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## Direct fit of experimental ro-vibrational intensities to the dipole moment function: Application to HCl

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### ABSTRACT

A dipole moment function (DMF) for hydrogen chloride (HCl) has been obtained using a direct fit approach that fits the best available and appropriately weighted experimental data for individual ro-vibrational transitions. Combining wavefunctions derived from the Rydberg–Klein–Rees (RKR) numerical method and a semi-empirical DMF, line intensities were calculated numerically for bands with  $\Delta\nu=0, 1, 2, 3, 4, 5, 6, 7$  up to  $\nu'=7$ . The results have demonstrated the effectiveness of inclusion of rotational dipole moment matrix elements and appropriate weighting of the experimental data in the DMF fitting. The new method is shown to be superior to the common method of fitting only the rotationless dipole moment elements, while at the same time being simple to implement.

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### 1. Introduction

The knowledge of accurate spectroscopic line parameters of hydrogen chloride (HCl) is important in modeling and interpreting spectra of stellar [1] and planetary [2] atmospheres. It is also required for the remote sensing of the Earth atmosphere [3,4], laser physics [5,6] and precision measurements. Due to their importance, spectral parameters of HCl have been included in the HITRAN spectroscopic database [7] for three decades [8]. In the most recent HITRAN compilation [7] (with the exception of the pure rotational band) the line positions were calculated using the potential-energy surface of Coxon and Hajigeorgiou [9], while the intensities were based on the dipole moment function (DMF) of Ogilvie et al. [10], slightly modified to incorporate high-accuracy measurements of the fundamental band by Pine et al. [11].

We have recently embarked on the task of updating and extending the existing HITRAN data for all hydrogen

halides by improving existing line parameters and including more lines, bands and isotopologues [12]. During the evaluation of the existing intensity data for HCl, we have found significant discrepancies between most commonly used semi-empirical dipole moment functions [10,13–17]. It is unfortunate that almost none of these DMFs has been used for intensity calculations that can be compared with experimental values. In the evaluation process, it was found that the use of the dipole moment function derived by Kiriya et al. [17] leads to severe discrepancies in line intensities (up to 40% even for low vibrational levels) when compared with the best available experimental data. Moreover, being considered as the most recent and extensive semi-empirical work, Ref. [17] was used to construct a piecewise dipole moment function at near-equilibrium internuclear distances by Buldakov and Cherepanov [18]. It was also used as an “experimental” function in order to evaluate recent theoretical calculations by Harrison [19] and in the calculation of the Einstein *A*-coefficients for vibrational transitions in the HCl laser [20].

In 1955, Herman and Wallis derived a methodology to describe the influence of the vibration–rotation interaction on line intensities of ro-vibrational bands of diatomic molecules [21]. Subsequently, their approach was modified

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and widely used as a standard method of determining the rotationless dipole moment matrix element for the ro-vibrational bands by fitting the existing experimental data. These rotationless dipole moment matrix elements are employed in a second step to determine the power series (or Padé approximants) coefficients of the electronic dipole moment function [10,13,14]. However this method cannot be applied to a single line-intensity measurement since Herman–Wallis fitting is basically a polynomial fit of measurements of many lines within one ro-vibrational band.

There have been several new line-intensity measurements of HCl. Although these measurements are quite precise, they often only contain information for one or two lines of an entire vibrational band [22,23]. In order to utilize the individual high-quality measurements for intensity calculations, a direct fit approach was developed in this work. Furthermore, because the intensity measurements in the literature are often inconsistent, careful selection and appropriate weighting of the data were carried out. Ultimately, a new DMF for HCl was derived, fitted to the best available (and appropriately weighted) experimental data using this direct fit approach. The ro-vibrational line intensities derived from our function were compared with the ones based on previously reported DMF's, HITRAN, and experimental data.

## 2. Methodology and previous results

Traditionally the DMF of a diatomic molecule as a function of the internuclear distance,  $r$ , is given by the power series

$$M(r) = \sum_i M_i x^i, \quad (1)$$

where  $x = (r - r_e)/r_e$ ,  $r_e$  is the equilibrium separation and  $i = 0, 1, 2, \dots$ . Some of the previous works (Refs. [10,16] for instance) employed the accepted approach developed by Tipping and Herman [24] of using only pure vibrational matrix elements to determine the DMF. In order to obtain pure vibrational matrix elements, one can take available measurements and fit them separately for every band (in the case of HCl the measured bands used in this work have  $v = 0$  as a lower state) to the Herman–Wallis expression

$$|\langle vJ' | M(x) | 0J'' \rangle|^2 = |R_{v0}(0)|^2 (1 + C_v m + D_v m^2 + \dots), \quad (2)$$

where  $R_{v0}(0)$  is a rotationless part,  $C_v$  and  $D_v$  are the Herman–Wallis coefficients, with  $m = -J$  for the P-branch and  $J+1$  for the R-branch. In order to derive the  $M_i$

coefficients from Eq. (1), these obtained rotationless matrix elements  $R_{v0}(0)$  are then fit to

$$R_{v0}(0) = \sum_i M_i \langle v | x^i | 0 \rangle, \quad (3)$$

where the expectation values  $\langle v | x^i | 0 \rangle$  can be determined from the potential energy function. In the case of the HCl molecule, bands with  $v'' = 0$  and  $v' = 0-7$  are available in the literature, and in Eq. (3)  $i$  is usually taken to run from 0 to 7. The double and single primes correspond to lower and upper state, respectively.

In 2001, Kiriyaama et al. [17] had suggested that inclusion of rotational components into the fit can allow for a better determination of the  $M_i$  coefficients through fitting to a larger number of points

$$\langle vJ' | M(x) | 0J'' \rangle = \sum_{i=1}^n M_i \langle vJ' | x^i | 0J'' \rangle. \quad (4)$$

They had chosen experimental values from Pine et al. [11] for the fundamental band, Toth et al. [13] for the first overtone, Ogilvie and Lee [16] for the second overtone, and Zughul [25] for bands 4-0 through 7-0. These experimental values were fitted (in Herman–Wallis-type manner) to Eq. (5) (reproduced exactly from Eq. (3.6) in the Ph.D. thesis [26]) with the order of the polynomial being determined using the Gauss criterion [17,26]

$$\langle vJ' | M(x) | 0J'' \rangle = \sum_{i=1}^n c_i m^i. \quad (5)$$

Note that Eq. (5) is different from Eq. (2), where squares of transition dipole moments are fitted rather than the actual values. Although this probably does not have a dramatic impact, it is more physically correct to follow the traditional approach of fitting the squares, i.e., it is more correct to use Eq. (2).

The polynomials were then used to calculate ro-vibrational matrix elements, from which the  $M_i$  coefficients were determined using Eq. (4). The  $M_i$  coefficients determined in Ref. [17] are given in Table 1. Unfortunately, if one uses these coefficients to calculate ro-vibrational transition dipole moments, the results drastically differ from experimental values including those that were used as input in Ref. [17]. Moreover, if one compares the rotationless matrix elements from Ref. [17] with those determined in the original experimental works [11,13,16,27] one can notice significant differences even in these parameters, especially in the fundamental and

**Table 1**

Dipole moment function coefficients of HCl in units of Debye. The number listed in parentheses is the standard deviation in the last digits of a given value.

	Present study	Ogilvie and Lee [16]	Kiriyaama et al. [17]
$M_0$	1.093164(86)	1.093004(75)	1.095056(1)
$M_1$	1.23679(135)	1.23614(44)	1.076259(152)
$M_2$	0.01518(375)	0.02063(530)	-0.001429(155)
$M_3$	-1.5377(96)	-1.5318(131)	-1.252768(94)
$M_4$	-0.8729(342)	-0.9188(264)	-0.383620(52)
$M_5$	-0.4066(639)	-0.3519(425)	0.104152(100)
$M_6$	-0.7531(3011)	-0.4367(725)	-0.223482(1828)
$M_7$	1.9268(8062)	0.3513(2068)	2.024332(4263)

first overtone bands. The source of the discrepancy becomes obvious if one takes the ratios of the squares of the Kiriyaama et al. [17] rotationless matrix elements to the ones determined in the original work of Pine et al. [11] and Toth et al. [13]. Both ratios are very close to 0.76, a value matching the isotopic abundance of  $H^{35}Cl$  (0.757587), which mistakenly was not accounted for in the Kiriyaama et al. [17] analysis of the intensities directly measured in Refs. [11,13]. In Refs. [16,27] the reported experimental intensities are at 100% abundance (i.e. the actual experimental intensities were already divided by natural abundance), and therefore for the second through sixth overtones there is no error made by Kiriyaama et al. [17].

In order to derive the new DMF, we identified the best available experimental results for each band and fitted them with proper weights. In general we used the Pine et al. [11] results for the fundamental band, Toth et al. [13] for the 2-0 band, Ogilvie and Lee [16] for the second overtone, and Gelfand et al. [27] for bands 4-0 through 7-0. We also added several individual ro-vibrational transition dipole moments that were measured with lower uncertainty (for instance the  $R(3)$  line in the first overtone measured by Ortwein et al. [23]). The rotationless value in the pure rotational band was taken as 1.10857 according to the recommendation of Ogilvie and Tipping [28]. We then used an overdetermined system of linear equations (Eq. (4)), that were solved using a weighted least squares method [29].

### 3. Details of the calculations and the results

To begin with, a potential energy function for  $H^{35}Cl$  was constructed using the purely numerical RKR method [30] with the Dunham coefficients from Parekunnel et al. [31]. This RKR potential was then employed to calculate the transition wavenumbers, lower-state energies and the expectation values  $\langle v'J' | x^i | 0J'' \rangle$  using Le Roy's LEVEL program [32]. Then the dipole moment matrix elements were evaluated from the measured line intensities. A sequence of signs of the dipole moment matrix elements (+ - + - - + -) was adopted as in the previous studies [14,16]. Table 2 lists the dipole moment matrix elements derived in this study from the experimental intensities and their experimental uncertainties. A grand fit of all listed dipole moment matrix elements to the system of linear equations (Eq. (4), eighth order) was carried out using a weighted least squares fit program [29] that was modified for the present study. Eight coefficients of dipole moment function,  $M_0, M_1, M_2, \dots, M_7$ , were subsequently determined and their values are listed in Table 1. For comparison, the coefficients of the dipole moment function coefficients determined by Ogilvie and Lee [16] and Kiriyaama et al. [17] are included in Table 1. Finally, the three dipole moment functions listed in Table 1 are plotted against internuclear distance in Fig. 1. While the dipole moment function derived in this work does not differ drastically from the one derived in Ref. [16], it clearly differs from the one derived in Ref. [17]. Although, the coefficients of  $M_i$  in Table 1 were derived using slightly different potentials

**Table 2**

Matrix elements  $M_{v0}(m)$  of electric dipole moment of HCl in units of debye. The subscripts  $v$  and 0 of  $M_{v0}(m)$  represent the  $v$ th upper vibrational level and the ground vibrational level, respectively. Pine et al. [11] results were used for the fundamental band, Toth et al. [13] for the 2-0 band, Ogilvie and Lee [16] for the second overtone, and Zughul [25] for bands 4-0 through 7-0. Estimated uncertainties (in percents) are given after each value.

m	$M_{10}(m) \times 10^2$		$M_{20}(m) \times 10^3$		$M_{30}(m) \times 10^4$		$M_{40}(m) \times 10^5$		$M_{50}(m) \times 10^6$		$M_{60}(m) \times 10^6$		$M_{70}(m) \times 10^6$	
-10	8.25672	2%												
-9	8.16347	2%												
-8	8.05362	2%	-8.46115	15%										
-7	7.96856	2%	-8.32351	15%	5.75723	25%	-2.88234	10%	-8.08881	20%	5.90593	25%		
-6	7.88346	2%	-8.25410	15%			-2.86567	10%	-7.99619	20%	5.96547	25%	-2.80935	30%
-5	7.77839	2%			5.74559	25%	-2.85896	10%	-7.95635	20%	6.03207	25%	-2.89648	30%
-4	7.67912	2%	-8.03939	15%	5.62528	25%	-2.87052	10%	-7.97178	20%	6.11274	25%	-3.01341	30%
-4			-8.07161 <sup>b</sup>	4%										
-3	7.58356	2%			5.62737	25%	-2.90552	10%	-8.05581	20%	6.23252	25%	-3.24595	30%
-3					5.52761 <sup>c</sup>	8%								
-2	7.48244	2%	-8.19298	15%	5.55171	25%	-2.96318	10%	-8.20179	20%	6.39073	25%	-3.07238	30%
-1	7.38562	2%	-8.09780	15%	5.69102	25%	-3.05364	10%	-8.42494	20%	6.60576	25%	-3.15826	30%
1	7.19426	2%	-7.88354	15%	5.53129	25%	-3.15801	10%	-8.64716	20%	6.84937	25%	-3.28765	30%
2	7.10403	2%			5.67157	25%	-3.16065	10%	-8.62136	20%	6.86504	25%	-3.39395	30%
3	7.02272	2%			5.89590	25%	-3.19973	10%	-8.62304	20%	6.92039	25%	-3.49778	30%
4	6.94008	2%	-7.99267 <sup>a</sup>	1%	5.68341	25%	-3.23565	10%	-8.68729	20%	7.00533	25%		
4			-8.01496 <sup>b</sup>	4%										
5	6.84209	2%	-7.75373	15%	6.24240	25%	-3.28203	10%	-8.74468	20%	7.11035	25%		
6	6.76418	2%	-7.98751	15%	6.37095	25%	-3.34624	10%	-8.82735	20%	7.23259	25%	-3.62641	30%
7	6.66449	2%	-7.73836	15%			-3.41058	10%	-8.91616	20%	7.36529	25%	-3.76753	30%
8	6.56930	2%	-7.92135	15%	6.13255	25%	-3.47490	10%	-8.99751	20%	7.50939	25%	-3.80380	30%
9	6.45739	2%	-7.72395	15%	6.40364	25%	-3.53754	10%	-9.10332	20%	7.65756	25%	-3.80741	30%
10	6.39033	2%	-7.95144	15%			-3.60597	10%	-9.21302	20%	7.78105	25%		
11	6.29444	2%												

<sup>a</sup> Value calculated from line intensity reported by Ortwein et al.[23].

<sup>b</sup> Value calculated from line intensity reported by De Rosa et al.[22].

<sup>c</sup> Value calculated from line intensity reported by Stanton et al.[33].

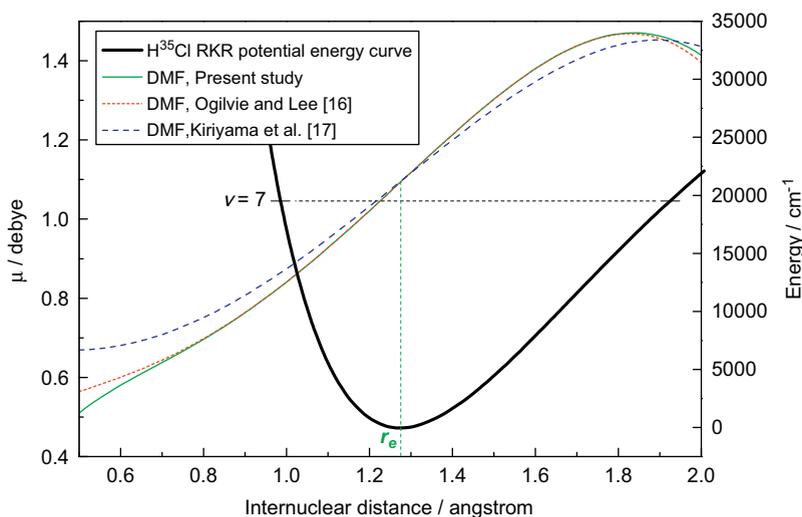


Fig. 1. Dipole moment functions of HCl using the  $M_i$  coefficients from Table 1.

and value of  $r_e$ , this cannot account for such a large difference. In the mean time we are confident in the quality of the RKR potential which is discussed in the last section of our paper. The reason for the discrepancy is an incorrect treatment of experimental intensities by Kiriya et al. [17].

It was found that adoption of the experimental uncertainties reported in the original publications (when available) did not offer the best fit to all the data. Thus adjustments were made (generally by increasing reported uncertainties) with the aim of reducing the overall deviation of the fitting. The uncertainties adopted for each line in our final fit are listed in Table 2.

The inner and outer classical turning points on the RKR potential for  $v=7$  were found to be approximately 0.986 and 1.925 Å, which suggests that the present DMF is valid within this range.

By combining the wavefunctions and the dipole moment function, the Einstein A-coefficients were calculated for  $\Delta v=0, 1, 2, 3, 4, 5, 6, 7$  up to  $v'=7$ , and were then converted to line intensities in HITRAN units. The corresponding file is given in the Supplementary material. The file contains only the  $H^{35}Cl$  lines, but the intensities for  $H^{37}Cl$ ,  $D^{35}Cl$  and  $D^{37}Cl$  isotopologues will be included in the global line list [12]. With the purpose of evaluating the influence of the DMF on reproducing line intensities, the line intensities calculated using LEVEL with the same wavefunctions but different DMFs were compared with experimental line intensities for the fundamental band and overtone bands up to  $v'=7$ . HITRAN intensities were also included in the comparisons. The results of the comparisons are plotted in Figs. 2–7.

### 3.1. Line intensity of the fundamental band

In Fig. 2, all the calculated line intensities for the fundamental band of  $H^{35}Cl$ , including HITRAN, are compared with measurements of Pine et al. [11] and the percentage differences were plotted against  $m$ -values. The results clearly show that the line intensities calculated in present study, Ref. [16], and HITRAN, are all within the 1% experimental

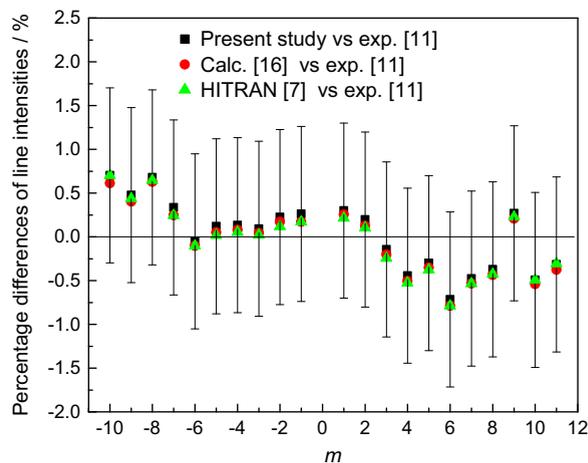


Fig. 2. Comparison of the empirical line intensities with Pine et al. experimental values [11] of the  $H^{35}Cl$  fundamental band.

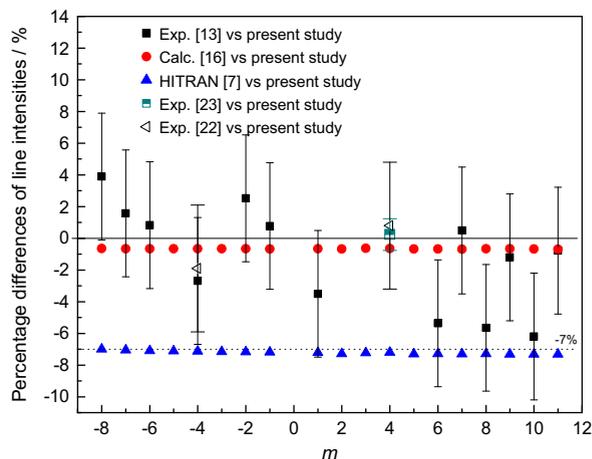


Fig. 3. Comparison of the line-intensities of the  $H^{35}Cl$  2-0 band comparison with present study as a reference.

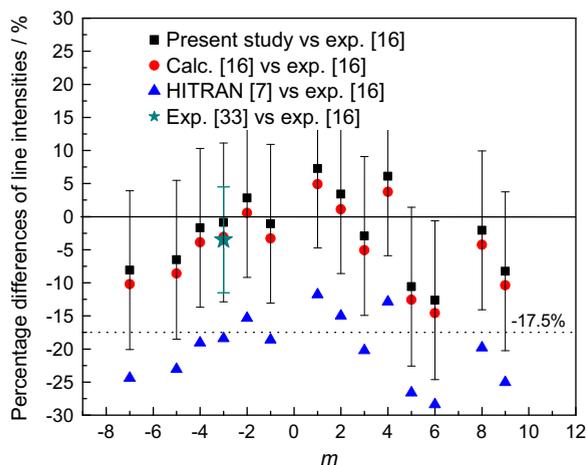


Fig. 4. Comparison of the line-intensities of the  $\text{H}^{35}\text{Cl}$  3-0 band with experimental values [16] as a reference.

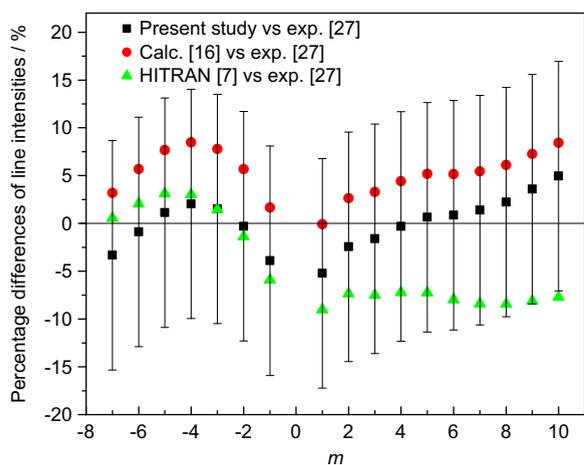


Fig. 5. Comparison of the line-intensities of the  $\text{H}^{35}\text{Cl}$  4-0 band with experimental values [27] as a reference.

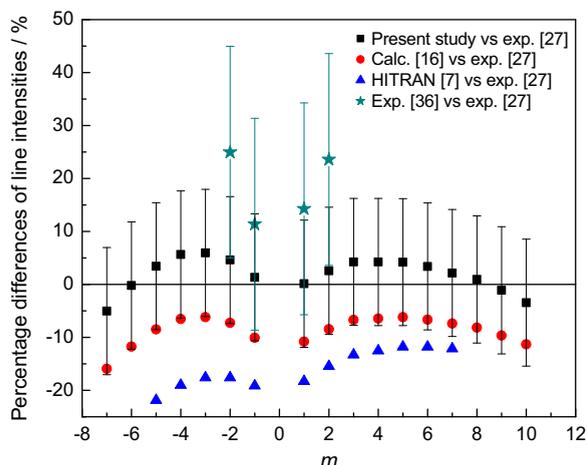


Fig. 6. Comparison of the line-intensities of the  $\text{H}^{35}\text{Cl}$  5-0 band with experimental values [27] as a reference.

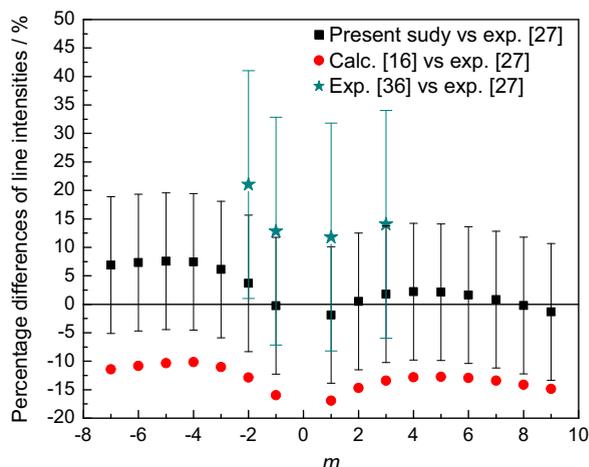


Fig. 7. Comparison of the line-intensities of the  $\text{H}^{35}\text{Cl}$  6-0 band with experimental values [27] as a reference.

error limit claimed by Pine et al. [11]. Furthermore, all three calculations agree well with each other in a unique pattern.

### 3.2. Line intensity of the first overtone band

In Fig. 3, measurements by Toth et al. [13], intensities derived from the DMF of Ogilvie and Lee [16], and HITRAN intensities for the 2-0 band of  $\text{H}^{35}\text{Cl}$  were compared with the present study. Additionally, the latest high-precision measurements by Ortwein et al. [23] and De Rosa et al. [22] were also compared with present study. From Fig. 3, it is apparent that both our DMF and the DMF by Ogilvie and Lee [16] reproduced the line intensities of the 2-0 band very well. However, HITRAN line intensities appear to be underestimated by about 7%. The intensity of the  $R(3)$  line calculated from our DMF has shown slightly better agreement to the measurement by Ortwein et al. [23] ( $\sim 0.2\%$ ) than the intensity derived from the DMF by Ogilvie and Lee ( $\sim 1\%$ ). However the differences are insignificant and both are within experimental uncertainties.

### 3.3. Line intensity of the second overtone band

A similar comparison was carried out for the 3-0 band (see Fig. 4). The HITRAN line intensities seem to be systematically underestimated by 17.5%. The reason for this is that in the semi-empirical DMF used for calculating HITRAN intensities, outdated low-resolution measurements by Benedict et al. [33] were used as an input. The values from Ref. [33] have shown large differences from more recent measurements by Ogilvie and Lee [16] and Stanton et al. [34] that were used as input parameters in this work. Interestingly, for the 3-0 band of  $\text{H}^{35}\text{Cl}$ , our calculation has shown better agreement with measurements by Ogilvie and Lee than the intensities derived from the semi-empirical DMF derived in the same work [16].

### 3.4. Line intensity of the 4-0, 5-0, 6-0 and 7-0 bands

Three papers have been published by Zughul et al. on the line intensity measurements of the 4-0 to 7-0 overtone

bands of HCl [25,27,35] which report analysis of the same spectra recorded at Kitt Peak Observatory with a Fourier transform spectrometer (FTS). However, the reported line intensities are inconsistent in Refs. [35 and 27]. Although Refs. [27 and 25] have reported the same line intensities for the 4-0, 5-0 and 6-0 overtone bands, the published dipole moment matrix elements derived from these intensities are different. No explanations for these discrepancies are offered in any of the three papers [25,27,35]. The only other intensity measurements for the 5-0 and 6-0 overtone bands were carried out by Reddy using the photoacoustic method [36] with much larger reported uncertainty. The discrepancies between line intensities reported by Reddy [36] and Ref. [27] are about 10–25%. Taking into account the reported uncertainty of their measurements, the line intensities reported in Ref. [27] were adopted. A sequence of uncertainties, 10%, 20%, 25% and 30% were employed for the 4-0, 5-0, 6-0 and 7-0 bands in our direct DMF fitting as relative weightings.

As shown in Figs. 5–8, line intensities calculated with the DMF derived here are in a better agreement with measurements from Ref. [27] for the 4-0 to 7-0 bands compared with both the intensities calculated from the DMF derived by Ogilvie and Lee [16] (that also used data from Ref. [27] as an input) and HITRAN intensities [7]. For the 5-0 and 6-0 bands, photoacoustic measurements by Reddy [36] were also included in the comparison and show a rather large discrepancy of +10% to +25%. Strangely, the difference between our calculations and intensity measurements from Ref. [27] shows a quadratic dependence on the rotational quantum number. The source of this unusual behavior is unclear. Additional experiments in these high overtones are desirable in order to confirm the values reported in Ref. [37].

#### 4. Conclusion

The coefficients of a power series expansion of the dipole moment function of HCl valid for an internuclear range of 0.986–1.925 Å have been determined using a direct fit

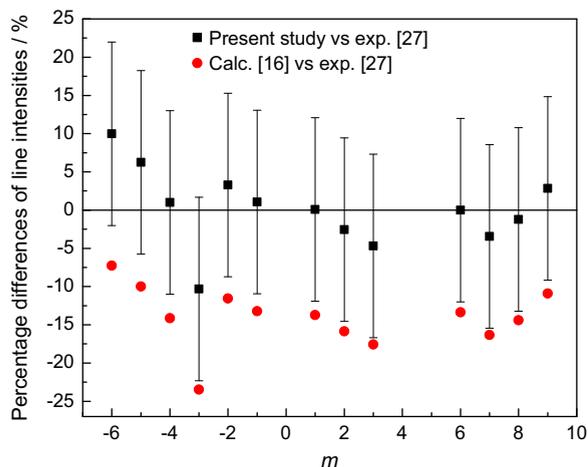


Fig. 8. Comparison of the line-intensities of the  $\text{H}^{35}\text{Cl}$  7-0 band with experimental values [27] as a reference.

approach using the best available and appropriately weighted experimental data. Using wavefunctions derived from the Rydberg–Klein–Rees method and our DMF, line intensities were calculated numerically for  $\Delta v=0, 1, 2, 3, 4, 5, 6, 7$  up to  $v'=7$  bands using the LEVEL program [32]. Calculation of the exact vibration-rotational matrix elements can involve complex algebra (see Refs. [38,39], for instance), but the use of LEVEL significantly simplifies the entire procedure. Comparisons were made between line intensities from the present study, the Ogilvie and Lee DMF [16], HITRAN, and experimental measurements. The results have clearly shown that the DMF can be constructed directly from the experimental ro-vibrational dipole moment matrix elements, thereby avoiding Herman–Wallis fits of the individual bands. Our method also allows inclusion of sparse data in the individual bands. Moreover, the inclusion of rotational dipole moment matrix elements gave a better prediction of line intensities for the high- $J$  lines. Appropriate weighting of the data in the fit is important and can be easily implemented. We would like to emphasize that the inclusion of experimental uncertainties is crucial in the construction of semi-empirical models.

#### 5. Future work

The methodology developed in this work will be applied to recalculate intensities of all hydrogen halides in the HITRAN database. In addition, intensities for the deuterated species, not presently available in HITRAN [7] will be produced [12]. Although the RKR potential used in this work seems to reproduce the experimental line positions quite accurately, it will be interesting to evaluate the effect on the result when using the exact experimental potential. We performed such an evaluation using an empirical potential provided to us by John Coxon and Photos Hajigeorgiou and inserted into LEVEL by Robert Le Roy [40]. This potential is an improved version over the one these authors published previously in Ref. [9].

Fig. 9 shows the comparison between transition dipole moments calculated using the RKR potential and the Coxon & Hajigeorgiou potential [40] with the experimental values from Table 2. It is apparent from this figure that the difference is marginal. This fact has clearly demonstrated that, for the purpose of calculating line intensities, the RKR potential is sufficient as long as it is based on an accurate set of spectroscopic constants. Based on this fact, even supposing Ref [17] had used a different potential from the current study, its influence on the intensity calculation is insignificant.

While the DMF in the polynomial form derived in this work is valid within the range of internuclear separations probed by experiments, a method of extrapolating the DMF will need to be developed. In particular, it is known that the fit of the data to Padé approximants rather than polynomials provides better predictions [10] beyond the range of experimental data. Alternatively, theoretical calculations, such as those in Ref. [19] need to be evaluated, as they can be used outside the range of validity of semi-empirical DMFs. In general, the idea of implementing piecewise a semi-empirical DMF as proposed by Buldakov and Cherepanov [18] seems to be attractive. Unfortunately, when constructing

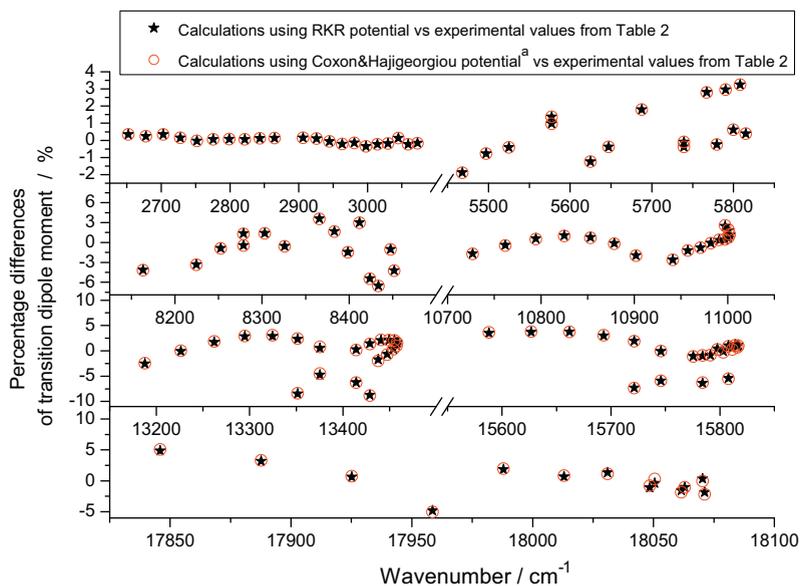


Fig. 9. Transition dipole moment comparison with experimental values of 1-0, 2-0, 3-0, 4-0, 5-0, 6-0 and 7-0 bands of  $\text{H}^{35}\text{Cl}$ . (a) Private communication with J. Coxon and P. Hajigeorgiou [40].

their piecewise DMF, Buldakov and Cherepanov used the erroneous values of Kiriya et al. [17], which undermined their results.

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### Appendix A. Supplementary Information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jqsrt.2011.03.014.

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