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Reference spectroscopic data for hydrogen halides. Part I: Construction and validation of the ro-vibrational dipole moment functions

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ABSTRACT

Knowledge of the infrared transition moments of hydrogen halides, namely HF, HCl, HBr, and HI, is essential for atmospheric, astrophysical, and laser applications. Recently, a new polynomial empirical dipole moment function (DMF) for HCl has been constructed using an efficient approach that involves a direct fit of experimental ro-vibrational intensities [Li et al. J Quant Spectrosc Radiat Transfer 2011;112:1543–50]. In the present study, this method was extended to the use of Padé approximation representations of the DMF and applied to all four hydrogen halides. To carry out the fits, the best available experimental data were collected and critically evaluated. Combining dipole moment functions with the wavefunctions obtained from highly-accurate empirical potential energy curves, line intensities were computed numerically for numerous ro-vibrational bands, and compared with the experimental values and with intensities calculated using the most recent *ab initio* dipole moment functions. Results obtained in this work form basis for calculating intensities of spectral lines of hydrogen halides and their isotopologues in the HITRAN 2012 database.

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1. Introduction

Hydrogen halides have been identified in various astrophysical objects such as the interstellar medium, planetary atmospheres, and carbon stars [1–7]. In the terrestrial atmosphere, HCl and HF are the main chlorine and fluorine reservoir gases in the middle atmosphere, and therefore are important in the ozone depletion process [8]. Hydrogen halides have attracted interest for their excellent properties as chemical lasers [9,10], and the tritium-containing species are important in the nuclear industry. Therefore, it is critically important to establish a reliable set of spectral parameters, such as transition frequencies, line intensities, and line-shape parameters of hydrogen halides for ready reference. These parameters will be used to update and extend hydrogen halide line lists in the HITRAN molecular spectroscopic database [11]. The present study focuses on the determination of the line intensities of hydrogen halides.

As discussed in many textbooks [12–14], line intensities of the ro-vibrational transitions of a diatomic molecule within an individual band, which can be measured experimentally, are usually refined with an empirical model suggested by Herman and Wallis in 1955 [15].

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According to their theory, the influence of the vibration–rotation interaction on the line intensity can be treated by fitting the squares of the matrix elements with a polynomial function. Such a method works well for individual bands whose intensities have already been measured, but to permit calculations for unmeasured bands, the molecular dipole moment function (dipole moment as a function of internuclear distance) is needed. In 1959, Trischka and Salwen [16] systematically studied the connection between the dipole moment function (DMF) of a diatomic molecule and its matrix elements. They suggested two approximate forms of the DMF when limited numbers of matrix elements are known. These two forms are: (1) the polynomial approximation; and (2) the wave-function approximation. The authors also proved that given the matrix element M_0^0 and all the off-diagonal matrix elements in a single column (or row), the DMF can be determined completely; however the diagonal matrix elements alone do not determine the dipole moment function. In the past few decades, the DMFs of hydrogen halides (using the polynomial approximation) have been studied in some detail, both experimentally and theoretically [17–34]. Recently, many new reliable laboratory measurements of the line intensities of these species have become available. It therefore seems timely to update the existing empirical DMFs and compare them with the most recent theoretical functions.

We have developed a direct fit approach to determine the DMFs of diatomic molecules in the form of a polynomial approximation. Its successful application to HCl [29] has demonstrated the effectiveness of inclusion of rotational dipole moment matrix elements and appropriate weighting of the experimental data in the DMF fitting. This efficient method has been shown to be superior to the conventional method which fits only the rotationless dipole moment elements, especially when the experimental data are sparse. It is fair to mention that fitting the individual rovibrational intensities directly was first attempted by Kiriyama et al. [28]. Unfortunately, as discussed in our previous paper, a number of mistakes had been made in the Kiriyama et al.'s work in the processes of converting units and formalisms of experimental intensities, and smoothing of the experimental values with Herman–Wallis approach which in addition was incorrectly interpreted. Apart from including the *ab initio* long range values in the fit, which will be discussed further, the advantage of our method is that we did not smooth the experimental data, but rather used experimental uncertainties in the fit. This proves especially useful when the experimental data in certain vibrational band are sparse, and therefore do not provide enough data for reliable Herman–Wallis fit.

In the present study, empirical DMFs of hydrogen halides are constructed using the direct fit approach. However, conventional polynomial DMFs are valid only near the equilibrium position since they diverge rapidly at long range. For that reason, we combine them with the most recent *ab initio* DMFs at large internuclear separation to obtain global DMFs using Padé approximation formulae. Using the new DMFs and highly accurate empirical potential energy functions (PEFs), the line intensities of hydrogen halides, including deuterium- and tritium-containing species and their halide isotopologues, were generated numerically for the pure rotational transitions and for numerous ro-vibrational bands. Results were compared with intensities calculated using the best experimental and most recent *ab initio* data as well as with values given in the current edition of the HITRAN database [11]. The line intensities for hydrogen halides in the current HITRAN database are largely based on unpublished work of Tipping in 1990 [35]. These intensities were calculated using DMFs derived from the rotationless matrix elements which were obtained from the Herman–Wallis fits of the pre-1990 ro-vibrational line intensity measurements of hydrogen halides. With the exception of the pure rotational intensities of HF, HCl, and HBr, these database intensities have remained unchanged since that time.

2. Method of the calculation

The direct fit method used in the present study has been applied previously to the HCl molecule [29], and therefore only a brief description is given here. Experimental ro-vibrational line intensities are first evaluated and converted to matrix elements, $M^{v'j'}_{v=0j''} = \langle v'j' | \mu(r) | 0j'' \rangle$, using the equations in Ref. [36]. Here, $\mu(r)$ is the electric dipole moment function, and the double and single primes correspond to the lower and upper states, respectively. Usually, a truncated polynomial approximation is assumed for $\mu(r)$ [14],

$$\mu(r) = \sum_{i=0}^{n} M_i x^i, \tag{1}$$

where M_i are the coefficients of the polynomial expansion, $x=(r-r_e)/r_e$ denotes the dimensionless Cartesian displacement, and r_e refers to the equilibrium bond length. Under this assumption, the following relation can be obtained for the ro-vibrational matrix elements,

$$\langle v'j' | \mu(r) | 0j'' \rangle = \sum_{i=0}^{n} M_i \langle v'j' | x^i | 0j'' \rangle, \tag{2}$$

where the expectation values $\langle v'j' | x^i | 0j \rangle$ can be determined from the potential energy function. At this point, the determination of the M_i coefficients becomes a problem of solving the over-determined systems of equations. In order to do this, a least-squares fit computer code by Le Roy [37] was accordingly modified and best sets of M_i coefficients were obtained.

It is worth mentioning that in the previous paper [29] we have also shown that the use of the RKR (Rydberg–Klein–Rees) potential energy function is sufficiently accurate for the purpose of line intensity calculation. Nevertheless, the best spectroscopically-determined potential energy functions [38] of hydrogen halides are used in the present study. These potential energy functions were determined using a modern direct potential fit (DPF) methodology. All available spectroscopic data on hydrogen halide ground electronic states were employed in the determination of highly accurate analytical functions that are also consistent with the expected inverse-power long-range expression for the potential energy. Pure rotational and ro-vibrational transition frequencies calculated with

these potentials are found to be in excellent agreement with the best available experimental values (within experimental uncertainties).

Owing to the fact that the polynomial approximation of a DMF has little physical meaning when extrapolating to short and long internuclear distances, its utility for predicting higher overtone and hot bands is very limited. The Padé approximation formula, Eq. (3), which has the correct asymptotic behavior, is often recommended for representing the form of a global DMF of a diatomic molecule [21]:

$$M(x) = M_0 \frac{(1+x)^3}{1+\Sigma_{i-1}^{7} e_i x^i}, \tag{3}$$

where M_0 is the zero-order of the M_i coefficients of the polynomial expansion of the DMF and e_i are the fitting coefficients of the Padé approximation. M_0 coefficients were held fixed in the fit.

To improve the determination of the e_i coefficients of the Padé formula, information on the DMF at large internuclear separation is needed to constrain the fitting. Unlike experiment, *ab initio* calculations are not subject to difficulties when dealing with high overtone and hot bands, and can thus provide information on the DMF with some validity, even for vibrational levels approaching the dissociation limit. Combining experimental intensity information near equilibrium and theoretical data at large separations, the semi-empirical global DMFs of hydrogen halides are constructed in the form of the Padé approximation formula.

3. HF

3.1. Padé representation of the dipole moment function of HF

A considerable amount of literature has been published on line intensity measurements of HF since the 1960s [18–20,39–45]. For the fundamental band, Pine et al. [43] have made a substantial advance in obtaining measurements with a tunable dye laser that are of superior accuracy over the early experimental studies based on low resolution grating spectroscopy. With extra care during sample handling, experimental condition control, and data reduction procedures, they were able to obtain line intensities of HF with an overall accuracy of better than 2%. For the 2-0 band, tunable diode laser measurements by Chou et al. [44] of the $P(3)$ and $P(6)$ line intensities complement the earlier measurement by Meredith in 1972 [19]. For the 3-0 band, the only available direct measurement is from Spellicy et al., that has an accuracy of 5% [18]. Rimpel [42] performed intensity measurements for the 4-0 and 5-0 bands in 1974. In that same year, Sileo and Cool [20] used a chemical laser source to carry out relative intensity measurements for many ro-vibrational bands up to $\Delta v \leq 6$. However, while their measurements are extensive, they have large reported uncertainties of 15%.

Furthermore, several attempts have been made to construct the DMF of HF using either *ab initio* calculations [17,34,46–48] or by empirical fitting of the rotationless matrix elements [19,21,23,49]. In contrast, in the present work a new DMF for HF is constructed by applying our efficient direct fit method with the best weighted experimental data. In summary, we adopt the results of Pine et al. [43] for the fundamental band, Meredith [19] for the 2-0 band, Spellicy et al. [18] for the 3-0 band, and Rimpel [42] for the 4-0 and 5-0 bands. The precise laser measurements of the $P(3)$ and $P(6)$ transitions of the 2-0 band by Chou et al. [44] are also included to improve the accuracy of our DMF. Because the inclusion of rotationless matrix elements from Sileo and Cool [20] would yield a large standard deviation for the fitting, we did not use their data in the present study. The ro-vibrational matrix elements and the corresponding weights used in the fit can be found in the Supplementary material.

The permanent dipole moment of the HF molecule has been measured by Muenter and Klemperer [50] for $v=0$, and by Bass et al. [49] for $v=0$ and $v=1$, by means of the Stark effect on a molecular beam. Such measurements also provide useful constraints for the determination of the DMF. For the permanent dipole moment measurement for $v=0$, $\langle 0|M(x)|0\rangle$, the value $1.826526 \pm 0.000007D$ reported by Muenter and Klemperer [50] does not agree with the Bass et al. [49] value $1.826567 \pm 0.000007D$ within their reported experimental uncertainties. Although the value from Bass et al. gives a slightly smaller standard deviation in our fits, the effect on the line intensities of the pure rotational and ro-vibrational bands was marginal ($<0.5\%$). The more recent values from Bass et al. were adopted in the determination of M_i coefficients that are listed in Table 1.

The experimental ro-vibrational intensities of HF have long served as benchmarks for *ab initio* studies. There is a large volume of published studies on the theoretical DMF of HF employing different methods [17,46–48]. In 2008, Harrison [47] analyzed the DMFs of hydrogen halides in terms of local moments constructed using the Hirshfeld method [51]. Another recent theoretical study by Kahn et al. [52] in 2011 involves direct calculation of the derivatives of the DMF, since ro-vibrational intensities are particularly sensitive to these derivatives as was discussed by Person and Newton [53]. The Kahn et al. theoretical DMF is expressed in the form of the power series expansion of Eq. (1) with the M_i coefficients determined up to M_5. To construct a DMF which is able to reproduce the power series expansion function over

Table 1
Coefficients of the power series expansion of the DMFs of hydrogen halides from the present study (in Debye)[a].

	HF	HCl	HBr	HI
M_0	1.802721 (17)	1.093080 (84)	0.817363 (43)	0.44716 (34)
M_1	1.4121 (16)	1.2367 (13)	0.6949 (19)	−0.07769 (20)
M_2	−0.0365 (37)	0.0152 (36)	0.3730 (39)	0.5469 (12)
M_3	−0.858 (26)	−1.5367 (93)	−1.742 (16)	−1.9634 (54)
M_4	−0.462 (65)	−0.874 (33)	−0.966 (59)	−5.091 (64)
M_5	−0.99 (43)	−0.384 (62)	1.17 (69)	−0.29 (31)
M_6		−0.86 (29)	6.0 (13)	
M_7		2.05 (78)	31 (15)	
M_8			−127 (43)	

[a] Numbers in parentheses are the estimated standard deviations in units of the last significant digit of the corresponding parameter.

Table 2
Comparison of the coefficients of the dipole moment functions in Padé approximate form.

	HF		HCl		HBr		HI	
	Present study	Ref. [21]	Present study	Ref. [21]	Present study	Ref. [21]	Present study	Ref. [21]
M_0 (Debye)	1.802721	1.80306	1.093080	1.09333	0.817363	0.81788	0.44716	0.44722
e_1	2.21800 (25)	2.227	1.86759 (22)	1.897	2.15246 (21)	2.199	3.1685 (37)	3.166
e_2	1.26541 (92)	1.331	0.8814 (11)	0.871	0.71905 (95)	0.808	2.2589 (13)	3.393
e_3	0.5092 (58)	0.550	1.4786 (99)	1.465	1.379 (11)	1.483	2.0633 (85)	2.243
e_4	1.286 (11)	1.044	1.202 (24)	1.829	3.694 (18)	3.868	13.178 (29)	11.794
e_5	0.661 (37)	1.112	0.26 (13)	−4.137	−1.24 (14)	−2.612	9.52 (20)	10.380
e_6	−0.032 (30)	12.095	11.55 (36)	13.886	2.64 (22)	13.209	6.56 (52)	7.423
e_7	4.5×10^{-16}	0.722	−12.92 (36)	0.416	6.17 (10)	0.255	0.84 (40)	−0.653
e_8	0.6781 (67)		6.76 (40)	–	–	–	–	–

Table 3
Valid ranges of power series expansion of the DMFs of hydrogen halides.

	Maximum v	Maximum J	x (MIN)	x (MAX)
HF	5	10	−0.2487	0.5152
HCl	8	10	−0.2293	0.5247
HBr	7	10	−0.2272	0.3529
HI	5	10	−0.1868	0.3702

the range of x covered by experiments, and also to have some validity at long range, we combined the empirical polynomial DMF in Table 1 and six *ab initio* data points at large nuclear separation from Harrison [47] to generate a global DMF using the Padé approximation formula of Eq. (3). The e_i coefficients thus determined from our non-linear least-squares fit are compared with those of Ogilvie et al. [21] in Table 2. It was found that the inclusion of higher order terms was necessary, even though some of them have large statistical uncertainties. In general, the differences between the Padé approximation and the power series expansions are less than 0.0004D over the range covered by experiments (as listed in Table 3). With that being said, the individual line intensities calculated using the resultant Padé formula differed from the experimental values for higher overtones by several percent. Therefore, in the calculation of the line-intensities for HITRAN in the range covered by experiments, we have employed the values calculated using a polynomial expression and a Padé approximation outside that range. In Fig. 1, our new DMF using the Padé approximation is plotted and compared with the theoretical results of Harrison [47]. They agree very well with each other at short ($x<0.5$) and long range ($x>1.5$). In the middle range ($0.5<x<1.5$), the dipole moments from Harrison are slightly larger than our semi-empirical values with a maximum difference of approximately 0.063D at $x=0.847$.

3.2. Line intensity comparison for HF

Since the ro-vibrational line intensities are very sensitive to the derivatives of the DMF, we have directly compared the ro-vibrational intensities calculated from the hydrogen halide DMFs instead of just comparing the shapes of these functions. The best empirical PEFs from Ref. [38] are used to calculate wavefunctions. Fig. 2 shows the percentage differences of the absolute line intensities

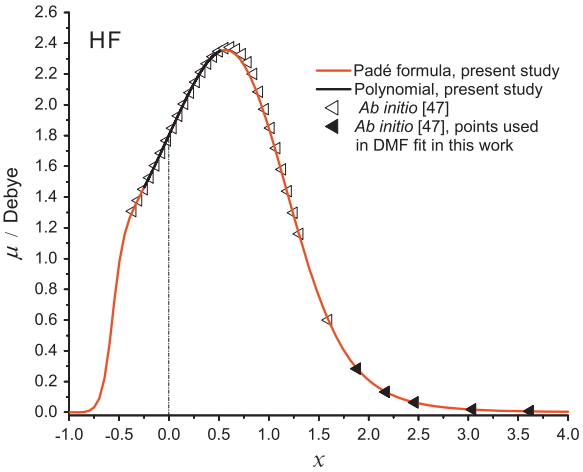

Fig. 1. Comparison of the semi-empirical DMF (present study) and *ab initio* DMF (Ref. [47]) of HF. $x=(r-r_e)/r_e$ is the reduced internuclear distance. Five *ab initio* points represented by solid triangles are used to constrain our Padé DMF at large internuclear separation.

from our calculated values of the experimental values, the best theoretical values, and the HITRAN database values for the 1-0 through 5-0 bands of HF. For the fundamental band, our result is almost identical to the HITRAN database, but with a slightly different J-dependence. Both of them agree well with experimental values from Pine et al. [43] with a difference less than 2%, while our results show better agreement for the $R(0)$ and $R(7)$ transitions which have the lowest experimental uncertainty. As one may notice, there is a clear trend of increasing of the differences of the intensities between our results and experimental values. It can be noted that the originally measured line intensities in Ref. [43] were divided by a factor of 1.018 owing to the difference between the calculated and measured line widths. Interestingly, if the undivided intensities are used, better agreement is achieved between the matrix elements M_0^1 and M_0^0, and the problem of the increasing trend is also eliminated. Nevertheless, no specific conclusion should be made at this stage and further investigation is needed. As for the theoretical studies, the fundamental band results from Harrison [47] are approximately 1% lower than those of the present study while showing a similar J dependence, whereas the results from Kahn et al. [52] are 2–3% larger

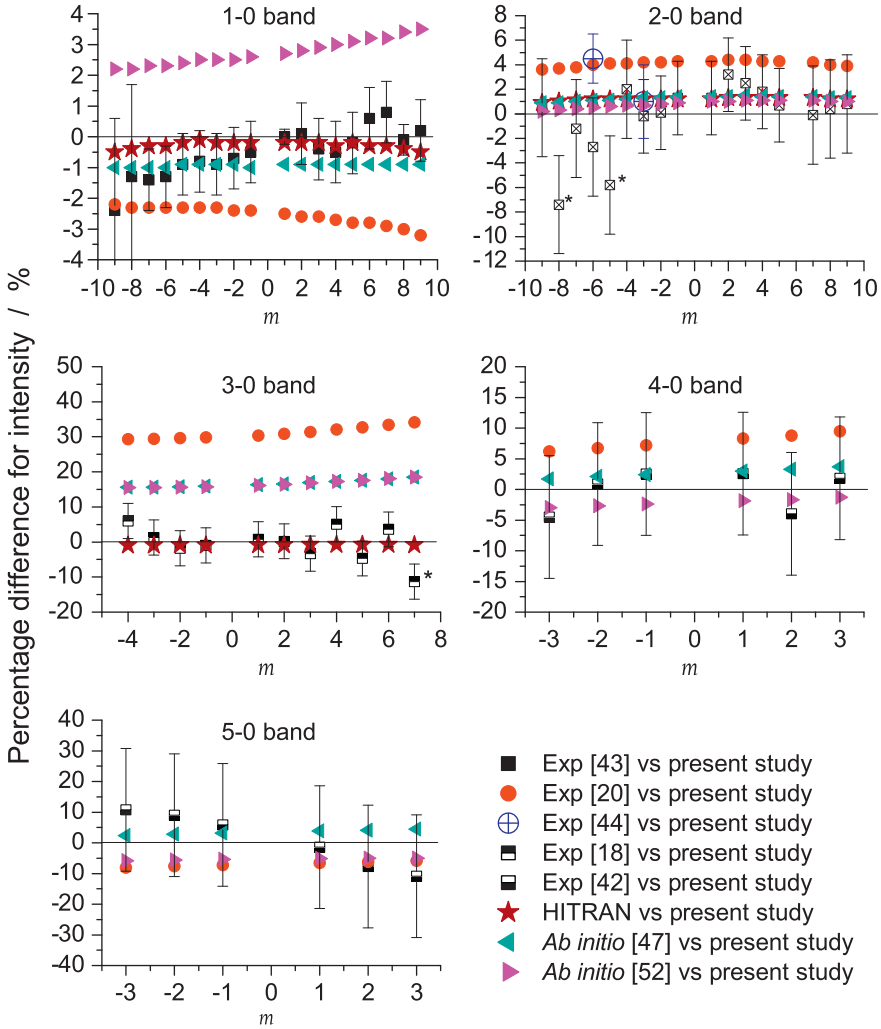

Fig. 2. Comparison of line intensities of the $H^{19}F$ ro-vibrational bands with the present study as a reference m is equal to $-J$ for P branch and $J+1$ for R branch lines. Note different scales in the panels of the plot.

than those of the present study. Results using the DMF constructed by Sileo and Cool [20] are 2–3% smaller than the present study.

In Fig. 2, experimental intensities [19,44], theoretical intensities [47,52] and the HITRAN database are also compared with the present study for the first overtone band of HF. Note that the uncertainties of the experimental data of Meredith [19] are obtained from Fig. 3 of that paper. The two outliers marked with an asterisk were disregarded in the determination of the DMF. The results obtained from the present study agree well with those of Meredith [19] within the experimental error (approximately 4–5%). HITRAN data are almost identical to the theoretical values of Harrison [47]. Both of them are approximately 1% higher than the present results. Another theoretical study by Kahn et al. [52] agrees very well with HITRAN for the R branch transitions but shows slightly poorer agreement for the P branch transitions. The experimental line intensity of the $P(3)$ transition by Chou et al. [44] agrees well with HITRAN and with the present study, while the line intensity

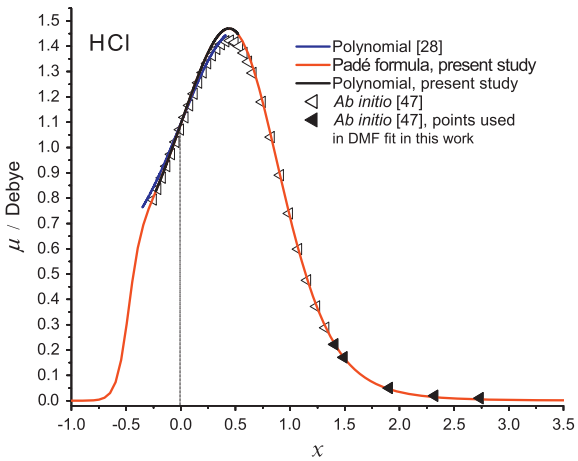

Fig. 3. Comparison of the semi-empirical DMF (present study) and *ab initio* DMF (Ref. [47]) of HCl. $x=(r-r_e)/r_e$ is the reduced internuclear distance. Five *ab initio* data represented by solid triangles are used to constrain our Padé DMF at large internuclear separation.

of the $P(6)$ transition from that same study does not agree well with either. Although HITRAN and the two theoretical results seem to have slightly better overall agreement with experimental data than the present study, the difference is marginal ($<1\%$) especially considering the large uncertainties of the experimental measurements.

A similar comparison was carried out for the 3-0 band in Fig. 2. It is clear that HITRAN and the present study are in good agreement with the experimental measurements of Spellicy et al. [18]. Note that the $R(6)$ line was disregarded in the present determination of the DMF. However, results from both theoretical studies [47,52] are much higher than the present study by approximately 16%. Moreover, the Sileo and Cool [20] measurements are about 30% higher than the present study, a difference which is twice as large as their estimated experimental uncertainty ($\sim$15%). In another recent *ab initio* study, by Futami et al. [54] in 2012, line intensities were calculated at the CCSD(T)/aug-cc-pVQZ level (Coupled-Cluster with Single and Double and Perturbative Triple excitations/augmented correlation-consistent polarized valence-only quadruple-zeta basis set). Their results for the 3-0 band are also approximately 15% higher than those of the present study. Further discussion of the line intensities of the 3-0 band can be found in Section 7.

For the 4-0 and 5-0 bands of HF, experimental intensities shown in Fig. 2 are averages of the three repeated measurements by Rimpel [42], with several outliers removed. As shown in this figure, the theoretical intensities of Harrison [47] are 2–3% higher than those of the present study, while the results of Kahn et al. [52] are 2–3% lower than the present study. Intensities computed using the DMF from Sileo and Cool are 6–9% higher than the present study. Since the single line intensity measurement of the $R(4)$ transition of the 5-0 band by Woody and Lynd [45] gives a value over an order of magnitude smaller than other measurements (and the *ab initio* calculations), it was not included in the present fit.

4. HCl

The construction of the DMF of HCl in the polynomial approximation and the associated line intensity comparison has been discussed in detail in our previous study [29]. Here, we have combined that DMF with long-range points from the *ab initio* dipole moment of Harrison [47] to construct a DMF using the Padé approximation (see Fig. 3). The derived e_i coefficients are listed in Table 2. As can be seen in Fig. 3, the DMF from the present study agrees well with that of Harrison [47] for $x<0$. However, for $x>0$, Harrison's calculation underestimates the dipole moment, and a maximum difference of $0.049D$ is observed at $x=0.412$. After that point, the difference becomes smaller, and good agreement is found again for the range $x>0.82$ to dissociation, which is largely due to the fact that we used *ab initio* points when fitting to the Padé approximant at long range. The DMF of Kiriyama et al. [28] is also plotted in Fig. 3 for the sake of comparison. As shown, this DMF deviates from both the present study and the theoretical DMF of Harrison [47]. The reason for this disagreement was discussed in our previous study [29]. Briefly, Kiriyama et al. [28] did not take into account the isotopic abundance of $H^{35}Cl$ when extracting

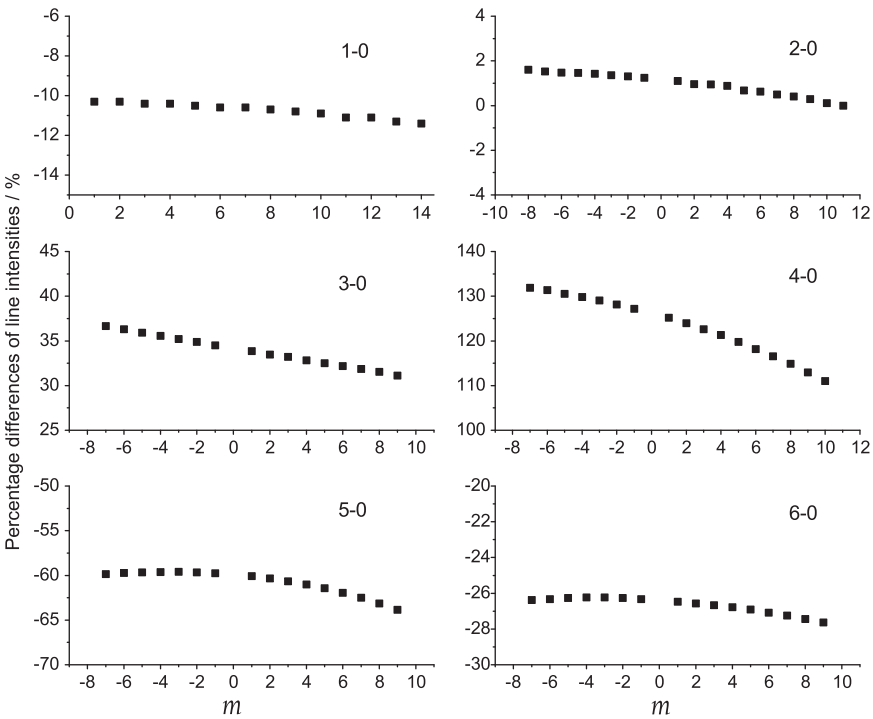

Fig. 4. Comparison of $H^{35}Cl$ line intensities using DMFs from the present study and a recent *ab initio* study of Harrison [47]. m is equal to $-J$ for P branch and $J+1$ for R branch lines. Note different scales in the panels of the plot.

the matrix elements from experimental intensities for the fundamental and first overtone bands. This resulted in an error of approximately 25% for the line intensities of the fundamental and first overtone bands.

Fig. 4 compares the line intensities calculated using Harrison's DMF and the present DMF for the 1-0 through 6-0 bands of $H^{35}Cl$. The corresponding differences of, approximately −11%, 1%, 34%, 127%, −60%, and −26% respectively, are much larger than the experimental uncertainties. It is thus tempting to conclude that the *ab initio* DMF of HCl is much less accurate than that of the HF molecule. These results also demonstrate the extreme sensitivity of calculated ro-vibrational intensities on the precise form (and derivatives) of the DMF.

5. HBr

5.1. Padé representation of the dipole moment function of HBr

A number of line intensity measurements for the fundamental and first overtone band of HBr have been published [30,55–58] with major discrepancies up to 50%, well outside the stated experimental errors (~10%). For example, the line intensities reported by Gustafson and Rao [55] for the fundamental band are approximately 40% lower than those reported by Babrov [57]. In 1985, Séoudi et al. [59] measured the line intensities of the fundamental band for both isotopologues $H^{79}Br$ (50.68%) and $H^{81}Br$ (49.31%) with an accuracy better than 5%. Their intensities agree satisfactorily with those of Babrov [57], but are approximately 50% larger than the intensities measured by Gustafson and Rao [55]. For the first overtone, the measurements of Babrov et al. [58] agree with recent diode laser measurements of the $R(7)$ and $P(2)$ lines by Chou et al. [60]. Both measurements are higher than those of Rao and Lindquist [56] by 25%, and those of Bernage and Niay [30] by 15%. For the 3-0 through 5-0 bands, the only line intensity measurements were carried out by Bernage and Niay [30]. For the 6-0 through 8-0 bands, the only available data are from Carlisle et al. [61]. After careful evaluation of all the available experimental data, we adopted the measurements of Séoudi et al. [59] and Babrov [57] for the fundamental band, Chou et al. [60] and Babrov et al. [58] for the 2-0 band, Bernage and Niay [30] for the 3-0 through 5-0 bands, and Carlisle et al. [61] for the 6-0 through 8-0 bands. The signs of the matrix elements used in the present study are the same as in Carlisle et al. [61]. A sanity check was performed by comparing the present sequence of signs with the ones calculated using the LEVEL program [62] with the derived DMF, and identical results were found. The DMF of HBr in the Padé approximation (Eq. (3)) is constructed in a similar fashion as those for HF and HCl and the results are plotted in Fig. 5. The derived e_i coefficients are listed in Table 2.

In 2001, Kiriyama and Rao [63] published a paper on the DMF of HBr. Large deviations are found between the polynomial dipole moment expansion coefficients M_i and those of Carlisle et al. [61]. Comparisons of the DMF in Ref. [63] and the *ab initio* calculations of Harrison [47] with

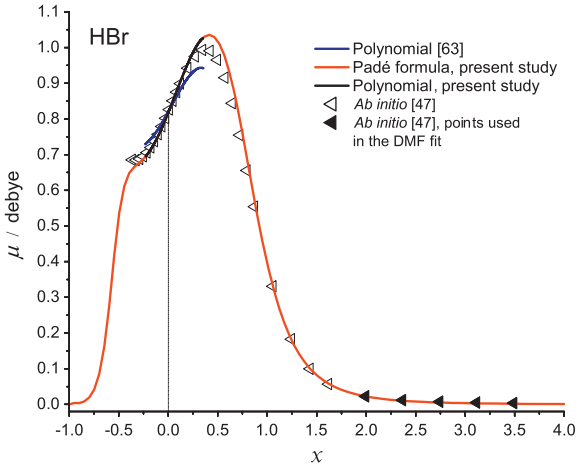

Fig. 5. Comparison of the semi-empirical DMFs (present study and Ref. [63]), and the Harrison [47] *ab initio* DMF for HBr. $x=(r-r_e)/r_e$ is the reduced internuclear distance. Five *ab initio* data points represented by solid triangles are used to constrain our Padé DMF at large internuclear separation.

the DMF determined in the present work are shown in Fig. 5. It is obvious that the DMF of Kiriyama and Rao is very different from the other two. It can be noted that the rotationless matrix element $M_0^1(0)=0.027664D$ used by Kiriyama and Rao [63] is much smaller than the values of $0.037036D$ used by Carlisle et al. [61]. This is due to the fact that Kiriyama and Rao used the fundamental band line-strengths measured by Gustafson and Rao [55], whereas Carlisle et al. used those from Babrov [57]. The latter values seem to be more accurate as they were corroborated by Séoudi et al. [59].

5.2. Line intensity comparison for HBr

Fig. 6 compares eight sets of experimental intensities [55,57,59], HITRAN, and *ab initio* intensities [47] with the present study for eight ro-vibrational bands of $H^{79}Br$. For the fundamental band, the present study agrees very well with the laser measurements by Séoudi et al. [59] but is higher than the measurements of Babrov [57] and Gustafson and Rao [55] at the band origin by approximately 11% and 50%, respectively. HITRAN entries are nearly identical to the measurements of Babrov at the band origin, but start to diverge for $J>5$.

For the first overtone band, a comparison with the present study is shown for four different experimental measurements [30,56,58,60], the HITRAN database, and the *ab initio* calculation [47]. As shown in Fig. 6, results from the present study are in excellent agreement with the recent laser measurements by Chou et al. [60] and the previous study by Babrov et al.[58]. HITRAN entries are approximately 10% lower than those in the present study and are close to the measurements of Bernage and Niay [30]. Interestingly, measurements by Rao et al. [56] have a similar J dependence to those of Babrov et al. [58], but are approximately 25% lower in magnitude. Lastly, line intensities calculated using the *ab initio* DMF of Harrison are about 32% higher than those of the present study.

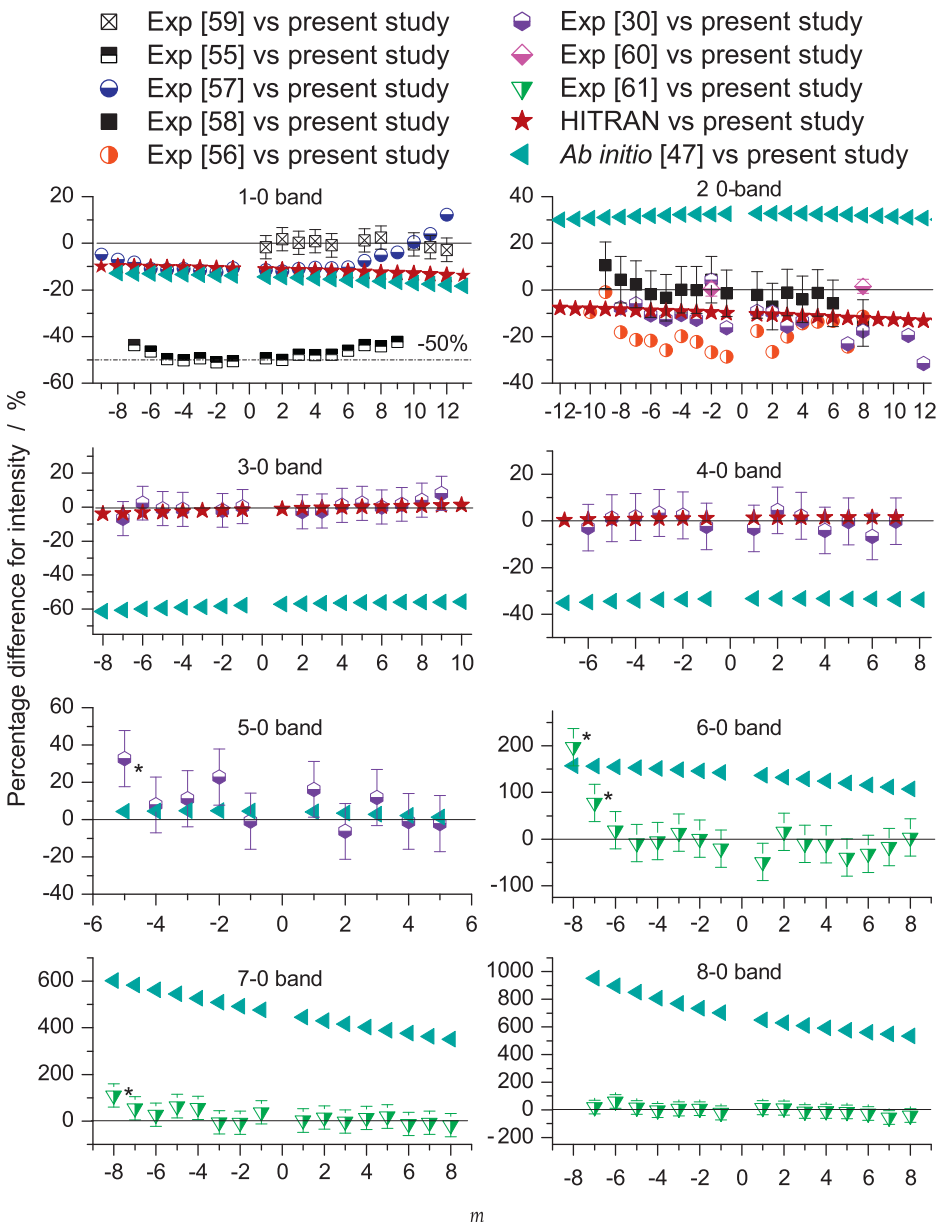

Fig. 6. Comparison of line intensities of the $H^{79}Br$ ro-vibrational bands with the present study as a reference. m is equal to $-J$ for P branch and $J+1$ for R branch lines. Note different scales in the panels of the plot.

For the 3-0, 4-0 and 5-0 bands, experimental data from Bernage and Niay [30], HITRAN, and the theoretical result [47] are compared with results of the present study. In all three cases, the present study agrees well with the measurements by Bernage and Niay, while the *ab initio* results of Harrison [47] differ from the present study by −58%, −34% and 4% for the 3-0 through 5-0 bands, respectively. For the 6-0 through 8-0 bands, we compared the only available experimental data by Carlisle et al. [61] and the *ab initio* values of Harrison [47] with the present study. Harrison's results are almost 14, 46 and 70 times larger than both the measurements of Ref. [61] and the present study. In general, despite the very similar appearances of our DMF and the *ab initio* DMF in Fig. 5 (in the range of x probed by experiments), the theoretical results for HBr are not in satisfactory agreement with the best experimental measurements. The calculated intensities are very sensitive to the precise form of the DMF and its derivatives, and simple "by eye" comparison of the DMF curves can be misleading.

6. HI

6.1. Padé representation of the dipole moment function of HI

There have been several theoretical studies on the electric dipole moment of the HI molecule, both at the equilibrium bond length and as a function of internuclear

separation [64,65]. Experimental infrared line intensities of HI have been reported by Benesch [66], Riris et al. [32], and Niay et al. [31]. Recently, Bulanin et al. [67–69] and Domanskaya et al. [70] published a series of papers on the line intensity measurements of HI. Their measured values are more precise and self-consistent than those of previous studies. A Stark measurement by Van Dijk and Dymanus [71] gives a value of $0.4477 \pm 0.0005D$ for the permanent dipole moment. No experimental measurements of the intensities of the pure rotational transitions of HI have been reported.

Domanskaya et al. [70] have derived an empirical DMF using rotationless matrix elements $M_0^v(0)$, $v=1,2,3,4$ retrieved from the HW fit of ro-vibrational experimental data (which did not include uncertainty-related weights). In the present study, all ro-vibrational matrix elements with appropriate weights were incorporated in the fit of the DMF. A similar approach as in the other hydrogen halides was used to construct the DMF in the form of a Padé approximation. The only difference is that only three *ab initio* dipole moment points at long range were used at this time since the *ab initio* calculation is not as reliable for HI. The derived e_i coefficients are listed in Table 2. The derived DMF together with the *ab initio* data from Harrison [47] are plotted in Fig. 7.

6.2. Line intensity comparison for HI

Fig. 8 compares the line intensities of five ro-vibrational bands calculated using the present DMF with the best available experimental and theoretical studies [33,47]. For the fundamental band, the present study agrees with the experimental values, within uncertainties provided to us by authors of Ref. [67]. However, neither of the theoretical results is in satisfactory agreement with the experimental measurements, with differences of +46% and −78% at the band origin, respectively. Fig. 9 shows the comparison of Einstein A coefficients for the fundamental band calculated using the present DMF, the empirical DMF of Domanskaya et al. [70], and the *ab initio* DMF by Harrison [47]. As is immediately apparent, the Einstein A coefficient in the *P* branch transition is predicted to diminish dramatically. However, the minima of the dips for the empirical DMFs occur at a value of $m=-14$ that differs from $m=-7$ for the theoretical DMF. This dip is a classic example of centrifugal distortion smoothly shifting the algebraic sign of a matrix element overlap integral from positive to negative (see Ref. [72]). In general, PEF anharmonicity will cause the inner loop of the $v=1$ wavefunction to have slightly less amplitude than the outer loop. For the HI molecule, the slope of the DMF is negative near r_e and this has the effect of increasing the amplitude of the overlap integral $\langle v_{=1}|M|v_{=0}\rangle$, giving rise to near perfect cancellation when centrifugal distortion shifts the wavefunction the other way around. This behavior does not occur for the lighter halides, HF, HCl and HBr, because the positive slope of the DMF near r_e magnifies the dominant contribution of the outer loop of the $v=1$ wavefunction to this overlap integral.

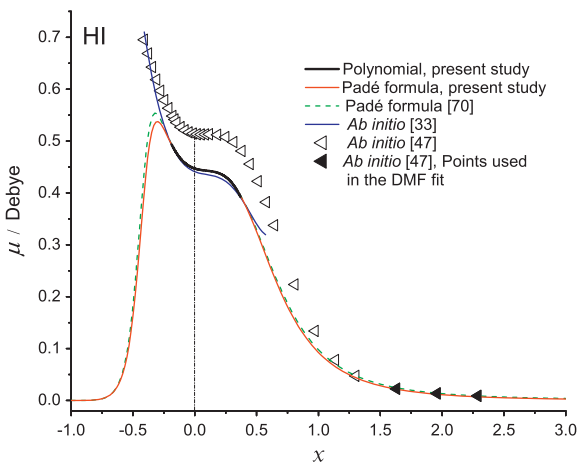

Fig. 7. Comparison for HI of the semi-empirical DMF (present study) with the *ab initio* DMF of Harrison [47]. $x=(r-r_e)/r_e$ is the reduced internuclear distance. Three *ab initio* data points represented by solid triangles are used to constrain our Padé DMF at large internuclear separation.

Fig. 8 shows the comparison between the measurements of Bulanin et al. [68], the theoretical study by Harrison [47], the theoretical study by van Stralen et al. [33], HITRAN, and the present study for the 2-0 through 5-0 bands of $H^{127}I$. In all cases, results from the present study are in excellent agreement with experiments. HITRAN intensities appear to be underestimated by approximately 20%, 7% and 5% for 2-0, 3-0 and 4-0 bands, respectively. It is interesting that results of van Stralen et al. [33] are consistently larger than the experimental measurements, while results from Harrison [47] are smaller, except for the 5-0 band. Nevertheless, both *ab initio* studies are not in satisfactory agreement with experiment.

7. Comparison of the pure vibrational matrix elements

It has been found previously that, for some systems such as the CO molecule [73], the vibrational matrix elements R_0^v decrease smoothly as a function of increasing vibrational quantum number v. A polynomial fit can usually be obtained if one plots the logarithm of R_0^v against quantum number v. Such plots for the hydrogen halides are shown in Fig. 10, for the *ab initio* study of Harrison and the present study. It is clear that no regular pattern is found except for the HF molecule. However, it is reassuring that the semi-empirical and *ab initio* values of R_0^v follow the same patterns.

In the case of HF in Fig. 10, vibrational matrix elements R_0^v from Harrison [47] are in excellent agreement with experimental values except for R_0^3. If one tries to fit the experimental log R_0^v values using a 3rd order polynomial expansion, the only point that fits poorly is R_0^3. In contrast, all theoretical R_0^v, $v=0,1,2,3,4\ldots$, are represented well by a 3rd-order polynomial curve. In addition, two other theoretical results of Kahn et al. [52] and Futami et al. [54] agree well with the Harrison's results for all bands. In detail, the differences between Futami et al. results and the present study are approximately 6%, 1%, 15%, −2% for the 1-0 through 4-0 bands. Since all three independent

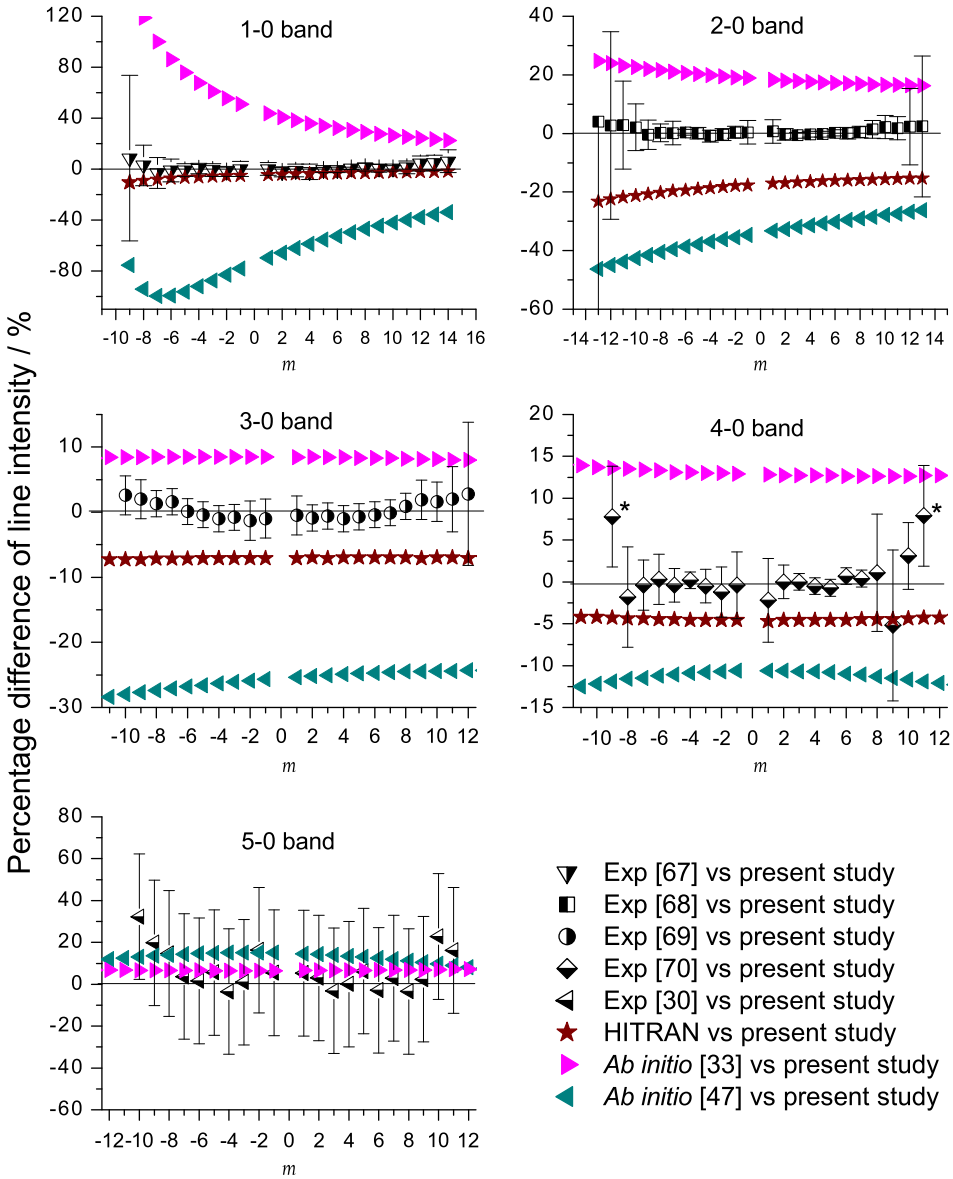

Fig. 8. Comparison of line intensities of the $H^{127}I$ ro-vibrational bands with the present study as a reference. m is equal to $-J$ for P branch and $J+1$ for R branch lines. Note different scales in the panels of the plot.

theoretical studies using different methods consistently predict higher intensities than the current experimental values of Spellicy et al. [18] for the 3-0 band, it would be highly desirable to re-measure the line intensities of this band.

8. Conclusion

Experimental ro-vibrational line intensity measurements for hydrogen halides molecules in their ground electronic states have been carefully evaluated. The best available experimental data were selected to determine the coefficients of the dipole moment power series expansions. For the purpose of extrapolation, we combined these DMFs with theoretical dipole moments at long range to obtain the global DMF in the form of a Padé approximation which is constrained to agree with the power series near equilibrium, and also has some validity at large internuclear separations. The DMFs thus obtained were compared with recent *ab initio* DMFs. Good agreement was found in terms of the shapes of the DMFs for HF, HCl, and HBr. Ro-vibrational line intensities calculated using our semi-empirical model were compared with those calculated from pure *ab initio* DMFs. Except for HF, the *ab initio* intensities were found to be of insufficient quality to replace semi-empirical results. Nevertheless, the *ab initio* study provides a useful constraint for the correct long range behavior of our Padé approximation.

In summary, the DMFs derived in the present study cannot only reproduce the experimental line intensities

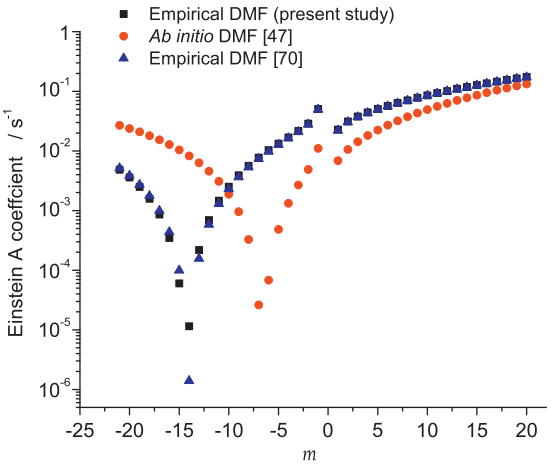

Fig. 9. Einstein A coefficients as a function of m for the HI fundamental band calculated from two empirical DMFs and the theoretical DMF of Ref. [47]. m is equal to $-J$ for P branch and $J+1$ for R branch lines. The dips in the graphs occur at values of m where the Einstein A coefficient in the P branch transition is predicted to diminish dramatically ($\sim 10^{-4}$ Einstein A coefficient following regular pattern). Similar intensity loss phenomenon has also been observed in other systems, such as OH [74].

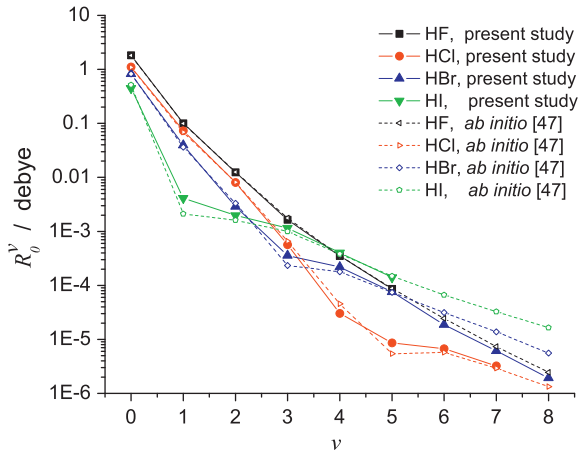

Fig. 10. Experimental and theoretical vibrational dipole moment matrix elements, R_0^v, for hydrogen halides. v is the upper vibrational level.

within experimental errors, but also can be used to estimate the intensities of any other bound state that has not yet been probed experimentally. There are, however, remaining issues with regard to quality and extent of the available experimental data. In particular, the following bands should be revisited experimentally: (1) the 3-0 band of HF, (2) the 4-0 to 7-0 bands of HCl, (3) the 6-0 to 8-0 bands of HBr.

The unusually rapid intensity drop phenomenon for P branch transitions of the fundamental band of HI molecule was observed. This behavior is common in systems that possess strong vibration–rotation interactions, for example, the OH molecule [74].

As will be described in a subsequent publication, the intensities of hydrogen halides and their isotopologues for the next edition of HITRAN were calculated using results of this work. In brief, we have used the polynomial expressions derived here to predict intensities in the range covered by experiments and a Padé approximant was used beyond that. One exception is the $\Delta v=3$ transitions of HF for which *ab initio* values were used due to inconsistencies discussed above. The line lists will constitute the HITRAN2012 data for hydrogen halides but they are already available in the update section of the HITRAN website (http://www.cfa.harvard.edu/hitran/).

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jqsrt.2013.02.005.

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