MARVEL analysis of the high-resolution rovibrational spectra of $\text{H}^{16}\text{O}^{35}\text{Cl}$ Balázs Rácsai^a, Tibor Furtenbacher^b, Luciano Fusina^c, Gianfranco Di Lonardo^c, Attila G. Császár^{b,*}^a Mihály Fazekas High School, Budapest, Hungary^b Institute of Chemistry, ELTE Eötvös Loránd University and ELKH-ELTE Complex Chemical Systems Research Group, H-1518 Budapest 112, P.O. Box 32, Hungary^c Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Bologna, Italy

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ABSTRACT

The experimentally measured high-resolution rovibrational spectra of $\text{H}^{16}\text{O}^{35}\text{Cl}$, collated from 16 sources, have been analyzed using the MARVEL (Measured Active Rotational–Vibrational Energy Levels) procedure. The compilation presented, the most extensive up to now, considers a total of 21 464 transitions, allowing the derivation of 6277 empirical energy levels, extending up to $17\,161\text{ cm}^{-1}$, corresponding to 15 vibrational parent states. Experimental transitions data from three older sources, not published explicitly in the original papers, are presented for the first time; they represent about one half of all the transitions investigated.

1. Introduction

There are a number of reasons why high-resolution, usually rotationally-resolved spectra and the related nuclear dynamics of $\text{H}^{16}\text{O}^{35}\text{Cl}$, the parent isotopologue of hypochlorous acid, HOCl, have been studied in detail *via* experimental [1–35] as well as theoretical [29,36–50] means. Interest in the spectroscopy of HOCl stems from the facts that HOCl is (a) considered to be an important temporary reservoir of chlorine atoms, as well as of the OH radical, in the earth's atmosphere; (b) an important member of a catalytic cycle providing a mechanism for mid-latitude stratospheric depletion of ozone by ClO_x radicals (HOCl is believed to convert relatively stable chlorine reservoir compounds, like ClONO_2 , into more reactive ClO_x radicals via heterogeneous chemistry on polar stratospheric clouds) [51–53]; (c) prone to destruction in the atmosphere by ultraviolet (UV) irradiation, necessitating the detailed understanding of its UV absorption spectra and the related cross sections [17]; (d) ideal to study rovibrational resonance (quasibound) [54] states in the continuum [46,47]; and (e) one of the favorite molecules for the study of unimolecular dissociation reactions [24,25,27,32] and intramolecular vibrational redistribution (IVR) [22], as its simple structure and relatively well separated fundamentals, apart from a 2:1 resonance between the HOCl bend (ν_2) and the OCl stretch (ν_3) at higher energies, make the dynamical treatment at high energies less complicated. The ν_2 band of HOCl happens to lie in an atmospheric window; thus, it provides a good opportunity to detect and measure HOCl in the stratosphere. In fact, spectroscopic information related to the ν_2 band is used to determine the column abundance of HOCl over the Antarctic [55], as well as to estimate the mixing ratio of HOCl in

the Arctic stratosphere [56]. Nevertheless, detailed knowledge of other spectral regions may provide opportunities for other applications.

The significance of HOCl for atmospheric modeling is highlighted by the fact that it is molecule #21 in the canonical spectroscopic database HITRAN [57,58]. It is important to note that there were no changes introduced in HITRAN 2020 [58] compared to HITRAN 2016 [57] for HOCl, neither in the spectral range, $1\text{--}3800\text{ cm}^{-1}$, nor in the number of lines, 8877 and 7399 for $\text{H}^{16}\text{O}^{35}\text{Cl}$ and $\text{H}^{16}\text{O}^{37}\text{Cl}$ (in natural abundance the ratio of the two chlorine isotopes is approximately 3:1). High-resolution spectroscopic data about HOCl are also accessible in the GEISA database [59]. Remote sensing [15,55,56] of HOCl in the upper atmosphere requires the availability of a large amount of spectroscopic parameters, including positions, intensities, and shapes of the observable lines. The principal aim of the present study is to validate the available measured rovibrational transitions and to provide empirical energy levels for $\text{H}^{16}\text{O}^{35}\text{Cl}$, both through the use of the MARVEL (Measured Active Rotational–Vibrational Energy Levels) technique [60–63].

The dissociation energy of HOCl, through the reaction $\text{HOCl} \rightarrow \text{OH} + \text{Cl}$ and involving ground-state species, is $D_0 = 19\,290\text{ cm}^{-1}$; thus, the corresponding potential energy hypersurface (PES) [40,44,46] supports only a limited number of pure vibrational states. In fact, the number of bound vibrational states of $\text{H}^{16}\text{O}^{35}\text{Cl}$ is estimated to be around 800 [22,29,41,45]. According to the usual convention, the vibrational fundamentals of HOCl, ν_1 (at about 3609 cm^{-1}), ν_2 (at about 1239 cm^{-1}), and ν_3 (at about 724 cm^{-1}), correspond to OH stretch, HOCl bend, and OCl stretch, respectively. HOCl is only a very slightly

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asymmetric rotor, with a Ray-asymmetry parameter [64] of $\kappa = -0.998$. Thus, its spectra have the appearance of those of prolate symmetric-top molecules characterized by a -type transitions.

The first study of the infrared (IR) spectrum of HOCl was performed by Hedberg and Badger [1]. A number of studies followed on ν_1 [2,5,9,10,12,20], ν_2 [8–10,12,14,20], and ν_3 [9,10,12,14,20]. The $2\nu_2$ band was first observed by Deeley and Mills [12], while $2\nu_1$ and $3\nu_1$, as well as the combination bands $\nu_1 + \nu_3$, $\nu_1 + \nu_2$, $\nu_1 + 2\nu_2$ were all assigned by Fusina and co-workers [18,19]. In addition, 49 highly rotationally excited transitions were measured for the $2\nu_3$ band [33]. No experimental data have been reported for the $\nu_2 + \nu_3$ combination band. As to the higher end of the spectrum, Charvát et al. [65] investigated the $3\nu_1 + \nu_2$ combination band, while Troe et al. [22] made measurements on the $3\nu_1 + 2\nu_2$ band. Even closer to the dissociation limit, the $n\nu_1$ bands, with $n = 4 - 7$, and the $4\nu_1 + \nu_2$ band have been studied [24–27,30,32,34]. Unfortunately, these papers do not report assigned rovibrational transitions; thus, they could not be considered for the present MARVEL analysis of the experimental rovibrational data of $\text{H}^{16}\text{O}^{35}\text{Cl}$. Overall, even after these considerable number of studies, only few of the about 800 possible bound vibrational states of $\text{H}^{16}\text{O}^{35}\text{Cl}$ have been probed experimentally.

The considerable number of theoretical studies [29,36–46,48–50] performed on HOCl yielded a detailed understanding of its rovibrational spectra. Since we do not use this information in a direct way, only a few highlights are given here. In 1979, Murrell et al. [38] obtained a PES of HOCl from spectroscopic data. There are more recent PESs generated for HOCl in the literature [43,44,46,48]. Also in 1979, Botschwina [36] made a good estimation of the vibrational spectrum. By now, “nearly-exact” variational nuclear-motion computations provided information about a large number of rovibrational bound and resonance states of HOCl [29,46,47,49]. Nevertheless, further computations would be needed to produce dependable theoretical line lists for at least the two main HOCl isotopologues, $\text{H}^{16}\text{O}^{35}\text{Cl}$ and $\text{H}^{16}\text{O}^{37}\text{Cl}$. These studies would be helped significantly by the availability of accurate empirical rovibrational energies of $\text{H}^{16}\text{O}^{35}\text{Cl}$, obtained during this study, allowing an advantageous mixing of the experimental and theoretical information, as done, for example, in Ref. [66].

2. Data sources

We made a concerted effort to collate *all* measured and assigned rovibrational transitions of $\text{H}^{16}\text{O}^{35}\text{Cl}$ from the literature. As a result, the number of transitions included in the present study is 21 464, of which 21 317 have been validated via a detailed MARVEL-based analysis. The analysis is based on 16 sources. The tags of the literature sources, see Table 1, are given according to the convention established in Ref. [67].

The microwave (MW) spectrum of HOCl was first reported in 69LiLi-mi [4]. They measured the hyperfine structure of the $1_{01} - 0_{00}$ transitions for altogether four isotopologues and subsequently derived a very approximate molecular structure for HOCl. Even after a lot more measurements and improved rotational constants, the approximate molecular structure for HOCl was determined, in 67Ashby [2], as $r_{\text{OH}} = 0.97(2)$ Å, $r_{\text{OCl}} = 1.689(6)$ Å, and $\angle_{\text{HOCl}} = 104(5)^\circ$, suffering from quite significant uncertainties. Later, 71MiScCa [7] reported millimeter-wave a -type transitions for five isotopologues, the 17 transitions measured for $\text{H}^{16}\text{O}^{35}\text{Cl}$ have been used in the present MARVEL analysis. In 1975, 75SuGu [68] studied the MW Zeeman spectrum of HOCl, but they did not report pure rotational transitions; therefore, this source could not be used in our analysis. In 1984, Gillis Singbeil and co-workers [11] reported the largest set of MW transitions. This source contains both hyperfine and pure rotational transitions. All 73 measured rotational transitions have been used in the present MARVEL study (note that in this study we are not treating hyperfine-resolved lines). Interestingly, after 1984, no MW spectra were published for $\text{H}^{16}\text{O}^{35}\text{Cl}$. In 1995, a

Table 1

Sources of experimental rovibrational transitions utilized during the MARVEL analysis of the present study on $\text{H}^{16}\text{O}^{35}\text{Cl}$ ^a.

Source tag	Range/ cm^{-1}	A/V	Avg. unc.
84GiAnDaGe [11]	0.27–20.65	73/73	3.734e–06
98FIBiWaOr [28]	1.08–392.12	4094/4094	2.002e–04
71MiScCa [7]	1.98–6.01	17/17	1.395e–06
90CaLoFuTr [16]	30.47–207.52	1262/1262	1.329e–03
95BeNaFuMo [21]	30.47–178.11	41/41	2.925e–06
86LaOl [14]	679.02–1295.12	627/627	4.169e–04
00AuKlFlPa [33]	1178.67–1314.49	2108/2108	1.001e–03
80SaOl [10]	1203.02–1276.98	240/240	2.384e–03
97ShNeZa [69]	1247.32–1252.84	2/2	6.258e–04
96CaLoFu [23]	2337.12–2608.99	1010/1010	6.020e–04
96CaLoFu.S2 [23]	2260.99–2757.07	1032/1032	1.239e–03
79WeSaLa [9]	3252.51–3875.88	651/651	2.605e–03
94AzCaCrLo [19]	4201.15–10 428.49	2022/2022	2.223e–03
94AzCaCrLo.S2 [19]	4112.95–10 466.65	3237/3237	4.338e–03
93CaLoEsFu [18]	6906.60–7167.06	800/800	9.674e–04
93CaLoEsFu.S2 [18]	6718.51–7232.29	1254/1254	1.709e–03
97ChDeHaAb [65]	11 410.76–11 511.11	424/424	4.402e–03
96AbHaKaTr [22]	12 551.29–12 644.37	629/629	5.502e–03
97HaChAbKo [26]	13 227.10–16 321.16	1941/1794	4.513e–03

^a Within a given source, transitions with significantly different uncertainties are grouped into segments [63] and treated separately during the MARVEL analysis. The first segment, with the lowest uncertainty, does not have a special source tag, while the tag of the second segment of a given source is concatenated with the string “S2”. A and V denote the number of lines available and those validated in a given source, respectively. Avg. unc. = average uncertainty, in cm^{-1} .

pure rotational spectrum was published in the submillimeter-wave region; Bellini and co-workers [21] reported several high-lying rotational energy levels of the vibrational ground state.

The first report about the IR spectrum of $\text{H}^{16}\text{O}^{35}\text{Cl}$ is due to Hedberg and Badger [1], employing a small-prism instrument. The accuracy of this study is not sufficient for our present purposes. Later, Ashby [2,5] provided results of a study with much higher resolution; in fact, he obtained the earliest value of the A_0 rotational constant of $\text{H}^{16}\text{O}^{35}\text{Cl}$. The accuracy of this study is still not sufficient for our present purposes; therefore, we were forced to skip these results from the present analysis, as well. A high-resolution infrared spectrum of the HOCl molecule was reported in 79WeSaLa [9], containing more than 650 transitions of the ν_1 band. Somewhat later, 80SaOl [10], 85DeMi [12], and 86LaOl [14] analyzed the ν_2 and ν_3 bands of the HOCl molecule, with a spectral resolution of a few 0.01 cm^{-1} . More than 2000 transitions were assigned on the $2\nu_1$ band by 93CaLoEsFu [18]. Two different measurement accuracies characterize the lines reported in Refs. [18,19,23]; these transitions are included in the MARVEL analysis as two separate segments. The tag of the second segment contains the string “S2” at the end of the tag. More than 4000 lines were published by 98FIBiWaOr [28] in the far-infrared (FIR) region. 90CaLoFuTr [16] also measured the FIR spectrum of HOCl, reporting very high-lying (up to $J = 54$) ground-state rotational energy levels.

Due to interest in IVR dynamics, using HOCl as a suitable test molecule, near-infrared spectra of $\text{H}^{16}\text{O}^{35}\text{Cl}$ have been recorded around $12\,000\text{--}13\,000 \text{ cm}^{-1}$ [22]. The $3\nu_1 + 2\nu_2$ and $3\nu_1 + \nu_2$ bands were analyzed by 96AbHaKaTr [22] and 97ChDeHaAb [65], respectively. 97HaChAbKo [26] published almost 2000 measured transitions for the $4\nu_1$ and $5\nu_1$ OH-stretch overtones as well as the weak $4\nu_1 + \nu_2$ combination band.

The full list of data sources used in the MARVEL analysis, along with some of their characteristics, is given in Table 1. As can be seen there, we found only one serious problem: the rovibrational lines of the $4\nu_1 + \nu_2$ band, from 97HaChAbKo [26], were in conflict with themselves; therefore, we had to skip this band from our analysis.

The uncertainties of the lines, employed during the MARVEL analysis, corresponding to each source were taken preferably from the original papers. Nevertheless, occasionally they had to be increased, first for

internal self-consistency of the data within a single data source and then for self-consistency within the complete MARVEL compilation of data.

Several older literature sources of transitions data do not contain the measured transitions in an explicit form. This means that these data are basically lost to the community [70]. It is in relation to this statement that we note that the present analysis makes data reported first in Refs. [18,19,23] available to the general public for the first time; these data form part of the MARVEL input file and they are reported in the Supplementary Information. Our MARVEL analysis validated all of the measured transitions of these sources. These three sources contain about half of all the transitions of $\text{H}^{16}\text{O}^{35}\text{Cl}$ treated during the present study.

3. MARVEL analysis

3.1. MARVEL

The MARVEL procedure [60–63] utilizes the theory of spectroscopic networks (SN) [71,72]. Recently, the algorithms employed by MARVEL have been systematically improved, the relationship of SNs to formal network theory considered [61,62,71,73], and the underlying methodology reviewed [63,72,74,75]. Therefore, it is sufficient to provide only a brief discussion about the most important features of MARVEL here.

The MARVEL protocol [60,61,63] yields what are called empirical energies, all with well-defined provenance and uncertainties, based on the available experimental transitions information. Thus, a MARVEL analysis starts with the construction of a SN, using the dataset of measured and assigned transitions collated from the literature. Using MARVEL requires that each transition treated has a *unique* (though not necessarily physically relevant) assignment, determining the transition's place within the SN, and an uncertainty. MARVEL then inverts the transitions information (wavenumbers, assignments, and uncertainties), yielding empirical energy levels with well-defined uncertainties, depending on the uncertainties of the transitions, within each component of the SN. Validation of the experimental information utilizes several elements of network theory.

MARVEL compilations of experimental high-resolution rovibronic transitions data currently exist for a considerable number of diatomic molecules (AlH [76], BeH [77], $^{12}\text{C}_2$ [66,78], ^{14}NH [79], $^{16}\text{O}_2$ [80], $^{48}\text{Ti}^{16}\text{O}$ [81], and $^{90}\text{Zr}^{16}\text{O}$ [82]), while rovibrational transitions data have been collated for triatomic molecules (H_2^{32}S [83] and isotopologues of H_2O [67,84–89], H_3^+ [90,91], and SO_2 [92]), and for larger species ($^{12}\text{C}_2\text{H}_2$ [93], $^{14}\text{NH}_3$ [94,95], $\text{H}_2^{12}\text{C}^{16}\text{O}$ [96], and $\text{H}_2^{12}\text{C}^{12}\text{C}^{16}\text{O}$ [97]), as well. Thus, there are ample studies demonstrating the utility of the MARVEL approach for the spectroscopic community and beyond.

3.2. Quantum numbers

In its ground electronic state, HOCl has an equilibrium structure with C_s point-group symmetry. $\text{H}^{16}\text{O}^{35}\text{Cl}$ is a very slightly asymmetric rotor, with $\kappa = -0.998$.

To label the vibrational part of the rovibrational states of $\text{H}^{16}\text{O}^{35}\text{Cl}$ we employ three quantum numbers, v_1 , v_2 , and v_3 , referring to the O–H stretch, HOCl bend, and O–Cl stretch modes, respectively [98]. For labeling the rotational states we use the standard asymmetric-top quantum numbers J , K_a , and K_c [99]. Thus, the rotation–vibration levels of $\text{H}^{16}\text{O}^{35}\text{Cl}$ are identified in this study by six quantum numbers: $(v_1 v_2 v_3) [J K_a K_c]$. In the literature, some states of $\text{H}^{16}\text{O}^{35}\text{Cl}$ have been labeled simply by J and $K (= K_a)$; these are cases when the value of K_c is unimportant or has not been resolved.

3.3. Spectroscopic network of $\text{H}^{16}\text{O}^{35}\text{Cl}$

Due to the fact that HOCl contains three different nuclei, the experimental spectroscopic network of $\text{H}^{16}\text{O}^{35}\text{Cl}$ built from the assigned transitions has a single principal component with 6277 energy levels, incorporating 21 464 transitions. There are only two other components, both of them contain only two energy levels; these minor components are not considered further in this paper.

Table 2

MARVEL-based vibrational band origins (VBO) of $\text{H}^{16}\text{O}^{35}\text{Cl}$ and their literature counterparts, the latter obtained from Ref. [26], except for $2\nu_2$, for which Ref. [23] is used^a.

Band	VBO(MARVEL)	Previous estimates ^b	N_{RL}	J_{max}	$K_{a,\text{max}}$
ν_0	0.0(0)	0.0	987	61	10
ν_3	724.358 15(57)	724.358 07(4)	587	44	8
ν_2	1238.624 73(40)	1238.624 60(4)	808	55	9
$2\nu_2$	2461.223 99(51)	2461.222 468(50)	454	44	6
ν_1	3609.479 7(30)	3609.482 48(4)	334	44	8
$\nu_1 + \nu_3$	4331.908 98(79)	4331.908 531(88)	346	35	5
$\nu_1 + \nu_2$	–	4820.432 330(110)	358	38	5
$\nu_1 + 2\nu_2$	6013.836 1(34)	6013.830 78(51)	304	38	4
$2\nu_1$	–	7049.813 190(69)	451	45	6
$3\nu_1$	10 322.289 5(30)	10 322.293 29(25)	454	41	7
$3\nu_1 + \nu_2$	11 478.001 4(20)	–	337	40	6
$3\nu_1 + 2\nu_2$	12 612.516 4(50)	12 612.551 9(6)	344	40	5
$4\nu_1$	13 427.397 4(20)	13 427.393 6(4)	418	40	6
$5\nu_1$	–	16 374(2)	73	28	5

^aAll VBO values are given in cm^{-1} . The uncertainties of the last VBO digits are given in parentheses. The number of rotational levels, N_{RL} , and the maximum J and K_a values within a given vibrational band are given in the last three columns of this table.

^bThe previous (best) estimates are based on effective Hamiltonian calculation.

4. Results and discussion

4.1. MARVEL energy levels

In total, we obtained 6277 empirical rovibrational energies for $\text{H}^{16}\text{O}^{35}\text{Cl}$, they are provided in the Supplementary Material. The energy levels span up to $J = 61$ and energies up to 17160.81 cm^{-1} . It is interesting that the maximum value of K_a is 10, i.e., there are no measured transitions in the literature which involve a state with a K_a value larger than 10 (see Table 2).

The uncertainties of the empirical rovibrational energy levels derived clearly show the lack of a large number of MW measurements. There are only seven energy levels whose uncertainties are less than 10^{-5} cm^{-1} ; these energy levels are members of the $[J 0 J]$ series up to $J = 6$. The uncertainties of all the other empirical energy levels are larger than 10^{-4} cm^{-1} .

Table 2 presents the vibrational band origins (VBO) and a summary of the number of empirical rovibrational energy levels determined for each vibrational parent state. Table 2 also gives term values of previous studies, all of which are based on effective Hamiltonian calculations.

The vibrational fundamentals of $\text{H}^{16}\text{O}^{35}\text{Cl}$ have already been estimated in 1951 in Ref. [1]. These estimates, 3626, 1242, and 739 cm^{-1} for ν_1 , ν_2 , and ν_3 , respectively, are off by 5 – 20 cm^{-1} , and have been evolving over time. In 2003, Jacox presented the values of 3609.48, 1238.62, and 724.36 cm^{-1} , respectively [100], all correct within the number of digits given. The evolution of these values can be traced in the MARVEL input file. The present best estimates of the ν_1 , ν_2 , and ν_3 fundamentals of $\text{H}^{16}\text{O}^{35}\text{Cl}$ are 3609.479 7(30), 1238.624 73(40), and $724.358 15(57) \text{ cm}^{-1}$, respectively.

We are not aware of any high-accuracy first-principles rovibrational energies of the empirical energy levels derived during this study. Therefore, we had to rely on spectroscopic constants available in the literature to confirm the correctness of the empirical (MARVEL) rovibrational energy levels. We compared our empirical energy levels to the effective Hamiltonian results of 98FlBiWaOr [28]. Fig. 1 shows the differences between the MARVEL levels and the energy values calculated by the parameters of Ref. [28] up to $J = 20$ and $K_a = 7$. As shown in Fig. 1, for the energy levels of the ν_0 , ν_2 , and ν_3 bands the agreement is nearly perfect, but for the ν_1 band the average difference is slightly larger (about 0.001 cm^{-1}). These comparisons support the correctness of the related empirical energies derived during this study.

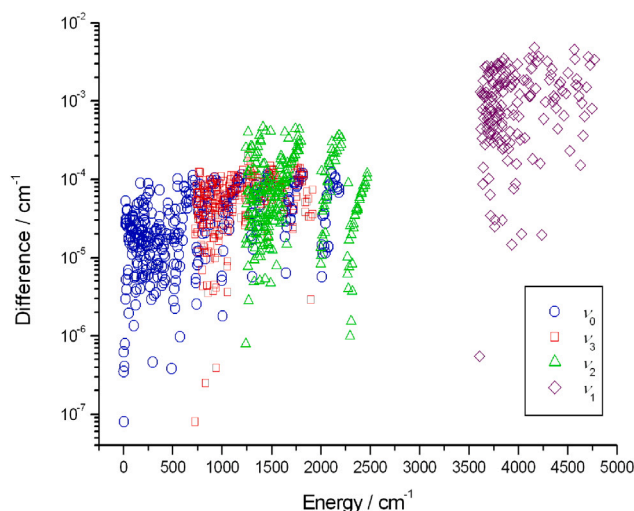


Fig. 1. Differences between the empirical (MARVEL) energy levels of this study and the earlier literature results of 98FIBiWaOr [28], up to $J = 20$ and $K_a = 7$, on the vibrational ground state (ν_0) and the vibrational fundamentals (ν_1 , ν_2 , and ν_3) of $\text{H}^{16}\text{O}^{35}\text{Cl}$.

4.2. Comparison to the HITRAN and GEISA databases

The canonical spectroscopic databases HITRAN [57,58] and GEISA [59] contain a considerable number of rovibrational transitions for the $\text{H}^{16}\text{O}^{35}\text{Cl}$ molecule. Therefore, it is worth comparing the three datasets and check the completeness of the MARVEL dataset.

For $\text{H}^{16}\text{O}^{35}\text{Cl}$, HITRAN 2016 [57] contains 8877 rovibrational transitions, going up to 3799.25 cm^{-1} . The HITRAN2016 database was constructed using the transitions and spectroscopic parameters reported in 84GiAnDaGe [11], 98FIBiWaOr [28], and 00AuKIFiPa [33]. Our collection of experimental data has 21 464 validated transitions, a considerably larger number. Our treatment also goes to much higher wavenumber values, up to 17161 cm^{-1} . Furthermore, a lot of the HITRAN 2016 line positions are based on effective Hamiltonian calculations, while the present dataset contains measured data. After checking the correctness of the HITRAN 2016 energy-level entries, it was found that altogether 611 lines contain invalid rotational labels. In each case the value of K_c is set to zero. The problematic lines are provided in the Supplementary Material.

Since HITRAN 2016 utilizes effective Hamiltonian results, it is not surprising that there are about 2300 lines in the $3400\text{--}3800\text{ cm}^{-1}$ region that are not available in our experimental database. Nevertheless, our MARVEL database contains 227 extra lines which are not part of the HITRAN 2016 dataset. There are only 524 lines which contain rovibrational energy levels that cannot be found in our MARVEL energy set. All of these lines belong to the ν_1 band. It is important to emphasize that all other HITRAN 2016 lines can be reproduced by the empirical energy levels of this study within 0.01 cm^{-1} .

For $\text{H}^{16}\text{O}^{35}\text{Cl}$, the GEISA database contains 9293 rovibrational transitions, extending up to 3799.25 cm^{-1} . These lines were seemingly constructed using the spectroscopic parameters of 98FIBiWaOr [28] and 00AuKIFiPa [33] and with the help of a private communication with J.-M. Flaud. Unfortunately, there are 1182 lines in the GEISA-2020 database with invalid rovibrational labels. Similar to HITRAN, in most of these cases the value of K_c is set to zero, but in a few cases these labels are simply incorrect. There are 408 lines where the discrepancy between the GEISA and MARVEL lines are larger than 0.01 cm^{-1} . In 49 cases the GEISA database uses the ν_2 vibrational label instead of $2\nu_3$, as mentioned in 00AuKIFiPa [33]. In the rest of the cases J is larger than 30; thus, in these cases the effective Hamiltonian used to construct the GEISA database might have resulted in incorrect line positions.

5. Conclusions

During this study, all available experimentally measured and assigned rovibrational transitions of the $\text{H}^{16}\text{O}^{35}\text{Cl}$ molecule have been collated into a single database. Using 21 464 experimental transitions from 16 sources, of which 21 317 could be validated, and the MARVEL protocol, we determined 6277 empirical rovibrational energy levels on the ground electronic state of $\text{H}^{16}\text{O}^{35}\text{Cl}$. Although the detailed knowledge of the spectroscopic properties of HOCl is important for several atmospheric reactions and processes, the present investigation revealed a few deficiencies in the high-resolution spectroscopy of $\text{H}^{16}\text{O}^{35}\text{Cl}$: (1) There are only relatively few experimentally measured MW transitions in which the value of K_a changes; therefore, these highly accurate lines do not create a connected component. This is why only seven MARVEL rovibrational energy levels have uncertainties less than 10^{-5} cm^{-1} , an accuracy typical of MW measurements. Several new measurements would be needed to connect these subcomponents, these experiments could be designed using the spectroscopic network of $\text{H}^{16}\text{O}^{35}\text{Cl}$ established in this study. (2) The maximum value of K_a in the database of experimentally measured transitions is 10. It would be desirable to extend the experimental studies for a connected set of $K_a > 10$ transitions. (3) It would be useful to experimentally observe and analyze the $2\nu_3$ and $\nu_2 + \nu_3$ bands, allowing the accurate estimation of the x_{33} and x_{23} anharmonic parameters (at present only known from theory [42]), completing the set of experimental vibrational anharmonicity constants of the molecule (see Table V of Ref. [19]).

We used the canonical spectroscopic databases and information systems HITRAN [57,58] and GEISA [59] to check the completeness of our experimental dataset. Detailed comparison of the three datasets revealed a number of significant differences. Most importantly, the present dataset is considerably more complete than the other two; for example, our MARVEL database contains 227 extra lines that are not present in the HITRAN dataset in the region covered there.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.jms.2021.111561>.

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