



Revisiting the integrated infrared intensities and atomic polar tensors of the boron trihalides



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ARTICLE INFO

Article history:

Received 11 March 2016

Received in revised form 1 April 2016

Accepted 5 April 2016

Available online 9 April 2016

Keywords:

Atomic polar tensors

Infrared intensities

Boron trihalides

GAPT

QTAIM

ABSTRACT

Integrated infrared intensities obtained from spectra of the Pacific Northwest National Laboratory (PNNL) database are reported for BF_3 , BCl_3 and BBr_3 . The BF_3 and BCl_3 intensities are compared with values reported much earlier whereas the asymmetric BBr_3 stretching intensity is reported for the first time. Although agreement is good for the BF_3 intensities, the result from the PNNL spectra for the asymmetric BCl_3 stretching vibration is about three times larger than the one reported earlier. The intensities obtained from the PNNL spectra are in excellent agreement with results from QCISD/cc-pVTZ quantum chemical calculations having an rms error of only 32.9 cm^{-1} or 5.9% of the average intensity. Revised experimental atomic polar tensors and GAPT charges are reported for all these molecules.

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1. Introduction

In our recent publication [1] in this journal a glaring inconsistency was reported between experimental [2] and theoretical intensity results for the BCl_3 asymmetric stretching vibration. Although the agreement between theory and experiment was very good for the in-plane and out-of-plane bending intensities, the reported experimental value of $231.3 \text{ km mol}^{-1}$ for the stretching mode was much smaller than the values calculated for 16 different basis sets at the MP2 and QCISD correlation treatment levels, that ranged between 629.6 and $838.4 \text{ km mol}^{-1}$. Even the employment of state-of-the-art computational protocols accounting for core–valence correlation consistent basis sets within the CCSD(T) theory [3] did not improve the results towards the experimental target. Infrared integrated intensity measurements made 50 years ago with low resolution spectrophotometers usually necessitated the use of pressure broadening techniques by means of a transparent inert gas to broaden the rotational lines of the investigated compound so that the band contour was relatively smooth over the slit width of the spectrophotometer. Inadequate pressure broadening can lead to underestimates of the absolute vibrational intensity values [4]. Indeed there is no mention that pressure broadening techniques were used to measure the BCl_3 intensities in Ref. [2].

Spectrophotometers used in the 1960's had typical resolutions [5] of 2 cm^{-1} whereas modern instruments have much smaller values. For example the recorded spectra of BF_3 , BCl_3 and BBr_3 in the Pacific Northwest

National Laboratory database [6] were measured with instruments having resolutions of the order of 0.1 cm^{-1} . For this reason we decided to determine the integrated intensities of BCl_3 along with BF_3 and BBr_3 from these new spectra to compare with existing literature data for these molecules. As will be seen the revised intensity values are in excellent agreement with high level quantum chemical results.

In the early 1970's our group reported experimental polar tensors, GAPT charges and other polar tensor invariant values for BF_3 and BCl_3 calculated from the experimental intensities of McKean [7] and Mandirola [2]. Here these values are revised using the intensities calculated from the PNNL data and the earlier experimental transformations used to transform derivatives from normal coordinates to atomic Cartesian coordinates. Furthermore, polar tensor values for the BBr_3 molecule are also reported for the very first time. These experimental polar tensor values are then used to further understanding of the electronic structures of the boron trihalides.

2. Methodology

The composite spectra were obtained directly from PNNL's website and the bands were numerically integrated using an in-house program by means of trapezoidal integration. To ensure that the program delivers the correct values for the integrals, and therefore for the band intensities, the band integrals reported by Sharpe et al. in their paper [6] were reproduced within a numerical precision of six digits.

The determination of the atomic polar tensors for the boron trihalides followed previous works on this subject [2,7–10]. This procedure requires values of the intensities of all fundamental vibrational modes, but unfortunately the PNNL's spectra are recorded only above

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Table 1
Experimental and calculated vibrational frequencies (in cm^{-1}) for BX_3 ($X = \text{F}, \text{Cl}, \text{Br}$) molecules.

Molecule	Mode	Sym.	Literature [2,7,8,17]		PNNL [6]		QCISD/cc-pVTZ	
			^{10}B	^{11}B	^{10}B	^{11}B	^{10}B	^{11}B
			BF_3	Q_2 δ_{oop}	A_2''	718	691	719
	Q_3 $\nu_{\text{B-X}}$	E'	1504	1453	1505	1453	1557	1502
	Q_4 $\delta_{\text{X-B-X}}$		482	480	–	–	488	486
BCl_3	Q_2 δ_{oop}	A_2''	475	455	–	–	479	465
	Q_3 $\nu_{\text{B-X}}$	E'	995	956	995	955	1019	978
	Q_4 $\delta_{\text{X-B-X}}$		260	249	–	–	259	258
BBr_3	Q_2 δ_{oop}	A_2''	385	370	–	–	418	399
	Q_3 $\nu_{\text{B-X}}$	E'	856	819	856	820	882	844
	Q_4 $\delta_{\text{X-B-X}}$		155	155	–	–	156	155

600 cm^{-1} , making some BX_3 band frequencies and intensities inaccessible. These molecules have three infrared active fundamental bands, two doubly degenerate in-plane modes and one out-of-plane deformation vibration. Since the in-plane bending modes of all the trihalides have frequencies below 500 cm^{-1} their spectra are not contained in the PNNL data bank.

To calculate the BF_3 polar tensor the out-of-plane bending and in-plane stretching intensities were integrated from the PNNL spectra. The in-plane bending intensity measured by McKean [7] was also used. For BCl_3 the in-plane stretching intensity from PNNL that is several hundred times larger than the very weak bending mode intensities measured by Mandirola [2] were used. The PNNL integrated value for the stretching mode, the experimental out-of-plane bending intensity from Pomposiello and Mandirola [8] and the QCISD/cc-pVTZ estimate of the in-plane bending intensity were used for the BBr_3 tensor. It should be noted that all the bending intensities for BCl_3 and BBr_3 are very small and have negligible contributions to the BCl_3 and BBr_3 polar tensors.

For BF_3 and BCl_3 , the \mathbf{A}^{UTL} matrices used to transform the polar tensor from normal coordinates to Cartesian coordinates [9] were the same as those of McKean [7] and Mandirola [2], respectively, but for BBr_3 this matrix from experimental data was not available. So the BBr_3 transformation matrix was calculated with Gaussian09 [11] at the QCISD/cc-pVTZ level, as recommended in the literature [12] for intensities. Although these calculations were carried out within the harmonic approximation there is no evidence of appreciable anharmonic character for any of the BBr_3 vibrations [13].

The molecular coordinates are as used previously [9] with the boron atom at the origin of the Cartesian system and the reference halogen

positioned on the x -axis. The polar tensor and its properties will be presented for just one halogen atom since the values for the others can be readily obtained through similarity transformations using the standard 2D rotation matrix [14].

3. Results and discussion

The experimental and theoretical vibrational frequencies of the boron trihalides are reported in Table 1. As can be seen there the QCISD/cc-pVTZ frequencies, as expected from anharmonicity considerations, are all higher than the experimental values except for the out-of-plane bend of BCl_3 whose values differ by only 1 cm^{-1} . It is worth mentioning that the PNNL spectra for the three molecules display a very good separation of the bands corresponding to the ^{10}B and ^{11}B isotopes, and the band center for each of them agrees very well with the values reported by McKean and Mandirola. As shown in Fig. 1, this low degree of overlap also made possible the integration of the two isotomeric bands separately. Isotopic effects from $^{35}\text{Cl}/^{37}\text{Cl}$ and $^{79}\text{Br}/^{81}\text{Br}$ pairs, on the other hand, are not so evident.

The available experimental and QCISD/cc-pVTZ intensities are presented in Table 2. The older literature values for BF_3 , which were not divided in terms of ^{10}B and ^{11}B moieties, are in good agreement with the theoretical values having a rms error of 35.4 km mol^{-1} . The PNNL values are in much better agreement with an error of only 8.6 km mol^{-1} or 0.8% of the experimental intensity sum, and the agreement is noticeable for both the summed and the individual isotomeric bands. The reader may notice that the ratio between the ^{10}B and ^{11}B intensities from the PNNL spectra are close to 4 as expected from the 80:20 abundance ratio between the two boron isotopes that was used for the theoretical estimates in Table 2. It is noteworthy that the PNNL and theoretical values are all a bit higher than McKean's values. The experimental intensity values given here are about 10% higher than those in Ref. [1] as the conversion factor from $\text{cm}^{-2} \text{ atm}^{-1}$ to km mol^{-1} used here corresponds to 296 K temperature rather than the 273 K value used previously, to make the comparison with the PNNL values easier.

PNNL values are only given for the stretching modes of BCl_3 and BBr_3 . The low frequency bending modes are outside the $600\text{--}6000 \text{ cm}^{-1}$ range reported overall the PNNL database. The large discrepancy between the older stretching band intensity and the PNNL and QCISD/cc-pVTZ values for BCl_3 can be seen in Table 2. The total PNNL value of $695.7 \text{ km mol}^{-1}$ is a sum of the intensities of the $^{10}\text{BCl}_3$ and $^{11}\text{BCl}_3$ bands of the recorded spectrum and is about three times the value of Ref. [2], $231.3 \text{ km mol}^{-1}$, and quite close to the QCISD/cc-pVTZ estimate of $734.3 \text{ km mol}^{-1}$. This corresponds to an error of only 5.6%, very good agreement when compared with errors normally

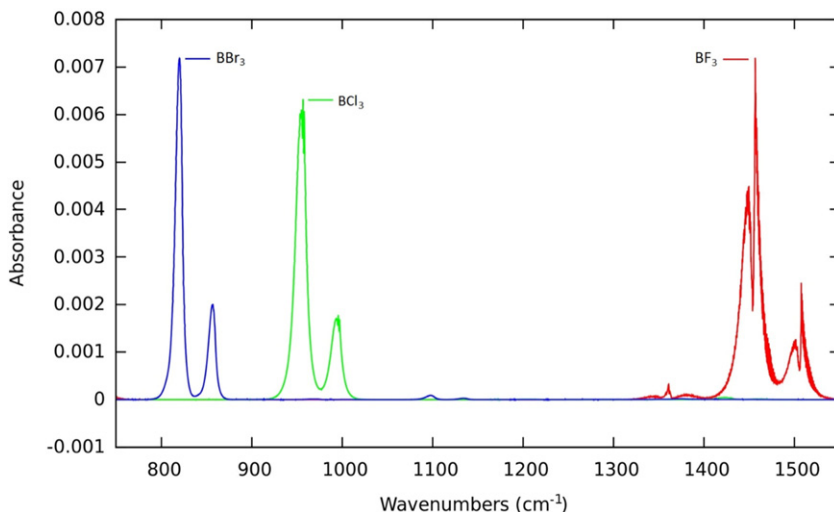


Fig. 1. The PNNL asymmetric stretching bands for the three boron trihalides.

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