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

G. Li a,1, I.E. Gordon b,*, P.F. Bernath a, L.S Rothman b

a University of York, Department of Chemistry, York YO10 5DD, UK
b Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge, MA 02138, USA

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 \( \Delta v = 0, 1, 2, 3, 4, 5, 6, 7 \) up to \( v' = 7 \). 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 Kiriyama 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...
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 available (and appropriately weighted) 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

\[
M(r) = \sum_i M_i r^i,
\]

where \( x = (r - r_e) / r_e \), \( r_e \) is the equilibrium separation and \( i = 0, 1, 2 \ldots \). 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

\[
\left| \langle v' | M(x) | 0 \rangle \right|^2 = |R_{0d}(0)|^2 (1 + C_v m + D_v m^2 + \ldots),
\]

where \( R_{0d}(0) \) 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 \( R_{0d}(0) \) are then fit to

\[
R_{0d}(0) = \sum_i M_i \langle v' | x^i | 0 \rangle,
\]

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 \( v_r = 0 \) and \( v_r = 0 \)–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, Kiriyama 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

\[
\left| \langle v' | M(x) | 0 \rangle \right|^2 = \sum_{i=0}^{n} c_i m^i.
\]

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] | Kiriyama et al. [17] |
| \( M_0 \)      | 1.093164(86)    | 1.093004(75)   | 1.095056(1) |
| \( M_1 \)      | 1.23679(135)    | 1.23614(44)    | 1.07629(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) |

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first overtone bands. The source of the discrepancy becomes obvious if one takes the ratios of the squares of the Kiriyama 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 $\text{H}^{35}\text{Cl}$ (0.757587), which mistakenly was not accounted for in the Kiriyama 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 Kiriyama 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 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

3. Details of the calculations and the results

To begin with, a potential energy function for $\text{H}^{35}\text{Cl}$ 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 $\langle \nu | \mathbf{J} \cdot \mathbf{J}' | 0 \rangle$ 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, $M_0, M_1, M_2, ..., M_7$, were subsequently determined and their values are listed in Table 1. For comparison, the coefficients of the dipole moment function determined by Ogilvie and Lee [16] and Kiriyama 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].

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3 Value calculated from line intensity reported by De Rosa et al. [22].
4 Value calculated from line intensity reported by Stanton et al. [33].

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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 Kiriyama 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 $\text{H}^{35}\text{Cl}$ lines, but the intensities for $\text{H}^{37}\text{Cl}$, $\text{D}^{35}\text{Cl}$ and $\text{D}^{37}\text{Cl}$ 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 $\text{H}^{35}\text{Cl}$, 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
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 H$^{35}$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] (~0.2%) than the intensity derived from the DMF by Ogilvie and Lee (~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 H$^{35}$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 discrepancies are different. No explanations for these discrepancies 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

![Graph showing comparison between transition dipole moments calculated using the RKR potential and the Coxon & Hajigeorgiou potential with experimental values from Table 2.](image-url)
their piecewise DMF, Buldakov and Cherepanov used the erroneous values of Kiriyama et al. [17], which undermined their results.

Acknowledgment

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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.

References


