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► **To cite this version:**

A.V. Nikitin, A.A. Rodina, A.E. Protasevich, L. Manceron, Michael M. Rey, et al.. New quantum assignment and preliminary High-Resolution Analysis of H₂CO in the range 3900-4450 cm⁻¹. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2024, 329, pp.109180. 10.1016/j.jqsrt.2024.109180 . hal-04780425v1

HAL Id: hal-04780425

<https://hal.science/hal-04780425v1>

Submitted on 13 Nov 2024 (v1), last revised 17 Dec 2024 (v2)

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New quantum assignment and preliminary High-Resolution Analysis of H₂CO in the range 3900-4450 cm⁻¹

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Number of Pages:

Number of Figures:

Number of Tables:

Number of supplemental files: 1

Keywords: high resolutions spectra; H₂CO; formaldehyde; vibration-rotation states; infrared absorption; effective Hamiltonian

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Abstract:

Four spectra of formaldehyde in natural isotopic abundance in the 3900-4450 cm^{-1} region were recorded at low temperature at Synchrotron SOLEIL for different pressures. Line positions and intensities were retrieved by non-linear least-squares curve-fitting procedures and analyzed using effective Hamiltonian and ab initio based effective dipole transition moment models. A new measured line list contains positions and intensities for 8929 features. Quantum assignments were made for 5536 new transitions, which represent ~XX% of the integrated line intensity observed in this region. The resulting list of lines is significantly new accurate line positions. All assigned 5536 line positions were fitted to RMS standard deviations of 0.00102 cm^{-1} . All intensities were received from the predicted value from ab initio variational calculations reported in the TheoReTS database (<http://theorets.univ-reims.fr> <http://theorets.tsu.ru>).

Introduction

Accurate knowledge of the spectroscopy of formaldehyde is important for the monitoring of this species in the atmosphere and also for detection of the presence of this molecule as an environmental pollutant indoors [1] [2] [3] [4]. Improving spectral parameters and line-by-line analyses are essential for the reliable interpretation of near infrared spectra returned by the ground-based and orbiting observatories [5] [6]. An assignment of infrared spectra corresponding to high-energy overtone and combination bands is known to be a tedious and difficult task. Recent *ab initio* calculations of potential energy surfaces (PES) and of dipole moment surfaces (DMS) together with a progress in variational nuclear motion calculations have permitted a significant progress in predictions of vibrational-rotational bands. Previous experience with some four- and five-atom molecules [7] [8] [9] [10] [11] have shown that *ab initio* based approaches could be useful for better modelling and assignments of high-resolution spectra. In the present work, we report theoretical vibrational levels of formaldehyde computed from new accurate *ab initio* PES using the algorithms similar to one recently applied for the methane molecule [12] and compare our results with other recent calculations [13] [14].

From the theoretical standpoint, the formaldehyde molecule is an interesting case because of the rapid basis set convergence of variational calculations and a possibility to compare different methods conducted in various coordinate systems using high-level quantum-chemical calculations. Burleigh et al. [15] have used the quadratic force field for formaldehyde obtained by refining the CCST(T)/cc-pVTZ *ab initio* quartic force field of Martin, Lee, and Taylor [16] by means of iteratively fitting a subset of the coefficients of a Taylor expansion of the potential energy surface (PES) to the observed transition frequencies. Yachmenev et al. [14] have calculated an *ab initio* PES using the CCSD(T) / aug-cc-pVQZ method in a wide range of geometries. A detailed review of earlier works refs [17] [15] [16] [18] [19] [20] that reported calculations of the formaldehyde PES and energy levels can be found refs. [13] [14].

The accuracy of *ab initio* calculations is in general lower than that of high-resolution experimental methods, except for studies of diatomic molecules with a small number of electrons. In the case of triatomics, very accurate *ab initio* calculations of PES and of dipole moment surfaces (DMS) led to a breakthrough in the extension of spectra analyses towards higher energy ranges. This was, for example, the case with the spectroscopy of water [21] [22] [23] [24], carbon dioxide [25] [26] [27], hydrogen sulfide [28] [29] and sulfur dioxide [30], as well as with the ozone spectra analyses [31] [32] [33]. In the latter case, *ab initio* predictions were mandatory for precise intensity quantification [34], for understanding the PES properties in the transition state range towards the dissociation threshold [35] [33], the interactions between

potential wells [36], and modeling of the isotopic exchange reactions [37]. [38] Many ab initio PESs have been subsequently refined by a fit to experimental data to achieve better accuracy in line positions. Theoretical line lists for ammonia [39] [27] and phosphine [40] [41] [42] are successful examples of this trend for four-atom species. New PESs and DMSs have been recently reported for five-atom [43] [44], six-atom molecules [45] [46], [47] and seven-atom [48] molecules.

Among the large number of ab initio calculations for many-electron systems, only two works reported calculations of the vibrational levels with the accuracy of about 0.1 cm^{-1} , at least in the low and medium energy ranges: ref [24] [49] for the water molecule, and ref [12] for methane. While both of these molecules contain 10 electrons, the formaldehyde molecule has 16 electrons. In the recent study by Morgan et al. [13] the high accuracy vibrational fundamentals of formaldehyde have been reported, but not all calculated vibrational energy levels were published.

In contrast to methane, formaldehyde is an experimentally much less studied molecule. One of the possible reasons for this is the unavailability of the cold spectra caused by the high temperature of condensation and a complex technique for creating the formaldehyde gas. While for methane about 200 assigned vibrational energy levels have been measured with high accuracy, in case of formaldehyde, no more than 20 vibrational levels could be accurately obtained from the high resolution rotationally resolved spectra. The calculations reported in this paper can be considered as an additional source of information that could be useful for extended assignment and modeling of high-resolution experimental spectra of formaldehyde and its isotopologues.

This work was dedicated to obtaining the list of lines of H_2CO in $3900\text{-}4450 \text{ cm}^{-1}$ region. The Polyad 3 band system corresponds to 28 upper state vibrational sublevels. In this work only 25 upper state vibrational sublevels included in the range were considered. The scheme of polyad is presented on **Fig. 1**.

This paper is structured as follows. The experimental conditions are described in Section 2. The CT-transformation of full Hamiltonian is considered in Section 3. Spectra modeling and assignment is described in Section 4. A detailed comparison with available experimental data in Sections 4 shows that the resulting full-dimensional ab initio PES provides currently the most accurate theoretical band origins for formaldehyde. We also discuss uncertainties and discrepancies in published experimental levels obtained from low- and high-resolution spectra. An empirically optimized PES obtained with a fine tuning of six PES parameters and the corresponding predicted vibrational levels are also reported.

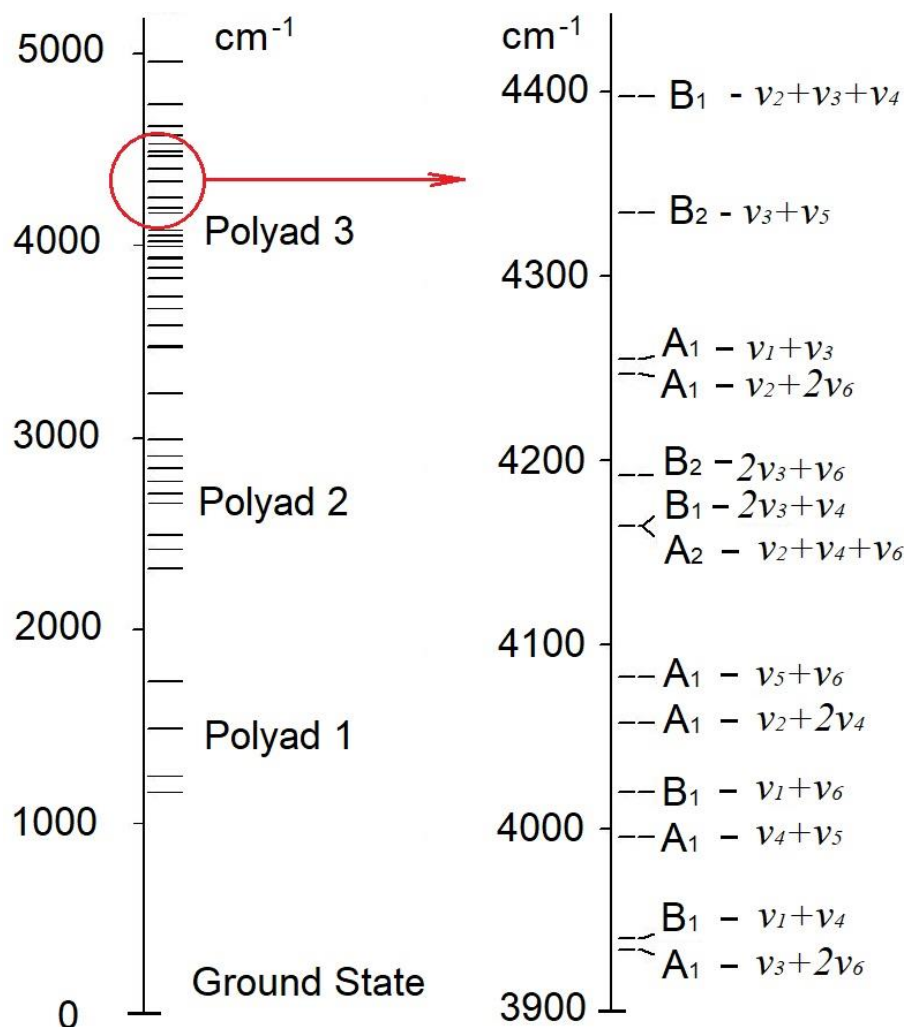


Fig. 1. Vibrational levels of the H₂CO polyads (left side), and the vibrational sublevels of a part of Polyad 3 (right side) corresponding to rovibrational bands analyzed in this work. The right hand side panel displays the principal vibration quantum numbers (notation ν₁ν₂ν₃ν₄ν₅ν₆), and symmetry types of vibration sublevels, and vibrational ranking numbers within the Polyad 3. The symmetry types correspond to irreducible representations of the C_{2v} point group.

1. Experiment

Four absorption spectra of formaldehyde were recorded with a Bruker IFS 125 HR high-resolution Fourier transform spectrometer (FTS) using the cryogenic long path optical cell located on the AILES beamline of the SOLEIL synchrotron [50]. The instrument was fitted with a tungsten source, an entrance aperture set to 1.0 mm, a Si/CaF₂ beam splitter, a 1.3 mm aperture and 418 mm focal length collimator, and an InSb detector cooled down to 77 K. Formaldehyde was generated by slow thermal decomposition of paraformaldehyde (Sigma Aldrich, 95% purity) in a high vacuum glass line. The resulting product was then distilled twice at low temperature (-90°C) and stored at low temperature in a glass bulb before being sublimed directly in the low

temperature cell. It contained a trace amount of CO₂ but did not present any evidence of decomposition or repolymerization at the low cell temperature about 160K). The pressures were measured with a Pfeiffer capacitance manometer of 10 mbar full-scale range, temperature stabilized at 45°C and characterized by an accuracy of reading of 0.1%.

An optical path length of 93 meters was adopted for all spectra. The spectra were successively recorded near 160K. About four days were needed to achieve this temperature with a 2 K temperature gradient. The varying parameters for all spectra are given in **Table 1**. All the interferograms were recorded with a maximum optical path difference (MOPD) of 150 cm, corresponding to a spectral resolution of 0.006 cm⁻¹ (0.9/MOPD, according to the Bruker definition of the spectral resolution) and were transformed without apodization function (Boxcar option) with a zero-filling factor of 8. The number of interferograms averaged to yield the single beam spectra is provided in **Table 1**. The transmittance spectra were obtained after division by a zero-absorption spectrum recorded with the cell evacuated and a 0.06 cm⁻¹ spectral resolution. The recordings cover the range 2500 to 7000 cm⁻¹ but are mostly dedicated to the 3900-6500 cm⁻¹ range where the absorption amplitude allows for quantitative measurements. At the low pressures and temperatures used here, the Doppler width are always larger than resolution and even the width of the sinc function (0.004 cm⁻¹).

Accurate calibration of the frequency axis was achieved using CO₂ impurity lines and a high resolution N₂O spectrum and line positions provided in the HITRAN database [ref] (uncertainties in the 10⁻³-10⁻⁴ cm⁻¹ range). After calibration, an RMS deviation of the position differences of about 3×10⁻⁴ cm⁻¹ was achieved.

Table 1. Experimental conditions for series of H₂CO spectra in the range of Polyad 3.

Spectrum ID	scan number	Pressure (Torr)	Temperature (K)
TrCH2O_2hPa	240	0.015	166
TrCH2O_7Pa	720	0.053	160
TrCH2O_22Pa	1620	0.165	165
TrCH2O_45Pa	360	0.315	163

2. *Ab initio* effective Hamiltonian

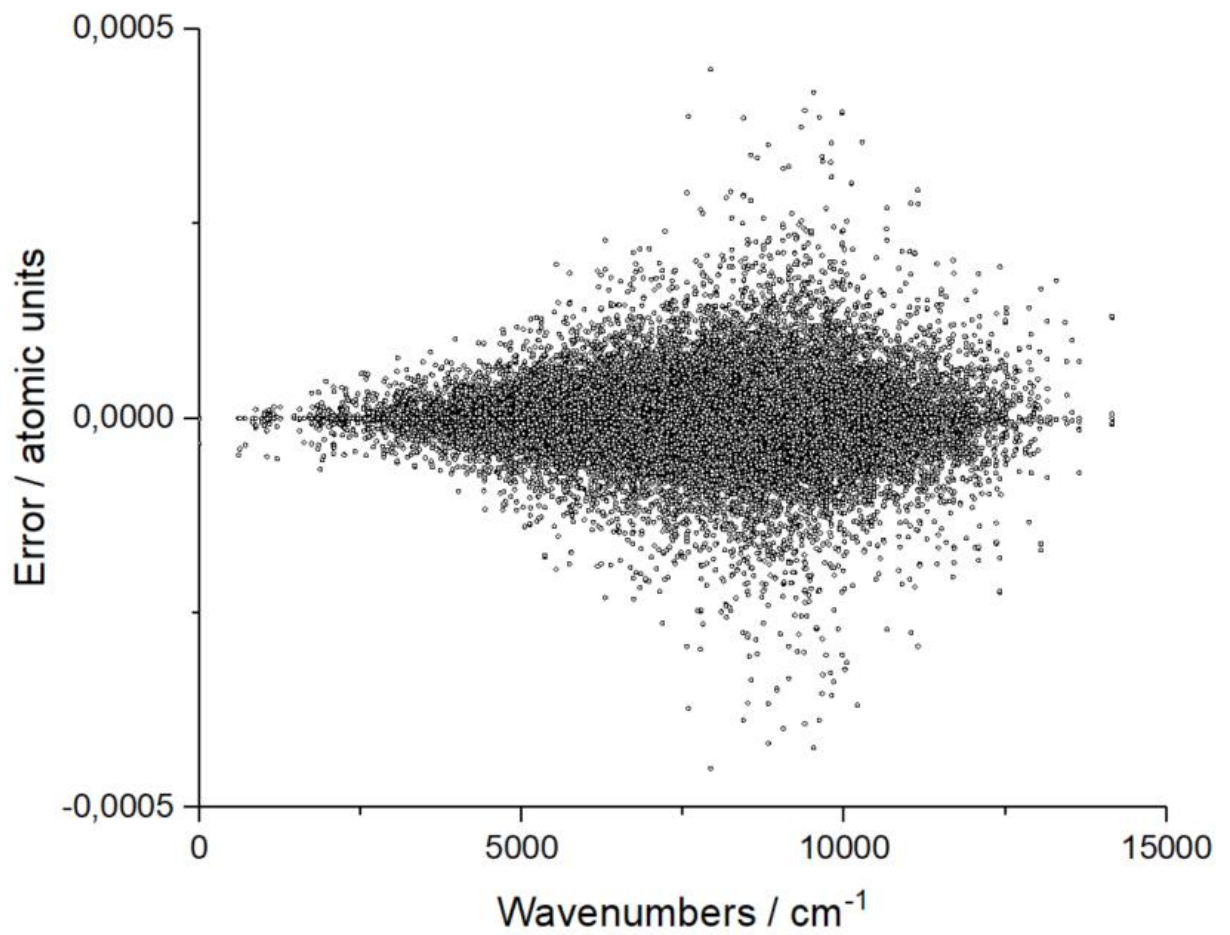
As an alternative to the contact transformation method described in Refs. [56], [57], [58], [59] [55], the numerical approach proposed recently in [55] and based on the transformation of some variational eigenfunctions was used in this work to derive an initial set of *ab initio* effective polyad Hamiltonian parameters to be refined on experimental data. Beyond obviating the need to make tedious algebraic calculations, the advantages of such an approach is threefold (i) For a full account of symmetry, the irreducible tensor operator formalism is used at the very first stage of calculation, even for molecules belonging to non-Abelian point groups, (ii) In order to improve the quality of the effective parameters, variational energies can be replaced with empirical energy levels during the numerical block-diagonalization procedure (iii) Last but not least, a set of dipole moment parameters can be easily derived from an *ab initio* DMS.

To construct the effective Hamiltonian, the PES from [51] is used. The accuracy of the vibrational levels obtained from this PES is $\sim 0.5 \text{ cm}^{-1}$. To improve the prediction, an empirical correction of the harmonic parameters of the PES was made.

The TENSOR code [51] [52] [53] [54] was then used to calculate the energy levels in normal coordinates using the Watson-Eckart KEO. We used contact transformation (CT) in form [55]. The contact transformation (CT) method that permitted deriving initial effective Hamiltonians from an *ab initio* PES as described in [56], [57], [58], [59] [55]

3. Effective dipole moment

To find the dipole moment surface (DMS), the X, Y, Z components of the dipole moment were calculated using the CCSD(T)/avtz method in 15000 geometries. Additionally, in 2120 geometries at the bottom of the potential well, the dipole moment was calculated using the CCSD(T)/acvqz method. The total DMS was obtained in the form of a 5th order Taylor series expansion, RMS fit $5\text{E}-5 \text{ au}$. Effective dipole moment was constructed using algorithm [56].



4. Spectra modeling and assignment and line parameters in the 3900–4450 cm⁻¹ region

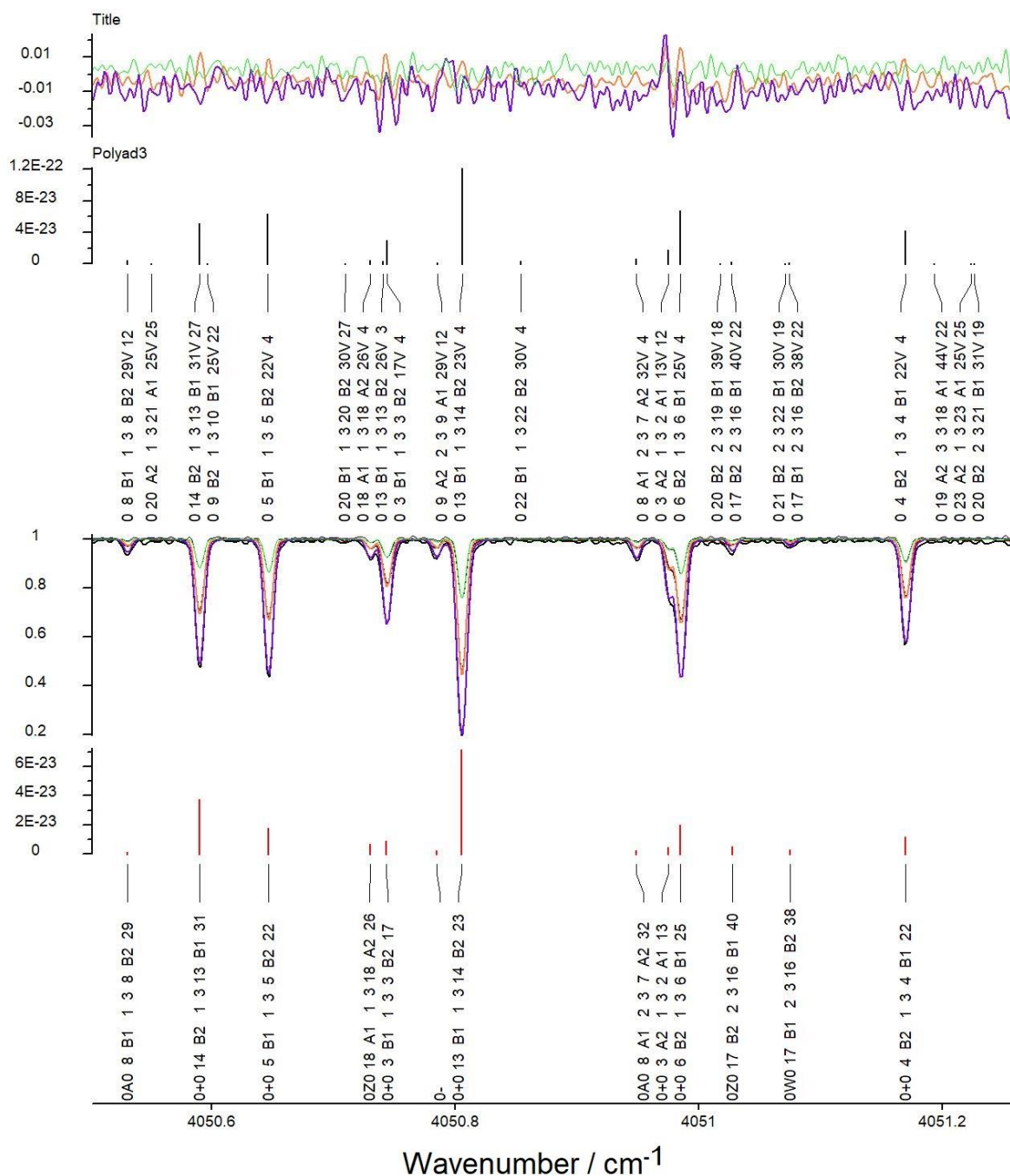


Fig. 2 Example of quantum number assignments in the H_2CO spectra. The upper panel shows residuals (obs-calc) for three spectra (green 0.053 Torr at 160 K, orange 0.165 Torr at 165 K and violet 0.315 Torr at 163 K). Next panel below shows the variation calculations at 296 K. Next panel below shows the comparison between three experimental spectra and simulation spectra (green 0.053 Torr at 160 K, orange 0.165 Torr at 165 K and violet 0.315 Torr at 163 K). Next panel shows assigned experimental line sticks and the lowest panel – our calculated intensity sticks at 296 K.

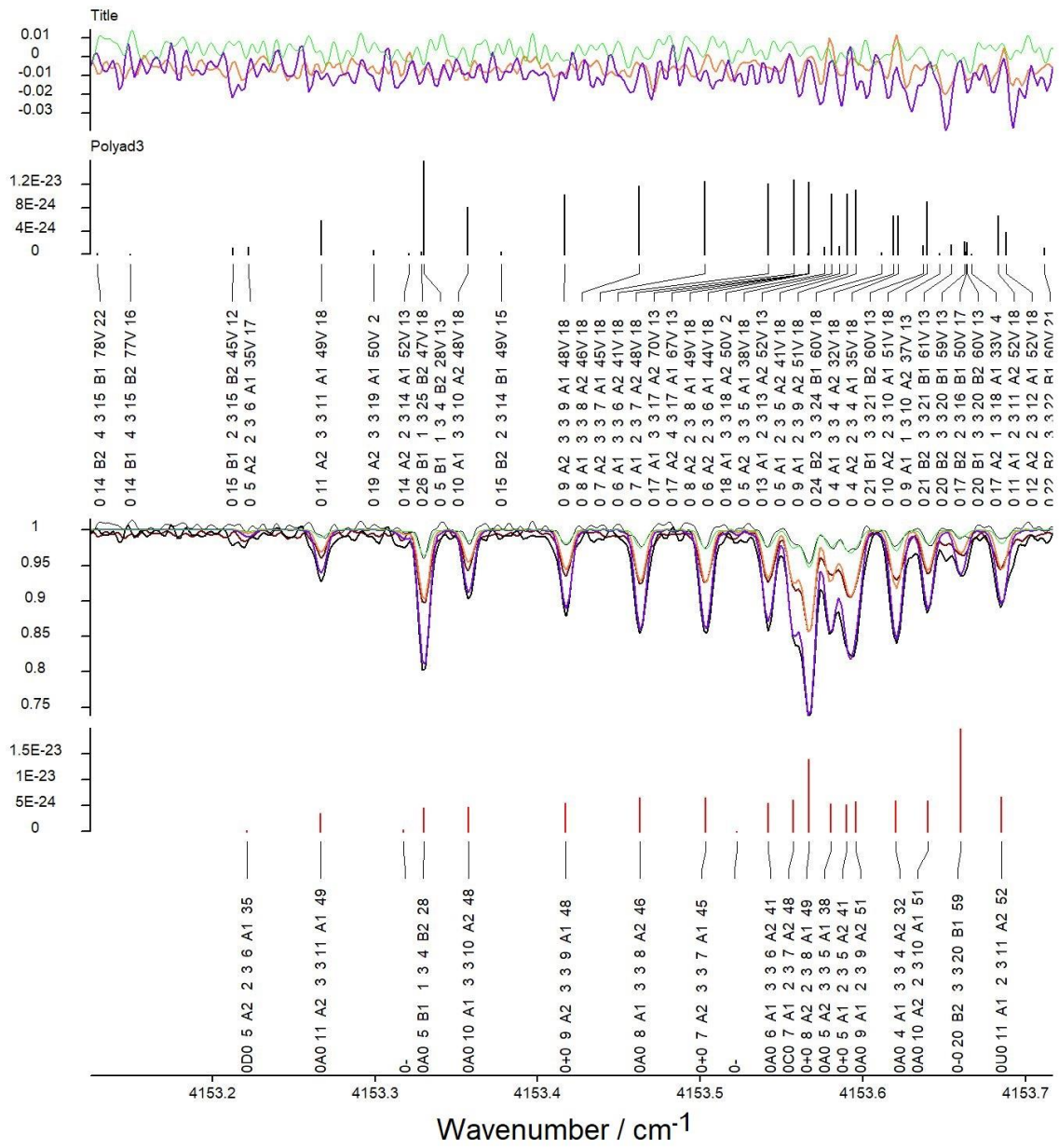


Fig. 3. The same as in Fig. 2, except for the spectral range of 4153.2-4153.7 cm⁻¹

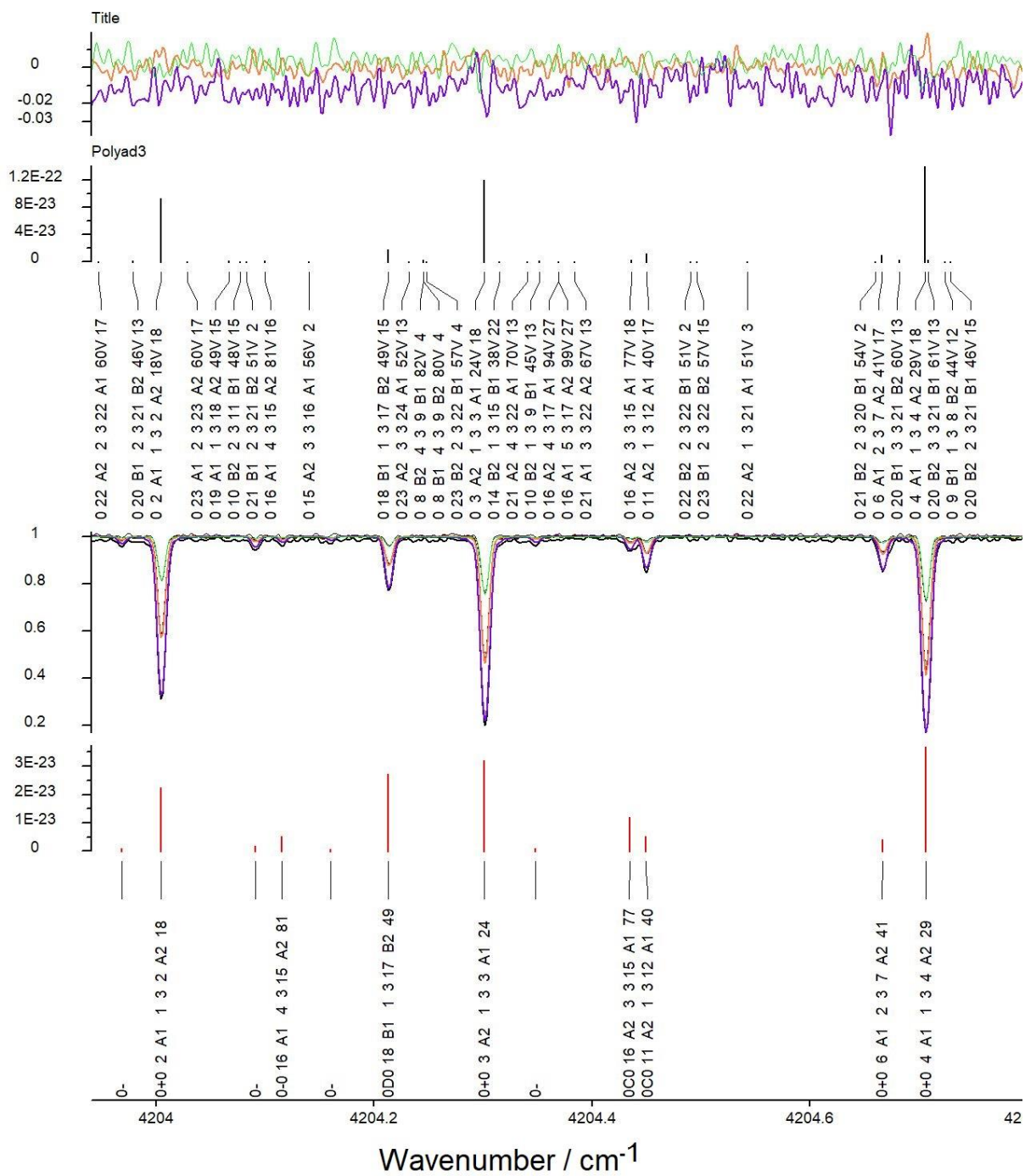


Fig. 4. The same as in Fig. 2, except for the spectral range of 4204-4204.6 cm⁻¹

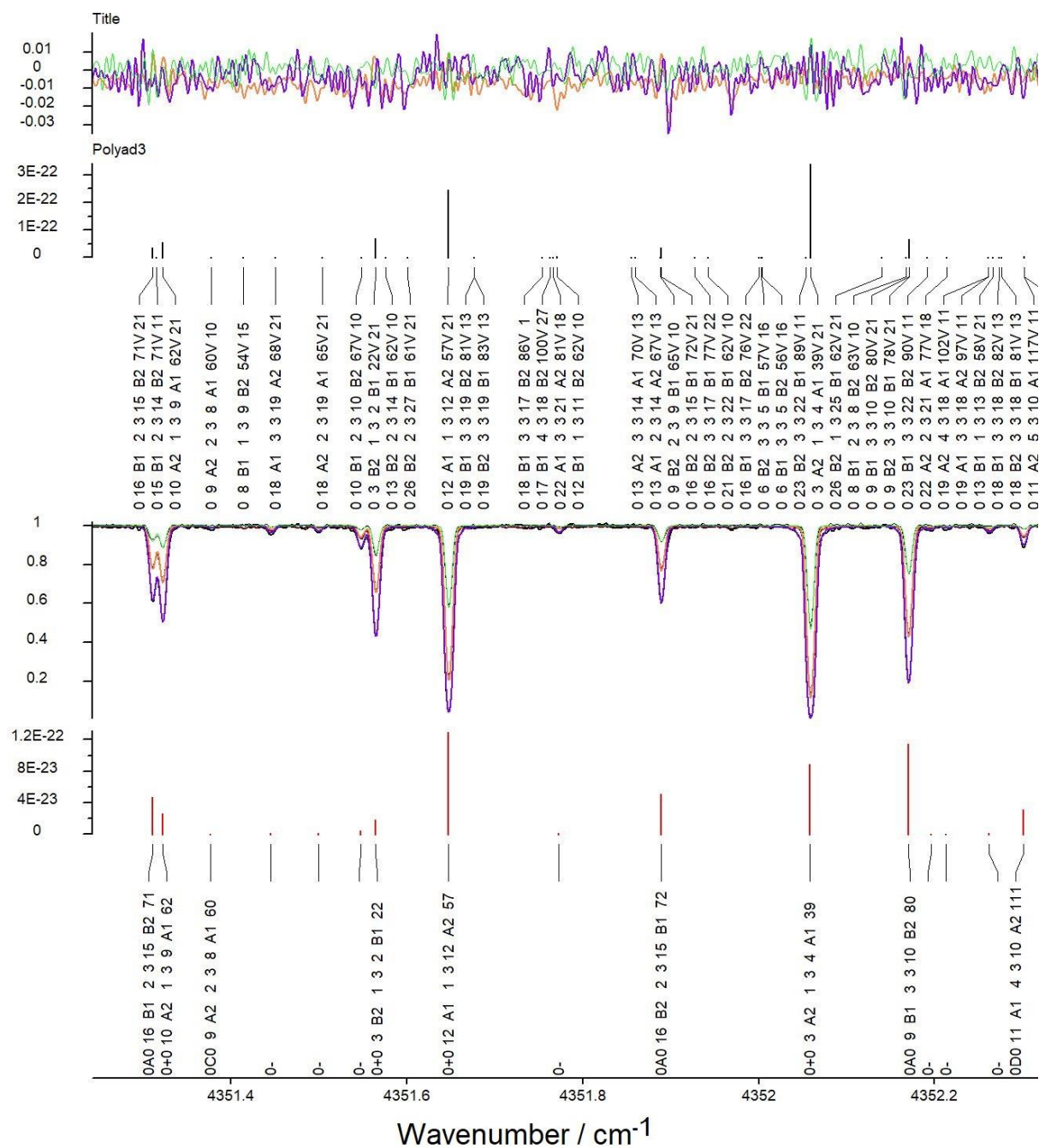


Fig. 5. The same as in Fig. 2, except for the spectral range of $4351.4\text{-}4352.2 \text{ cm}^{-1}$

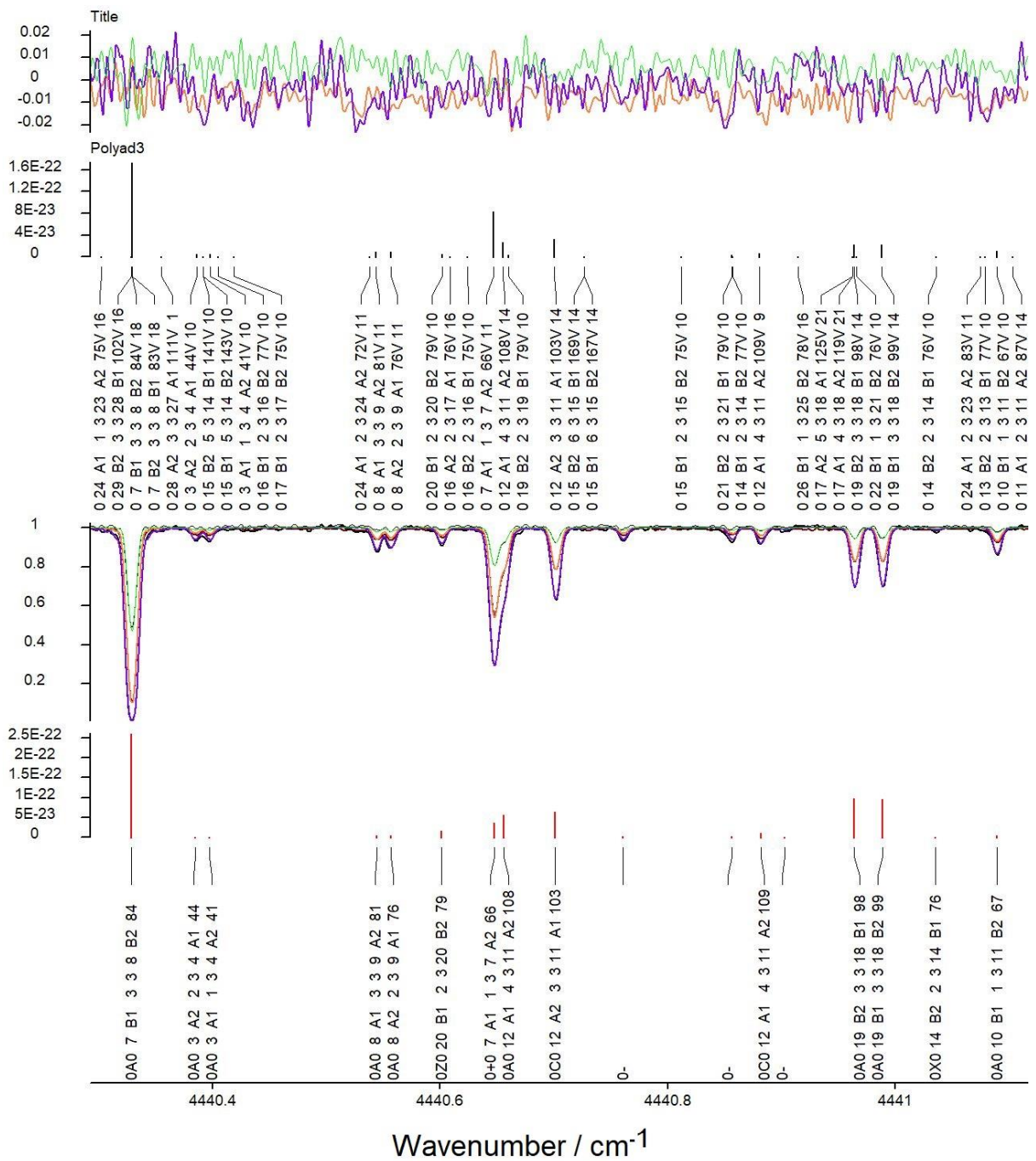


Fig. 6. The same as in Fig. 2, except for the spectral range of 4440.4-4441 cm^{-1}

Table 2. Line position statistic for H₂CO transitions corresponding to studied range

Vibrational upper state levels	Vibration Energy cm ⁻¹ This work	Positions			
		Number Fitted Transit.	RMS (10 ⁻³ cm ⁻¹)	J _{min}	J _{max}
(001002)A1	3935.513	96	1.218	1	17
(100100)B1	3941.531	406	1.045	0	21
(000110)A1	3996.519	302	1.398	1	18
(100001)B1	4021.082	843	0.733	0	21
(010200)A1	4058.358	353	1.053	0	20
(000011)A1	4082.992	268	0.732	0	19
(010101)A2	4164.719	394	0.825	1	20
(002100)B1	4165.179	456	1.266	1	21
(002001)B2	4192.383	728	0.758	0	21
(010002)A1	4247.664	338	1.010	0	20
(101000)A1	4255.457	75	1.292	3	16
(001010)B2	4335.098	980	0.854	0	24
(011100)B1	4397.746	295	1.073	4	23
	Total	5534	1.043		

Conclusion

In ref [60], vibrational energy levels were calculated from *ab initio* PES. The calculation accuracy was estimated to be no worse than 1 cm⁻¹. The empirical energy levels obtained with high accuracy coincided well with the calculated levels, but the levels obtained from low-resolution spectra or from dark states clearly go beyond the limits of the expected accuracy. Table 3 compares the new empirical levels with the calculated levels in [60]. It can be seen that the difference between the empirical and *ab initio* calculated levels does not exceed 1 cm⁻¹. Table 3 also shows a comparison with work [14]. Vibrational-rotational energy levels and lists of transitions will also be presented in the Theorets database.

Table 3. Comparison of calculated vibrational levels [60] [14] with empirical values in the range 3470 4400 cm⁻¹.

Vib. State	C		Calc	Exp-Calc	Calc [14]	Exp-Calc [14]
2v ₂	A ₁	3471.715	3472.69	-0.975	3469.39	2.33
3v ₄	B ₁	3481.494	3480.76	0.734	3478.04	3.45

$2v_4 + v_6$	B ₂	3587.022	3586.19	0.832	3581.09	5.93
$v_4 + 2v_6$	B ₁	3676.610	3676.03	0.58	3668.88	7.73
$3v_6$	B ₂	3735.970	3735.54	0.43	-	-
$v_3 + 2v_4$	A ₁	3826.074	3825.74	0.334	3822.43	3.64
$v_3 + v_4 + v_6$	A ₂	3888.412	3888.10	0.312	3883.37	5.04
$v_3 + 2v_6$	A ₁	3935.512	3935.09	0.422	3929.86	5.65
$v_1 + v_4$	B ₁	3941.530	3941.57	-0.04	3939.85	1.68
$v_4 + v_5$	A ₂	3996.519	3995.94	0.579	3994.75	1.77
$v_1 + v_6$	B ₂	4021.081	4021.18	-0.099	4017.7	3.38
$v_2 + 2v_4$	A ₁	4058.357	4058.28	0.077	4054.6	3.76
$v_5 + v_6$	A ₁	4082.992	4082.54	0.452	4078.88	4.11
$v_2 + v_4 + v_6$	A ₂	4164.719	4164.74	-0.021	4159.35	5.37
$2v_3 + v_4$	B ₁	4165.179	4165.37	-0.191	-	-
$2v_3 + v_6$	B ₂	4192.383	4192.51	-0.127	4189.62	2.76
$v_2 + 2v_6$	A ₁	4247.663	4247.79	-0.127	4241.02	6.64
$v_1 + v_3$	A ₁	4255.456	4255.86	-0.404	4253.86	1.60
$v_3 + v_5$	B ₂	4335.098	4335.05	0.048	4334.78	0.32
$v_2 + v_3 + v_4$	B ₁	4397.747	4398.14	-0.393	4394.05	3.70
RMS deviation				0.45		4.27

Experimental values are given also in Ref [61], [62], [63], [64], low precision data are given in [65].

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