters.

The parameters obtained reproduce the experimental band centres used in the fit with the $d_{rms} = 0.73\,cm^{-1}$. In order to illustrate the accuracy of the results derived, column 3 of Tables 12 and 13 give the values of the band centres calculated with our parameters from Tables 14 and 15. One finds a good agreement between the experimental and calculated band centres. The columns 2 of Tables 12 and 13 present, for comparison, the values of the same band centres calculated with the parameters from [64].

As can be seen from Table 14, the values of the parameters F_{22}, F_{33}, and F_{44} obtained from the fit are close to the values of the corresponding parameters from [64] and [9]. On the other hand, larger differences arise for the values of the F_{34} parameter. To understand the origin of this inconsistency, we repeated the fit with a fixed value of the parameter F_{34}. The results of this second fit are very close to the results of the first fit (see column 3 of Table 14, columns 3 and 6 of Table 15, and column 4 of Tables 12 and 13). The d_{rms} increases only a little, to $0.75\,cm^{-1}$. Comparison of results of the first and the second fit shows, that the fit to just the frequencies in our experimental data is not able to determine the parameter F_{34}.

6. Discussion and conclusion

Using the strategy of the direct assignment of the $J = 0$ states of excited vibrational levels [29,32,65] we have thus been able to identify and precisely determine a large number of pure vibrational state energies for CH_3D extending to about $6300\,cm^{-1}$ and for CHD_3 extending up to $8700\,cm^{-1}$. Essential to such an analysis are very high resolution spectra with reduced Doppler width taken at low temperatures of about 80 K and allowing for assignment of the low J transitions in these spectra. Besides applications in atmospheric and planetary science (particularly for the isotopomer CH_3D) these results open a window towards the complete nine-dimensional quantum dynamics of intramolecular vibrational motion and redistribution in the fundamental methane molecule. The present results are of sufficient accuracy to serve as benchmarks for further experimental and theoretical studies.

As one application of the present results we might compare with the results on the spectrum and femtosecond intramolecular vibrational redistribution by the strong Fermi-resonance within the CH-chromophore in CHD_3 [7,20,21,33,34,66]. Table 16 provides such a comparison for the lower polyads designated by the symbol N_j, where N is the polyad quantum number ($N = v_1 + v_5/2$ in the normal mode basis) and j gives a state index increasing with decreasing energy within each polyad. The polyads with A_1 symmetry have integer N, whereas polyads with E symmetry have half-odd integer N. One recognises a good agreement of the experimental level positions where overlap exists in Table 16. The differences between experiment and the effective hamiltonian fit as well as the three-dimensional vibrational variational calculations of [20] using 180 basis functions for the CH chromophore's stretching and bending levels remain modest and are of the expected magnitude for such model fits. This provides one confirmation for the validity of the time dependent wavepacket dynamics obtained from the variational calculations in the CH-chromophore subspace [19,33,34]. Table 16 indicates the obvious need to

Table 15. Vibrational spectroscopic parameters of the CH_3D and CHD_3 molecules (in cm^{-1}).

	CH_3D			CHD_3		
1	2	3	4	5	6	7
Parameter	Present work, I	Present work, II	[64]	Present work, I	Present work, II	[64]
ω_1	3072.6833[a]	3073.6784[a]	3071.4	3133.8793[a]	3136.1717[a]	3130.5
ω_2	2289.9925[a]	2288.7415[a]	2285.2	2192.8606[a]	2192.3649[a]	2191.3
ω_3	1339.8435[a]	1340.7082[a]	1339.8	1026.1678[a]	1026.0830[a]	1025.4
ω_4	3160.6238[a]	3163.8824[a]	3156.8	2343.7880[a]	2342.3602[a]	2337.0
ω_5	1504.4874[a]	1504.3008[a]	1508.1	1318.6017[a]	1319.0257[a]	1321.4
ω_6	1188.8961[a]	1188.2985[a]	1188.1	1054.2383[a]	1054.9672[a]	1055.5
x_{11}	−4.0633(818)	−5.3214(855)	−17.197	−58.7895(452)	−58.9936(486)	−59.221
x_{12}	−2.9308(787)	−2.5552(753)	−1.878	−2.4050(615)	−2.9045(640)	−2.204
x_{13}	5.6371(651)	488461(664)	−0.981	−9.0383(489)	−9.1934(502)	−9.731
x_{14}	−99.5704(782)	−99.0218(766)	−72.771	2.7796(381)	2.3367(363)	2.184
x_{15}	−9.5368(521)	−9.1793(542)	−19.016	−21.2261(337)	−21.3667(396)	−21.111
x_{16}	−7.4372(527)	−7.2330(570)	−5.612	−0.7920(333)	−1.4056(347)	−0.309
x_{22}	−28.0925(886)	−27.9443(898)	−31.167	0.7911(316)	1.1391(307)	−8.826
x_{23}	−7.3640(473)	−7.3118(433)	−6.739	3.1231(796)	3.0935(757)	15.727
x_{24}	−7.8757(779)	−7.7295(758)	1.639	−42.9968(658)	−42.7271(649)	−37.352
x_{25}	−3.6385(505)	−3.5220(550)	−3.331	−5.1721(857)	−5.2201(826)	−4.017
x_{26}	−17.8095(565)	−17.5869(550)	−22.266	−2.3816(904)	−2.4885(875)	4.674
x_{33}	−7.6676(813)	−7.7593(809)	−6.802	−6.1956(351)	−6.1883(368)	−7.230
x_{34}	−10.3564(459)	−10.5173(490)	−9.440	−7.0455(441)	−6.9765(464)	−8.449
x_{35}	−2.8660(632)	−2.9084(618)	−2.033	−2.9438(832)	−2.7954(798)	−1.029
x_{36}	−3.0865(617)	−3.0729(622)	−1.091	3.5503(873)	3.4450(824)	1.638
x_{44}	−31.8247(753)	−32.4024(774)	−31.611	−16.6579(791)	−16.3487(761)	−18.601
x_{45}	−8.1681(558)	−8.3727(578)	−14.611	−8.4413(424)	−8.4541(409)	−7.195
x_{46}	−9.3785(841)	−9.3041(850)	−7.686	−11.2718(978)	−11.0441(975)	−8.402
x_{55}	−4.4819(536)	−4.4168(547)	−1.874	−4.5233(368)	−4.5516(401)	−4.604
x_{56}	−5.1763(831)	−5.0898(800)	−4.068	5.1780(380)	4.9188(415)	0.055
x_{66}	0.261[b]	0.261[b]	0.261	−5.2427(860)	−5.3057(865)	−5.500
y_{666}	−0.2239(789)	−0.2166(807)				
g_{44}	27.0956(326)	28.5389(352)	12.636	8.5470(662)	8.5598(640)	8.252
g_{45}	−7.0826(727)	−7.0618(759)	−1.721	3.6205(449)	3.5837(422)	−0.060
g_{46}	3.1700(852)	3.1598(873)	−0.230	1.1200(874)	1.1429(854)	−0.729
g_{55}	2.4586(317)	2.3804(385)	0.384	5.1145(384)	5.0951(373)	5.403
g_{56}	−4.6803(674)	−4.6841(713)	−5.056	6.1304(751)	5.8940(730)	0.921
g_{66}	1.4987(830)	1.5158(789)	0.645	2.8833(910)	2.8714(889)	3.251
k_{155}	−56.3671(349)	−56.6885(342)		30.0[c]	30.0[c]	
k_{345}				−70.8100(638)	−70.6261(671)	
$F_{11,44}$	−70.1382(896)	−74.8129(912)				
$F_{33,56}$	15.7181(785)	15.3674(714)				
$F_{33,66}$				−18.0922(812)	−17.9093(824)	
$F_{1,333}$				8.2431(786)	8.1787(757)	

Notes: [a]Was not fitted, but calculated on the basis of the F_{ij} parameters given in columns 2 and 3 of Table 14.
[b]Was constrained to the value from [64].
[c]Was constrained to the value from [20], obtained including intensity information.

extend the present analyses to higher excitations, with currently available data from our cold samples extending to about 12,000 cm^{-1}. Indeed, our analysis of 1988 extended to about 19,000 cm^{-1} using also further results from the literature [67]–[74] (see also [4–9,19,33,66,75,76]).

While the present analysis confirms the results on the quantum dynamics in the three-dimensional subspace of the CH-chromophore, our current analyses extend well beyond this by including excitations of all vibrations in the full nine-dimensional coordinate space of normal modes. They thus will allow analyses of intramolecular vibrational redistribution to non-CH chromophore modes, which is generally expected on longer time scales than the 100 fs times for intrachromophore redistribution.

Table 16 illustrates a further important aspect. The approximate zero order assignments of the vibrational

Table 16. Results for CH-chromophore polyad states in CHD_3 (all term values $\tilde{\nu}/cm^{-1}$).

N_j	Exp. from Table 13, this work	Calc. I from table 13, this work	Exp. ref. [20]	Theory $\tilde{\nu}_{var}$ ref. [20]
$(1/2)_1$	1292.500	1292.12	1292.499	1292.63
1_2	2564.676	2564.63	2564.67	2568.42
1_1	2992.786	2992.73	2992.75	2990.85
$(3/2)_2$	3838.040	3838.48		3839.96
$(3/2)_1$	4261.662	4261.91	4262.1	4261.40
2_3	–	5092.73	–	5092.15
2_2	5515.603	5514.98	5515.7	5515.96
2_1	5865.004	5865.64	5864.98	5865.47
$(5/2)_3$	–	–	–	6346.88
$(5/2)_2$	–	–	–	6766.40
$(5/2)_1$	7115.499	–	7115.48	7113.98
3_4	–	7584.30	–	7582.97
3_3	–	7999.40	8005.4	8000.91
3_2	8346.919	8347.05	8347.1	8347.25
3_1	8623.349	8622.89	8623.32	8624.19

levels as given in columns 1 of Tables 12 and 13 have, of course, only a very rough, qualitative meaning. Only the symmetry assignments and band centre wavenumbers have a real significance. Similarly, the parameters of the effective hamiltonians used in the fits (Tables 14 and 15) have significance only in the framework of a given effective fit and should not be considered to be simply related to the parameters of the potential hypersurface (see discussion in [20,77]–[79]). Finally, the effective Hamiltonian used may not necessarily lead to very accurate level predictions, if far removed from the fitted range. This deserves a further test.

An aspect not analysed here in detail concerns the absorption intensities and dipole function related among other things to the important question of the dipole moment direction in CH_3D and CD_3H [4,80]. Analyses of our current results will provide further important experimental information on the multidimensional dipole function in these isotopomers [6,9,19]. The relation to the quantum dynamics in excited electronic states of methane [17] and in the limit of electronic excitation the Rydberg states and the cations of methane isotopomers [81] deserves mention as well as the use of understanding the true nature of the multidimensional coupled vibrational states in methane isotopomers reacting with reactive atoms [12]–[15]. Particularly for the isotopomer CH_3D our accurate experimental results and their analysis should prove useful in understanding features in planetary atmospheres including the moon Titan [82].

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References

[1] J.H. van't Hoff, *Vorlesungen über theoretische und physikalische Chemie* (Vieweg, Braunschweig, 1898).
[2] L. Pauling, *The Nature of the Chemical Bond*, 2nd ed. (Oxford University Press, London, 1940).
[3] R.N. Zare, *Angular Momentum: Understanding Spatial Aspects in Chemistry and Physics* (Wiley, New York, 1988).
[4] H. Hollenstein, R. Marquardt, M. Quack and M.A. Suhm, J. Chem. Phys. **101** (5), 3588 (1994).
[5] H. Hollenstein, R. Marquardt, M. Quack and M.A. Suhm, Ber. Bunsenges. Phys. Chem. **99** (3), 275 (1995).
[6] R. Marquardt and M. Quack, J. Chem. Phys. **109** (24), 10628 (1998).
[7] S.D. Peyerimhoff, M. Lewerenz and M. Quack, Chem. Phys. Lett. **109** (6), 563 (1984).
[8] D.W. Schwenke, Spectrochim. Acta A **58** (4), 849 (2002).
[9] R. Marquardt and M. Quack, J. Phys. Chem. A **108** (15), 3166 (2004).
[10] M. Quack and J. Troe, Ber. Bunsen-Ges. Phys. Chem. **81**, 329 (1977).
[11] M. Quack, J. Phys. Chem. **83** (1), 150 (1979).
[12] J.P. Camden, H.A. Bechtel, D.J.A. Brown and R.N. Zare, J. Chem. Phys. **124** (3), 034311 (2006).
[13] W.F. Hu, G. Lendvay, D. Troya, G.C. Schatz, J.P. Camden, H.A. Bechtel, D.J.A. Brown, M.R. Martin and R.N. Zare, J. Phys. Chem. A **110** (9), 3017 (2006).
[14] J.P. Camden, H.A. Bechtel, D.J.A. Brown, M.R. Martin, R.N. Zare, W.F. Hu, G. Lendvay, D. Troya and G.C. Schatz, J. Am. Chem. Soc. **127** (34), 11898 (2005).
[15] J.P. Camden, W.F. Hu, H.A. Bechtel, D.J.A. Brown, M.R. Martin, R.N. Zare, G. Lendvay, D. Troya and G.C. Schatz, J. Phys. Chem. A **110** (2), 677 (2006).
[16] M. Quack, Angew. Chem. Int. Ed. (Engl.) **28** (5), 571 (1989).
[17] M.J.M. Pepper, I. Shavitt, P.v. Ragué Schleyer, M.N. Glukhovtsev, R. Janoschek and M. Quack, J. Comput. Chem. **16** (2), 207 (1995).
[18] A. Bakasov, T.K. Ha and M. Quack, J. Chem. Phys. **109** (17), 7263 (1998).

[19] R. Marquardt, M. Quack and I. Thanopulos, J. Phys. Chem. A **104** (26), 6129 (2000).
[20] M. Lewerenz and M. Quack, J. Chem. Phys. **88** (9), 5408 (1988).
[21] T. Carrington, L. Halonen and M. Quack, Chem. Phys. Lett. **140** (5), 512 (1987).
[22] X.G. Wang and T. Carrington, J. Chem. Phys. **118** (14), 6260 (2003).
[23] X.G. Wang and T. Carrington, J. Chem. Phys. **119** (1), 94 (2003).
[24] X.G. Wang and T. Carrington, J. Chem. Phys. **119** (1), 101 (2003).
[25] H.G. Yu, J. Chem. Phys. **121** (13), 6334 (2004).
[26] S. Albert, S. Bauerecker, V. Boudon, L.R. Brown, J.-P. Champion, M. Loëte, A. Nikitin and M. Quack, Chem. Phys. **356** (1–3), 131 (2009).
[27] O.N. Ulenikov, E.S. Bekhtereva, S. Albert, S. Bauerecker, H.M. Niederer, M. Quack, in preparation.
[28] H.M. Niederer, S. Albert, S. Bauerecker, V. Boudon, J.P. Champion and M. Quack, Chimia **62** (4), 273 (2008).
[29] M. Hippler and M. Quack, J. Chem. Phys. **116** (14), 6045 (2002).
[30] O.N. Ulenikov, E.S. Bekhtereva, S.V. Grebneva, H. Hollenstein and M. Quack, Phys. Chem. Chem. Phys. **7** (6), 1142 (2005).
[31] O.N. Ulenikov, E.S. Bekhtereva, S.V. Grebneva, H. Hollenstein and M. Quack, Mol. Phys. **104**, 3371 (2006).
[32] O.N. Ulenikov, E.S. Bekhtereva, S. Albert, S. Bauerecker, H. Hollenstein and M. Quack, J. Phys. Chem. A **113** (10), 2218 (2009).
[33] R. Marquardt and M. Quack, J. Chem. Phys. **95** (7), 4854 (1991).
[34] R. Marquardt and M. Quack, in *Encyclopedia of Chemical Physics and Physical Chemistry, Vol. 1 (Fundamentals)*, edited by J.H. Moore and N. Spencer (IOP, Bristol, 2001), pp. 897–936.
[35] H.R. Dübal and M. Quack, J. Chem. Phys. **81** (9), 3779 (1984).
[36] J. Segall, R.N. Zare, H.R. Dübal, M. Lewerenz and M. Quack, J. Chem. Phys. **86** (2), 634 (1987).
[37] A. Amrein, M. Quack and U. Schmitt, J. Phys. Chem. **92** (19), 5455 (1988).
[38] O.N. Ulenikov, E.S. Bekhtereva, A.S. Bulavenkova, S. Bauerecker, H. Hollenstein and M. Quack, in *Proceedings Nineteenth Colloquium on High Resolution Molecular Spectroscopy, Salamanca, Spain, 11–16 September 2005*, edited by D. Bermejo, J.L. Doménech, and M.A. Moreno (Sociedad Española de Óptica, Salamanca, 2005), paper N10.
[39] E.S. Bekhtereva, O.N. Ulenikov, E.A. Sinitsin, S. Albert, S. Bauerecker, H. Hollenstein and M. Quack, in *Proceedings of the 20th Colloquium on High-Resolution Molecular Spectroscopy*, edited by V. Boudon (Université de Dijon, Dijon, 2007), paper J 30, p. 268.
[40] A.V. Nikitin, J.P. Champion and L.R. Brown, J. Mol. Spectrosc. **240** (1), 14 (2006).
[41] S. Albert, K.K. Albert and M. Quack, in *Trends in Optics and Photonics (TOPS)* (Optical Society of America, Washington, DC, 2003), Vol. 84, pp. 177–180.
[42] S. Albert and M. Quack, Chem. Phys. Chem. **8** (9), 1271 (2007).
[43] S. Albert, S. Bauerecker, M. Quack and A. Steinlin, Mol. Phys. **105** (5), 541 (2007).
[44] S. Bauerecker, M. Taraschewski, C. Weitkamp and H.K. Cammenga, Rev. Sci. Instrum. **72** (10), 3946 (2001).
[45] S. Bauerecker, Phys. Rev. Lett. **94** (3), 033404 (2005).
[46] S. Bauerecker, F. Taucher, C. Weitkamp, W. Michaelis and H.K. Cammenga, J. Mol. Struct. **348**, 237 (1995).
[47] A.G. Maki and J.S. Wells, NIST Spec. Publ. 821 (1991).
[48] L.S. Rothman, D. Jacquemart, A. Barbe, D.C. Benner, M. Birk, L.R. Brown, M.R. Carleer, C. Chackerian, K. Chance, L.H. Coudert, V. Dana, V.M. Devi, J.M. Flaud, R.R. Gamache, A. Goldman, J.M. Hartmann, K.W. Jucks, A.G. Maki, J.Y. Mandin, S.T. Massie, J. Orphal, A. Perrin, C.P. Rinsland, M.A.H. Smith, J. Tennyson, R.N. Tolchenov, R.A. Toth, J. Vander Auwera, P. Varanasi and G. Wagner, J. Quant. Spectrosc. Radiat. Transfer **96** (2), 139 (2005).
[49] M. Quack, Mol. Phys. **34** (2), 477 (1977).
[50] M. Quack, in *Symmetries and Properties of Non-rigid Molecules: A Comprehensive Survey*, edited by J. Maruani and J. Serre, in series Studies in Physical and Theoretical Chemistry, Vol. 23 (Elsevier, Amsterdam, 1983) pp. 355–378.
[51] E.B. Wilson, J.C. Decius and P.C. Cross, *Molecular Vibrations the Theory of Infrared and Raman Vibrational Spectra* (McGraw-Hill, New York, 1955).
[52] H.C. Longuet-Higgins, Mol. Phys. **6** (5), 445 (1963).
[53] E.R. Cohen, T. Cvitas, J.G. Frey, B. Holmström, K. Kuchitsu, R. Marquardt, I. Mills, F. Pavese, M. Quack, J. Stohner, H.L. Strauss, M. Takami and A.J. Thor, *Quantities, Units and Symbols in Physical Chemistry*, 3rd ed., second corrected printing (IUPAC and Royal Society of Chemistry, RSC Publishing, Cambridge, 2008).
[54] O.N. Ulenikov, G.A. Onopenko, N.E. Tyabaeva, J. Schroderus and S. Alanko, J. Mol. Spectrosc. **200** (1), 1 (2000).
[55] O.N. Ulenikov, G.A. Onopenko, N.E. Tyabaeva, S. Alanko, M. Koivusaari and R. Anttila, J. Mol. Spectrosc. **186** (2), 293 (1997).
[56] O.N. Ulenikov, G.A. Onopenko, N.E. Tyabaeva, J. Schroderus, S. Alanko and M. Koivusaari, J. Mol. Struct. **517–518**, 25 (2000).
[57] E.P. Wigner, *Quantum Theory of Angular Momentum* (Academic Press, New York, 1965).
[58] V.N. Saveliev and O.N. Ulenikov, J. Phys. B – At. Mol. Opt. Phys. **20** (1), 67 (1987).
[59] Y.S. Makushin, O.N. Ulenikov and A.E. Cheglokov, *Symmetry and Its Applications to the Problems of*

Molecular Vibration–Rotation Spectroscopy, Parts I and II (in Russian) (Tomsk State University Press, Tomsk, 1990).
[60] D.A. Varshalovitch, A.N. Moskalev and V.K. Khersonsky, *Quantum Theory of Angular Momentum* (Nauka, Leningrad, 1975).
[61] U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic Press, New York, 1959).
[62] O.N. Ulenikov, G.A. Onopenko, N.E. Tyabaeva, J. Schroderus and S. Alanko, J. Mol. Spectrosc. **193** (2), 249 (1999).
[63] O.N. Ulenikov, G.A. Onopenko, N.E. Tyabaeva, S. Alanko, M. Koivusaari and R. Anttila, J. Mol. Spectrosc. **186** (2), 230 (1997).
[64] T.J. Lee, J.M.L. Martin and P.R. Taylor, J. Chem. Phys. **102** (1), 254 (1995).
[65] M. Quack, Chimia **57** (4), 147 (2003).
[66] T.K. Ha, M. Lewerenz, R. Marquardt and M. Quack, J. Chem. Phys. **93** (10), 7097 (1990).
[67] L.F.H. Bovey, J. Chem. Phys. **21** (5), 830 (1953).
[68] J.K. Wilmshurst and H.J. Bernstein, Can. J. Chem. – Rev. Can. Chim. **35** (3), 226 (1957).
[69] T.A. Wiggins, E.R. Shull, J.M. Bennett and D.H. Rank, J. Chem. Phys. **21** (11), 1940 (1953).
[70] G.J. Scherer, K.K. Lehmann and W. Klemperer, J. Chem. Phys. **81** (12), 5319 (1984).
[71] G.A. Voth, R.A. Marcus and A.H. Zewail, J. Chem. Phys. **81** (12), 5494 (1984).
[72] J.W. Perry, D.J. Moll, A. Kuppermann and A.H. Zewail, J. Chem. Phys. **82** (3), 1195 (1985).
[73] A. Campargue and F. Stoeckel, J. Chem. Phys. **85** (3), 1220 (1986).
[74] A. Campargue, F. Stoeckel, M. Chenevier and H. Ben Kraiem, J. Chem. Phys. **87** (10), 5598 (1987).
[75] D. Permogorov, A. Campargue, M. Chenevier and H.B. Kraiem, J. Mol. Spectrosc. **170** (1), 10 (1995).
[76] C. Domingo, A. Delolmo, R. Escribano, D. Bermejo and J.M. Orza, J. Chem. Phys. **96** (2), 972 (1992).
[77] M. Quack, Annu. Rev. Phys. Chem. **41**, 839 (1990).
[78] A. Beil, D. Luckhaus, M. Quack and J. Stohner, Ber. Bunsenges. Phys. Chem. **101** (3), 311 (1997).
[79] D. Luckhaus and M. Quack, Chem. Phys. Lett. **205** (2–3), 277 (1993).
[80] R. Signorell, R. Marquardt, M. Quack and M.A. Suhm, Mol. Phys. **89** (1), 297 (1996).
[81] H.J. Wörner and F. Merkt, Angew. Chem.-Int. Edit. **48** (35), 6404 (2009).
[82] D.E. Jennings, P.N. Romani, G.L. Bjoraker, P.V. Sada, C.A. Nixon, A.W. Lunsford, R.J. Boyle, B.E. Hesman and G.H. McCabe, J. Phys. Chem. A **113** (42), 11101 (2009).
[83] O.N. Ulenikov, A.B. Malikova, S. Alanko, M. Koivusaari and R. Anttila, J. Mol. Spectrosc. **179**, 175 (1996).

Appendix 1. Tables of line wavenumbers

The appendix contains tables of observed transition wavenumbers for more than 9000 lines for CH_3D and CD_3H with their preliminary assignments as used for the final assignment of transitions leading to the $J = 0$ levels of excited vibrational states. The Appendix can be viewed online. These tables contain as Table A the results for CH_3D and as Table B the results for CHD_3. These tables have nine columns with the following content:

(I) Observed wavenumbers, $\nu^{\text{exp.}}$ (in cm^{-1}).
(II, III) Quantum numbers of the upper ro-vibrational state, J', K'.
(V, VI) Quantum numbers of the lower ro-vibrational state, J'', K''.
(IV, VII) Symmetry of the upper and lower ro-vibrational states, respectively. Index 0 corresponds to A_1 symmetry; indices 1 and 2 correspond to A_2 and E, respectively; index 'a' corresponds to a pair of degenerate A_1/A_2 ro-vibrational states (not split under the conditions of our experiment).
(VIII) Band.
(IX) Symmetry of the vibrational state.