The pulsed field ionization-photoelectron (PFI-PE) spectrum of boron trichloride (BCl3) in the region of 93 590–95 640 cm⁻¹ has been measured using vacuum ultraviolet (VUV) laser. At energies 0–1100 cm⁻¹ above the adiabatic ionization energy (IE) of BCl3, the bending vibration progression of BCl3⁺ is clearly resolved in the PFI-PE spectrum, whereas the spectrum at energies 1200–1900 cm⁻¹ above the IE(BCl3) is found to exhibit dense vibrational structure. This observation unambiguously shows that BCl3⁺ in its ground state has $C_{2v}$ symmetry. Ab initio calculations performed at the CCSD(T)/CBS level with high-level corrections are consistent with this observation, indicating that the BCl3⁺($X˜ \;2A_1$) ground state has two long and one short B–Cl bonds.

Furthermore, the CCSD(T)/CBS calculations predict the existence of two BCl3⁺ transitional structures with $D_{3h}$ and $C_{2v}$ symmetries lying ≈800 and 1300 cm⁻¹, respectively, above the BCl3⁺($X˜ \;2B_2$) ground state. This prediction is also consistent with the dense features observed in the PFI-PE spectrum in the region of 1200–1900 cm⁻¹ above the IE(BCl3). The assignment of the PFI-PE vibrational bands gives the $E(x \;2B_2)$ ground state is $X˜ \;2B_2$ lies above the IE(BCl3) is found to exhibit dense vibrational structure.

I. Introduction

Due to the importance of BCl3 in the semiconductor industry, the structure of BCl3 has been subject to studies by various experimental methods and theoretical ab initio quantum chemical calculations. The ground state of neutral BCl3 is known to have a $D_{3h}$ structure with the dominant electronic configuration:

\[ \ldots (5a_1^3)(5e^3)(6a_1^2)(6e^2)(2a_2^2)(2e^2)(2c^2)^2 \times 1A_1. \]

Thus, the ground electronic state of the ion might be expected to be $X \;\bar{2}A_2$, which corresponds to a delocalized positive charge over the whole molecule. However, theoretical calculations showed that three local minima in the potential energy surface may exist, one with $D_{3h}$ and the other two with $C_{2v}$ symmetries.

One $C_{2v}$ structure has one short and two long B–Cl bonds (1S2L) and the other with 2S1L B–Cl bonds. The differences in energy among these minima are around a tenth of an eV. Therefore, it is claimed that at present, ab initio quantum chemical calculations are unable to accurately predict which is the most stable structure. From the structures of infrared (IR) absorption bands for Cl isotopomers of the B–Cl anti-symmetric stretching vibration observed in previous Ne-matrix isolation studies, it has been concluded that BCl3(X) has $D_{3h}$ symmetry. However, as pointed out below, the interpretation of the experimental observation leading to the latter conclusion is not unique. In the previous HeI photoelectron study, only a structureless peak is found in the first electronic band. In the recent threshold photoelectron (TPE) study, partially resolved irregular structures in the region between 11.60 and 11.85 eV were tentatively associated with excitation of the in-plane and out-of-plane bending vibrations. However, owing to the relatively low resolution of the TPE spectrum, a definite determination of the vibrational band positions could not be made. At present, the only known vibrational frequency for BCl3(X) is that of the anti-symmetric B–Cl stretching mode obtained in previous IR absorption studies using the Ne-matrix isolation technique. An accurate adiabatic ionization energy (IE) of BCl3 is also very important to the thermochemistry of the BCl3⁺ ion. The present literature values for the IE range from 11.60 to 11.64 eV and were measured about three decades ago by photoelectron spectroscopy and photoionization mass spectrometry.

Obviously, further experimental and theoretical studies are needed to characterize the structure of BCl3⁺(X) and the IE(BCl3).

On the basis of the Franck–Condon principle, if both the BCl3(X) neutral and the BCl3⁺(X) ion have $D_{3h}$ symmetries, the bending vibration of BCl3(X) should not be excited upon threshold photoionization of BCl3(X), and we should observe only excitation of the B–Cl stretching vibrations of BCl3⁺(X) in the photoelectron spectrum. However, if BCl3⁺(X) is of $C_{2v}$ symmetry with the Cl–B–Cl bond angles different.
from 120°, vibrational bands associated with excitation of the bending vibrations of BC13 \(^+\) are expected to be observed in photoelectron measurements. Therefore, a high-resolution photoelectron study of BC13 can provide direct experimental determination of the BC13 \(^+\) (X) ion structure. In this report, we present a \(\Delta V\)-pulsed field ionization-photoelectron (PFI-PE) study of BC13 near its ionization threshold. The PFI-PE spectrum obtained in the present study exhibits well-resolved vibrational structures, which can be assigned to bending vibrational progressions for BC13 \(^+\). This observation, together with high-level \textit{ab initio} calculations presented in this study, shows that the ground electronic state for BC13 \(^+\) has a \(C_2v\) structure. In addition to obtaining the bending vibrational frequencies for BC13 \(^+\), the assignment also yields a highly precise adiabatic IE for BC13.

The dissociative photoionization process,

\[
\text{BC13} + h\nu \rightarrow \text{BC13}^+ + \text{Cl} + e^-,
\]

was examined previously in a photoionization efficiency (PIE) measurement, yielding a value of 12.30 \pm 0.02 eV for the 0 K threshold or appearance energy (AE) for the formation of BC13 \(^+\) from BC13. We have also examined process (1) using the synchrotron based PFI-PE-photon coincidence (PFI-PEPICO) time-of-flight (TOF) method. \(\Delta V\) has been demonstrated in previous studies that highly precise 0 K AE values for dissociative photoionization processes of small molecules can be determined by the disappearance energy of the parent ion in PFI-PEPICO TOF measurements. \(\Delta V\) and \(\Delta V\) for (process 1) determined in the present synchrotron based PFI-PEPICO experiment, together with the IE(BC13) value obtained in the VUV laser based PFI-PE study, has allowed the determination of the 0 K bond dissociation energy \((D_0)\) for Cl-B-Cl with an error limited only by the precision \((\pm 2 \text{ meV})\) of the PFI-PEPICO measurements. Using the known 0 K heats of formation \((\Delta H^0)\) for Cl and BC13, along with the IE and AE values obtained in the present study, we have determined highly precise \(\Delta H^0\) values for BC13 \(^+\) and BC13 \(^+\).

For guiding the assignment and interpretation of the PFI-PE spectrum for BC13, we have carried out theoretical \textit{ab initio} quantum calculations for the harmonic vibrational frequencies of BC13 and BC13 \(^+\) and Franck-Condon factors (FCF) associated with the BC13 \(^-\) (X) \rightarrow BC13 \((X)\) photoionization transition. \(\Delta V\) The highly precise values for the IE(BC13), the AE(BC13 \(^+\)) for process (1), and the \(D_0(\text{Cl}-\text{B}-\text{Cl})\) obtained in this study can be used to benchmark state-of-the-art theoretical predictions. For this reason, we have undertaken high-level \textit{ab initio} quantum calculations on BC13 and BC13 and their ions at the coupled cluster level with single and double excitations plus quasi-perturbative triple excitations [CCSD(T, Full)] along with approximations to the complete basis set (CBS) limits. \(\Delta V\) Furthermore, high-level corrections were also made in these calculations.

II. Experiment

A. VUV laser PFI-PE measurements

The VUV photoelectron and photoion spectrometer used in this experiment has been described previously. \(\Delta V\) The apparatus is similar to those built by other groups. \(\Delta V\) Briefly, coherent VUV radiation was generated by using the resonance-enhanced four-wave sum-frequency mixing in a pulsed Xe jet. The fundamental frequencies were generated by two dye lasers, which were pumped by the same Nd-YAG laser (20 Hz). One dye laser frequency \((\omega_1)\) was fixed to match the two-photon (20\(\Delta V\)) resonance frequency of the Xe 5\(\Delta V\)5(\(\Delta V\))5P(\(\Delta V\))6P(\(\Delta V\))1(\(\Delta V\)) transition at 80 119.0 cm\(^{-1}\). The frequency \((\omega_2)\) of the other dye laser was tuned from 741 to 634 nm by using four different laser dyes. The two fundamental laser beams were merged by a dichroic mirror and focused by an achromatic lens into a pulsed Xe jet. The apparatus consists of four vacuum chambers; namely, the beam-source chamber, which houses a pulsed valve (nozzle diameter = 0.7 mm) to produce a pulsed molecular beam; the frequency-mixing chamber, which houses the Xe jet (nozzle diameter = 1 mm); the monochromator chamber, which is equipped with a gold coated toroidal grating; and the ionization chamber, which houses ion and electron time-of-flight (TOF) spectrometers together with a set of dual microchannel plate (MCP) detectors for charged particle detection. The drift lengths for the ion and electron TOF spectrometers are 80 and 26 cm, respectively. Two layers of \(\mu\)-metal shield are installed inside the ionization chamber. A separate MCP detector is used in this chamber to monitor the VUV laser intensity.

The PFI-PE and VUV laser signals were fed into two identical boxcars (SR 245, Stanford Research Systems) before further processing by a personal computer. The pulses use to synchronize the two pulsed valves and the Nd-YAG laser were provided by a digital delay generator (DG 535, Stanford Research Systems). The PFI voltage pulses for field ionization were provided by another DG 535 unit with the high voltage option.

The BC13 gas sample (purity = 99.5%) was premixed with He (He 80\%, BC13 20\%) prior to entering the photoionization region as a skinned pulsed (20 Hz) supersonic beam (stagnation pressure = 1000 Torr, stagnation temperature = 298 K). During the experiments, the pressures for the beam source and ionization chambers were maintained at \(\approx \) 1.5 \times 10\(^{-7}\) and 1.5 \times 10\(^{-7}\) Torr, respectively. To avoid sampling of BC13 dimers and clusters, we find that it is necessary to time the VUV laser to hit the early part of the molecular beam pulse. The frequencies of the dye lasers were calibrated by He/Ne and He/Ar opto-galvanic lamps.

B. VUV synchrotron PFI-PEPICO TOF measurements

The PFI-PEPICO TOF measurements for BC13 were conducted using the high-resolution VUV photoelectron-photoion facility of the Chemical Dynamics Beamline at the Advanced Light Source (ALS). \(\Delta V\) The procedures for PFI-PEPICO TOF measurements have been described in detail previously. \(\Delta V\) The experiment was performed at the multi-bunch mode (period = 656 ns, dark gap = 104 ns). In this experiment, Ar was used in the gas filter to suppress higher undulator harmonics with photon energies greater than 15.759 eV. A 1200 lines mm\(^{-1}\) grating was used to disperse the first order undulator harmonic with entrance/exit slits set at 50/50 \(\mu\)m for PFI-PEPICO measurements. The resulting monochromatic VUV beam was focused into the photoionization center of the photoelectron-photoion apparatus. The application of the PFI pulse (height = 9 V \(\text{cm}^{-1}\), width = 200 ns) was delayed by 10 ns with respect to the beginning of the dark gap. The PFI pulse also served to extract photons toward the ion detector. The average accumulation time for the PFI-PEPICO spectrum was about 30 min. The VUV energy calibration was performed by measuring known Rydberg resonances of Xe (88\(\Delta V\), 96\(\Delta V\)) and H-atom absorption lines at the gas filter with monochromator entrance/exit slits set at 30/30 \(\mu\)m. The Stark shift correction of the energy scale for the PFI-PEPICO measurement of BC13 was made based on the assumption that the Stark shifts of the present PFI-PEPICO measurements are identical to those observed for the rare gases measured under the same experimental conditions. \(\Delta V\) The BC13 gas sample (purity = 99.9\%) was obtained from Aldrich and was introduced into the photoionization region as a pure, continuous skinned supersonic beam (stagnation pressure = 700 Torr, nozzle diameter = 127 \(\mu\)m, stagnation temperature = 298 K) as described previously. \(\Delta V\)
photoionization chamber was maintained at a pressure of \(<10^{-6}\) Torr during the experiment.

III. Theoretical ab initio quantum calculations and spectral simulation

A. Semi-empirical simulation of the origin band

As shown below, the PFI-PE origin band for BCl\(_3\)(X) observed in this experiment exhibits a full-width at half-maximum (FWHM) of \(\approx 20\) cm\(^{-1}\). In order to determine the adiabatic IE with a higher precision, it is necessary to simulate the origin band profile by using the rotational line strengths for photoionization transitions. A variety of approaches based on the Buckingham–Orr–Sichel (BOS) scheme to calculate the rotational line strengths for simulation of PFI-PE spectra have been developed.29–31 In the previous PFI-PE study of SO\(_2\), the rotational line strengths for transitions between the neutral and the ion are assumed to be the same as those between the neutral and the Rydberg state.31 We found that this method cannot be used to obtain a satisfactory simulation in the present BCl\(_3\) case. Because the BOS scheme only takes into account direct photoionization processes and excludes interchannel couplings, the latter finding indicates that photoionization of BCl\(_3\) may involve strong perturbations by near resonance intermediate autoionizing states. Thus, we use a semi-empirical method proposed previously by Ng and co-workers to fit the PFI-PE origin band of BCl\(_3\)(X).32 The main purpose of this simulation is to determine a more precise value for the IE(BCl\(_3\)).

The rotational state for BCl\(_3\)(X) and its ion can be labeled by \((\tau^oJ\tau^oM^o)\) and \((\tau^+N^+M^+)\), respectively, where \(J^o\) and \(N^+\) are the rotational quantum numbers for the neutral and ion, respectively. For the ion, we neglect the coupling between the electronic spin and the nuclear rotation. Here, \(\tau^o\) and \(M^o\) (\(\tau^+\) and \(M^+\)) are the numberings of rotational energy levels and the magnetic quantum numbers in the space fixed coordinates for the neutral molecule (ion). The rotational wave functions for the neutral molecule and ion are expressed by linear combinations of the symmetric top wave functions, \(|J^oM^oK^o\rangle\) and \(|N^+M^+K^+\rangle\), respectively, as shown in eqns. (2a) and (2b):32

\[
|\tau^o J^o M^o\rangle = \sum_{K^o} c_{\tau^o K^o} |J^o M^o K^o\rangle \quad (2a) \\
|\tau^+ N^+ M^+\rangle = \sum_{K^+} c_{\tau^+ K^+} |N^+ M^+ K^+\rangle \quad (2b)
\]

Here, \(K^o\) and \(K^+\) are the respective projections of \(J^o\) and \(N^+\) on the molecular fixed frame for the neutral and ion, respectively. We assume the rotational line strength \(I(N^+ \tau^+ J^o \tau^o)\) can be expressed by the equation,

\[
I(N^+ \tau^+ J^o \tau^o) = \alpha(\Delta J)(2J^o + 1)(2N^o + 1) \\
\sum_{K^o K^+} c_{\tau^o K^o} c_{\tau^+ K^+} \beta(\Delta K) \exp\left(-\frac{E_{\text{rev}}}{k T}\right), \quad (3)
\]

where \(\Delta J = N^+ - J^o, \Delta K = K^+ - K^o\) and \(\alpha(\Delta J)\) and \(\beta(\Delta K)\) are the scaling factors for different rotational branches and subbands, respectively. That is, the \(\alpha(\Delta J)\) and \(\beta(\Delta K)\) values can be adjusted to give the best fit of the experimental spectrum. The Boltzmann rotational distribution of the neutral is taken into account in eqn. (3) in the calculation of the intensities for the rotational transitions.

B. High-level ab initio quantum calculations

The adiabatic IE values for BCl\(_2\) and BCl\(_3\) and the 0 K AE(BCl\(_3^+\)) for process (1) were calculated with the CCSD(T, Full)/CBS extrapolation methods.30 Specifically, the geometry optimizations were calculated at the CCSD(T)/aug-cc-pVTZ level of theory. Based on the optimized geometry, single point energy calculations were carried out at the CCSD(T)/aug-cc-pV\(X\)\((\text{X} = Q, 5, 6)\), aug-cc-pV\(X\)\((\text{X} = 5, 6)\) and aug-cc-pV\(X\)\((\text{X} = 3, 3)\) basis sets were used on B and Cl atoms, respectively.33,34 Only the 2s/2p (on B) and 3s/3p (on Cl) valence electrons are correlated in the calculations. The CBS energies were then estimated by a mixed exponential Gaussian function of the form,35

\[
E(X) = E_{\text{CBS}} + B \exp(-X) + C \exp(-X^2), \quad (4)
\]

where \(X = 4, 5\) and 6 for aug-cc-pV\((\text{Q} + \text{d})\)Z, aug-cc-pV\((\text{5} + \text{d})\)Z, and aug-cc-pV\((\text{6} + \text{d})\)Z, respectively. The zero-point vibrational energy \(E_{\text{ZPE}}\) corrections were evaluated according to the sum \(\frac{1}{2} \sum_\omega \omega, \) where \(N = 3\) is the number of atoms and \(\omega,\) values are the vibrational frequencies obtained at the CCSD(T)/aug-cc-pVTZ level.36 The core-valence electron correlation \((1s)\) electrons on B and \(2s/2p\) electrons on Cl) contributions \((E_{\text{CBS}})\) were obtained at the CCSD(T) level using aug-cc-pwCVQZ basis set.37,38 The scalar relativistic effect \((E_{\text{R}})\) was computed at the configuration interaction with singles and doubles (CISD) level of theory with cc-pVQZ basis set, and is taken as the sum of the mass-velocity and one-electron Darwin terms in the Breit–Pauli Hamiltonian.39 The atomic spin–orbit correction \((E_{\text{SO}})\) of \(-0.036\) eV for Cl is based on the experimental excitation energies of Moore.40 All CBS energy calculations and correlation contributions were performed using the MOLPRO 2002.6 program suite41 and individual energetic contributions to IE(BCl\(_3\)), IE(BCl\(_3^+\)) and AE(BCl\(_3^+\)) are listed in Table 1. We have also calculated the \(\Delta H_0\) for BCl\(_3^+\), BCl\(_3\) and BCl\(_3^+\) at the CCSD(T, Full)/CBS level for comparison with experimental determination. In the \(\Delta H_0\) calculation, the experimental values \(\Delta H_0(B) = 133.27\) kcal mol\(^{-1}\) and \(\Delta H_0(Cl) = 28.58\) kcal mol\(^{-1}\) are used.

Table 1 also lists the CCSD(T, Full)/CBS energetic predictions for the ground state structure of BCl\(_3\) and the three BCl\(_3^+\) structures, i.e., BCl\(_3^+\) (\(C_{2\text{v}}, 1\text{S}_{2\text{L}}\)), BCl\(_3^+\) (\(D_{3\text{h}}, 1\text{S}_{2\text{L}}\)) and BCl\(_3^+\) (\(C_{2\text{v}}, 2\text{S}_{1\text{L}}\)). As expected, the ground state for BCl\(_3\)(X) is predicted to have a \(D_{3\text{h}}\) symmetry. However, the CCSD(T, Full)/CBS calculation predicts that the most stable geometry for BCl\(_3^+\) is the BCl\(_3^+\) (\(C_{2\text{v}}, 1\text{S}_{2\text{L}}\)) structure. This prediction is contrary to the results of previous DFT calculations which predict a \(D_{3\text{h}}\) structure for BCl\(_3^+\)(X).10,11 The BCl\(_3^+\) (\(D_{3\text{h}}, 1\text{S}_{2\text{L}}\)) and BCl\(_3^+\) (\(C_{2\text{v}}, 2\text{S}_{1\text{L}}\)) structures are transition structures (as found to have one imaginary frequency for each) lying at energies 0.10 eV (806 cm\(^{-1}\)) and 0.16 eV (1290 cm\(^{-1}\)), respectively, above the ground BCl\(_3^+\) (\(C_{2\text{v}}, 1\text{S}_{2\text{L}}\)) structure. We note the IE prediction of 11.606 eV for the formation of BCl\(_3^+\) (\(1\text{S}_{2\text{L}}\)) from BCl\(_3\)(X) is lower than the IE value of 11.62 eV obtained in the recent CCSD(T)/CBS calculation by 0.013 eV. The lower IE value obtained in the present calculation is due to the fact that the CCSD(T)/CBS calculation of ref. 10 has not taken into account the \(E_{\text{ZPE}}\) correction. As expected, the bond angle between the two long B–Cl bonds for BCl\(_3\)(\(1\text{S}_{2\text{L}}\)) is found to be smaller than 120°, whereas the bond-angle between the two short B–Cl bonds for BCl\(_3^+\)(\(2\text{S}_{1\text{L}}\)) is larger than 120°.42 The bond lengths (\(r\)) and bond angles (\(\angle\)) calculated for the ground state structures of BCl\(_3\) and BCl\(_3^+\)(\(1\text{S}_{2\text{L}}\)) at the CCSD(T)/aug-cc-pVTZ level are compared in Table 2.

The harmonic vibrational frequencies calculated at the CCSD(T)/aug-cc-pVTZ level and MP2/aug-cc-pVPTZ levels for BCl\(_3\) and BCl\(_3^+\)(\(1\text{S}_{2\text{L}}\)) are summarized in Table 3 to compare with known experimental vibrational frequencies. We have also obtained vibrational frequencies for BCl\(_3^+\) with anharmonicity corrections. However, the calculation of the anharmonic frequencies for BCl\(_3^+\)(\(1\text{S}_{2\text{L}}\)) was unsuccessful, leading to physically unacceptable values, indicating the ground potential surface for BCl\(_3^+\) is highly anharmonic. This
observation is consistent with the expectation that the ground state potential surface for BCl$_3$ is highly perturbed by the close proximity of the BCl$_3$($D_{3h}$) and BCl$_3$($C_{2v}$, 251I) transition structures.

IV. Results and discussion

A. PFI-PE spectrum for BCl$_3$($X$)

The PFI-PE spectra of BCl$_3$ near its ionization onset in the VUV energy range of 93 600–95 000 cm$^{-1}$ and 95 065–95 740 cm$^{-1}$ obtained using a PFI field of 0.5 V cm$^{-1}$ are shown in Figs. 1 and 2, respectively. For the VUV energy range of 94 940–95 065 cm$^{-1}$, the efficiency for four-wave sum-frequency mixing is too low such that reliable PFI-PE signals could not be measured. The energy scales of the PFI-PE spectra have been corrected for the Stark shift ($\Delta E$), which is assumed to obey the relation of $\Delta E = 4.1\sqrt{F}$ cm$^{-1}$, where $F$ is the PFI field in V cm$^{-1}$.42 We note that the PFI-PE intensities shown in the region of 93 600–93 800 cm$^{-1}$ represent the average of several scans made at higher PFI fields ($\leq 1$ V cm$^{-1}$). As shown in Fig. 1, the PFI-PE signals in this energy range are essentially within the noise level. Table 4 lists the positions of PFI-PE vibrational bands resolved in the PFI-PE spectrum of Fig. 1.

There are several BCl$_3$ isotopomers with significant intensities, including $^{35}$Cl$^{11}$B$^{35}$Cl$_3$, $^{35}$Cl$^{13}$B$^{35}$Cl$_3$, $^{37}$Cl$^{11}$B$^{35}$Cl$_3$ and $^{37}$Cl$^{13}$B$^{35}$Cl$_3$. The $^{35}$Cl$^{12}$B$^{35}$Cl$_3$ and $^{37}$Cl$^{12}$B$^{35}$Cl$_3$ isotopomers with the natural abundance ratio of 3:1 are expected to have the largest contributions to the PFI-PE spectrum. The only known vibrational frequency of BCl$_3$($X$) is the antisymmetric B–Cl stretching frequency obtained by IR absorption studies using the Ne-matrix isolation technique.4,6 In the latter studies, the IR absorption band was assigned as the degenerate B–Cl antisymmetric stretching ($\nu_5$) band of BCl$_3$($X$), suggesting a $D_{3h}$ symmetry for BCl$_3$($X$).4,6 The rationale for such an assignment was that the IR absorption band profile has a multiplet structure, which is consistent with a doubly degenerate vibration of a BCl$_3$($D_{3h}$) structure.4 However, this assignment is not unique. The multiplet structure of the IR band observed at 1100 cm$^{-1}$ in the matrix isolation study6 can be attributed to excitation of the B–Cl stretching ($\nu_2$) mode of the isotopomers $^{35}$Cl$^{11}$B$^{35}$Cl$_2$ and $^{37}$Cl$^{11}$B$^{35}$Cl$_2$ with a $C_{2v}$ structure. Our $ab initio$ MP2 vibrational frequency calculation shows that the $\nu_2$ ($\sigma_a$) frequencies of $^{35}$Cl$^{11}$B$^{35}$Cl$_2$ and $^{37}$Cl$^{11}$B$^{35}$Cl$_2$ differ by $\approx 3$ cm$^{-1}$. The fact that the two major peaks of the IR multiplet have the relative intensities of 3:1 and the separation of $\approx 3$ cm$^{-1}$ as reported in ref. 6 can be taken as strong support of a $C_{2v}$ structure for BCl$_3$($X$).

For the symmetric B–Cl bending vibrational frequency of BCl$_3$($X$), theoretical calculations show that the frequency spread due to different isotopomers is $\approx 4$ cm$^{-1}$. Because of the limitation of the achieved signal-to-noise ratios and PFI-PE resolutions, we are not able to resolve the contributions from different isotopomers. The band position given in Table 4 should be regarded as those from $^{35}$Cl$^{35}$B$^{35}$Cl$_2$.

On the basis of the theoretical calculations, the PFI-PE vibration bands resolved in Fig. 1 should be associated with the BCl$_3$($X$ $^2$B$_2$) $\leftrightarrow$ BCl$_3$($X$ $^2$A$^1$) photoionization transition. Because the equilibrium $\angle$($C$–B–Cl) and ($B$–Cl) of BCl$_3$ ($X$ $^2$A$^1$) are different from those of BCl$_3$($X$ $^2$B$_2$), we expect that the symmetric bending mode $\nu_2$ ($\sigma_a$) and the symmetric B–Cl stretching modes, $\nu_1$ ($\sigma_a$) and $\nu_5$ ($\sigma_g$), for BCl$_3$($X$ $^2$B$_2$) are excited upon photoionization of BCl$_3$($X$ $^2$A$^1$) ($\theta$). As shown in Table 2, the differences in $\angle$($C$–B–Cl) and ($B$–Cl) between the neutral molecule and the ion are predicted to be 24$^\circ$ and 0.029–0.077$^\circ$, respectively. We have performed FCF calculations based on the predicted harmonic frequencies. The FCF calculations18 predict the dominant excitation of the $\nu_2$ ($\sigma_a$) vibration progression. However, the calculated FCFs based on $ab initio$ harmonic frequencies match poorly with the vibrational bands resolved in the PFI-PE spectrum, indicating that the potential energy surface for BCl$_3$($X$ $^2$B$_2$) is highly anharmonic. A more sophisticated FCF calculation beyond the harmonic approximation is required to simulate the observed PFI-PE spectrum of Fig. 1. The perturbation by near resonance autoionizing Rydberg states can also contribute to the

<table>
<thead>
<tr>
<th>BCl$_3$</th>
<th>BCl$<em>3$($D</em>{3h}$)</th>
<th>BCl$<em>3$($C</em>{2v}$, 251I)</th>
<th>BCl$<em>3$($C</em>{2v}$, 251I)</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extrapolated CBS$^b$</td>
<td>$-1403.232$</td>
<td>$-1403.797$</td>
<td>$82$</td>
<td>$-1403.797$</td>
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<tr>
<td>$E_{PFI}$$^{c}$</td>
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<td>22</td>
<td>0.007</td>
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<tr>
<td>$E_{CV}$$^{d}$</td>
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<td>54</td>
<td>$-1.022$</td>
<td>25</td>
</tr>
<tr>
<td>$E_{SR}$$^{e}$</td>
<td>$-4.218$</td>
<td>04</td>
<td>$-4.218$</td>
<td>63</td>
</tr>
<tr>
<td>$\Delta E_{corr}$</td>
<td>11.832</td>
<td>11.627</td>
<td>$0.008$</td>
<td>$0.009$</td>
</tr>
<tr>
<td>CBS IE or AE$^f$</td>
<td>IE = 11.707$^b$</td>
<td>IE = 11.606$^b$</td>
<td>IE = 11.766$^b$</td>
<td>IE = 7.383$^b$</td>
</tr>
</tbody>
</table>

This work, IE or AE |

IE = 11.6410 ± 0.0002$^d$ |

AE = 12.492 ± 0.002$^d$ |

$^a$ Total energies are given in Hartrees, energy differences (IEs) and IE are in eV. $^b$ Extrapolated from the frozen-core total energies using eqn. (1). $^c$ Taken as the sum $\left(\sum_{n=1}^{N} \omega_n\right)$ of all vibrational frequencies at CCSD(T)/aug-cc-pVTZ. $^d$ Core-valence electrons correlation obtained as the difference of all-electron and frozen-core energies at CCSD(T) using aug-cc-pwCVQZ basis set. $^e$ Scalar relativistic effect calculated at CSDI/aug-cc-pV5Z. $^f$ Atomic spin–orbit coupling for chlorine is taken from ref. 40.
poor match between experimental vibrational band intensities and theoretical FCFs. Because of the poor match with experimental vibrational band intensities, the calculated FCFs based on the harmonic approximation are not shown here.

An inspection of the pattern of PFI-PE vibrational bands shows that the PFI-PE peaks can be grouped into two progressions with spacings in the range of ≈140–210 cm⁻¹ (see markings in Fig. 1). We note that these spacings are significantly lower than the theoretical harmonic ν₊(a₁) frequency of 231–249 cm⁻¹. We assume that the strong vibrational progression results from photoionization transitions from the BCl₃(X 1A₁; 00) ionization transition with the PFI-PE origin band. Fig. 3 compares the best simulated curve (lower spectrum) for the BCl₃(X 2B₂; 00) → BCl₃(X 1A₁; 00) ionization transition with the PFI-PE origin band (upper spectrum). The agreement between the experimental and simulated spectra are reasonable, but not perfect. Because all rotational transitions within a rotational branch or sub-branch are scaled with the same scaling parameter, the present simulation scheme cannot account for forced rotational autoionization and local perturbation by near resonance autoionizing states, which is known to occur in PFI-PE measurements. The parameters used in the simulation are listed in Table 5. The rotational constants for BCl₃(X 2B₂) and BCl₃(X 1A₁) used in the simulation are calculated based on the theoretical structures of the CCSD(T)/aug-cc-pVTZ calculations (see Table 2). The instrumental function for PFI-PE measurements is assumed to be a Gaussian function with a FWHM of 1.6 cm⁻¹. The scaling factors [ς(ΔJ) and β(ΔK)] for the rotational branches are: ς(1) = ς(−1) = 1, ς(0) = ς(±2) = 3 and β(0) = β(±2) = 1. The simulation shows that the rotational temperature for BCl₃ molecules achieved in the supersonic expansion is ≈50 K. Most importantly, the simulation yields the IE(BCl₃) = 93 891 ± 2 cm⁻¹ (11.6410 ± 0.0003 eV) after taking into account the Stark shift correction. The main contributions to the error limit arise from the wavelength

Theoretical and experimental vibrational frequencies (cm⁻¹) of BCl₃(X 1A₁) and BCl₃(X 2B₂)

<table>
<thead>
<tr>
<th>Vibrational frequencies</th>
<th>BCl₃(D₁₉)</th>
<th>Theoretical and experimental methods</th>
<th>ν₁(d')</th>
<th>ν₁(b')</th>
<th>ν₂(a₂')</th>
<th>ν₂(a')</th>
<th>ν₃(b')</th>
<th>ν₃(a')</th>
<th>ν₄(b')</th>
<th>ν₄(a')</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theory⁵</td>
<td>MP2/aug-cc-pVTZ</td>
<td>256/255</td>
<td>256/255</td>
<td>460/457</td>
<td>482/477</td>
<td>977/963</td>
<td>977/963</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSD(T)/aug-cc-pVTZ</td>
<td>252/251</td>
<td>252/251</td>
<td>460/457</td>
<td>471/467</td>
<td>972/957</td>
<td>972/957</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment⁷</td>
<td>243.0</td>
<td>243.0</td>
<td>407.6</td>
<td>471.0</td>
<td>986.3</td>
<td>986.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BCl₃(IS2L)</td>
<td>ν₁ (b₂)</td>
<td>ν₂ (a₁)</td>
<td>ν₂ (b₁)</td>
<td>ν₃ (a₁)</td>
<td>ν₅ (a₁)</td>
<td>ν₆ (b₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Theory⁵</td>
<td>MP2/aug-cc-pVTZ</td>
<td>235</td>
<td>249</td>
<td>384</td>
<td>400</td>
<td>1169</td>
<td>3138</td>
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<td></td>
</tr>
<tr>
<td>CCSD(T)/aug-cc-pVTZ</td>
<td>226</td>
<td>231</td>
<td>385</td>
<td>474</td>
<td>1146</td>
<td>715</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment</td>
<td>IR/Ne Matrix⁶</td>
<td>194</td>
<td>209</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3

Vibrational frequencies

VUV Energy (cm⁻¹)

9300 9375 9400 9425 9450 9475 9500 9525 9550 9575 9600 9625 9650 9675 9700 9725 9750 9775 9800

VUV intensity (arb. units)

0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

Fig. 1 The PFI-PE spectra of BCl₃ in the VUV energy range of 93 600–95 000 cm⁻¹ (top energy scale). The bottom energy scale represents the measure with respect to the IE(BCl₃) at 93 891 cm⁻¹. The relative intensities have not been normalized by the corresponding VUV intensities.

VUV Energy (cm⁻¹)

9400 9500 9600 9700 9800

VUV intensity (arb. units)

0.0 0.1 0.2 0.3 0.4 0.5

Fig. 2 The PFI-PE spectra of BCl₃ in the VUV energy range of 95 000–96 800 cm⁻¹ (top energy scale). The bottom energy scale represents the measure with respect to the IE(BCl₃) at 93 891 cm⁻¹. The relative intensities have not been normalized by the corresponding VUV intensities.

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Table 4 Assignments of PFI-PE vibrational bands for BCl$_3$(X $^2$B$_2$)

<table>
<thead>
<tr>
<th>Main progression$^a$</th>
<th>Hot band progression$^b$</th>
<th>Band positions(cm$^{-1}$)</th>
<th>Relative energy(cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta^+$</td>
<td>$v_1^+$ = 1</td>
<td>93 891</td>
<td>93 841</td>
</tr>
<tr>
<td></td>
<td>$v_1^+$ = 2</td>
<td>93 976</td>
<td>94 037</td>
</tr>
<tr>
<td></td>
<td>$v_2^+$ = 2</td>
<td>94 071</td>
<td>94 100</td>
</tr>
<tr>
<td></td>
<td>$v_2^+$ = 3</td>
<td>94 206</td>
<td>94 206</td>
</tr>
<tr>
<td></td>
<td>$v_2^+$ = 4</td>
<td>94 367</td>
<td>94 367</td>
</tr>
<tr>
<td></td>
<td>$v_2^+$ = 5</td>
<td>94 516</td>
<td>94 516</td>
</tr>
<tr>
<td></td>
<td>$v_2^+$ = 6</td>
<td>94 662</td>
<td>94 662</td>
</tr>
<tr>
<td></td>
<td>$v_2^+$ = 7</td>
<td>94 771</td>
<td>94 771</td>
</tr>
<tr>
<td></td>
<td>$v_2^+$ = 8</td>
<td>94 907</td>
<td>94 907</td>
</tr>
</tbody>
</table>

$^a$ Vibrational progression for the transitions BCl$_3$(X $^1$A$_1$; $\theta^+$) $\rightarrow$ BCl$_3$(X $^2$B$_2$; $\nu_1^+$ = 1, 2, 3, 4, 5 and 6).

$^b$ Band positions are peak positions of the vibrational bands except that for BCl$_3$(X $^2$B$_2$; $\theta^+$), which is determined by simulation. Because the band positions for different isotopomers are not resolved, the band position given here are assumed to be from $^1$ClI/$^1$B/$^1$Cl.$^1$. $E$ Energies measured with respect to the BCl$_3$(X $^2$B$_2$; $\theta^+$) origin band. $^2$ Calculated based on the theoretical geometries for BCl$_3$(X $^1$A$_1$) and BCl$_3$(X $^2$B$_2$) obtained at the CCSD(T)/aug-cc-pVTZ level.

Table 5 Parameters used to simulate the PFI-PE origin band for the photoionization transition BCl$_3$(X $^2$B$_2$) $\rightarrow$ BCl$_3$(X $^1$A$_1$)

<table>
<thead>
<tr>
<th>Fitting parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotational constants/cm$^{-1}$ a</td>
<td>BCl$_3$(X $^1$A$_1$); $A$ = 0.104, $B$ = 0.104, $C$ = 0.052</td>
</tr>
<tr>
<td>Scaling factors</td>
<td>$\beta(\Delta \Omega) = \beta(\Omega = 1 = \Omega = 2 = 1 = \Omega = 3); \beta(\Delta \Omega) = \beta(\Omega = 1 = \Omega = 2 = 1)$</td>
</tr>
<tr>
<td>Rotational temperature</td>
<td>50 K</td>
</tr>
<tr>
<td>Instrumental resolution</td>
<td>Gaussian function: FWHM = 1.6 cm$^{-1}$</td>
</tr>
</tbody>
</table>

Calibration of the dye lasers and the uncertainty of the Stark shift correlation. The IE value determined in the present PFI-PE study agrees with one of the previous photoelectron studies, but has a significantly smaller error limit (see Table 6). The IE value determined in the present study is 0.035 eV higher than the theoretical CCSD(T)/CBS prediction of 11.606 eV. This discrepancy of 0.035 eV could be partly due to the use of harmonic vibrational frequencies such as the ZPVE correction in the IE calculation. As mentioned previously, the potential energy surface for BCl$_3$ is highly anharmonic. Thus, the use of theoretical harmonic vibrational frequencies of BCl$_3$(X $^2$B$_2$) for the ZPVE correction may not be appropriate. A multi-dimensional vibrational frequencies calculation beyond the harmonic approximation is required for a more precise ZPVE correction.

VUV Energy(cm$^{-1}$)

93 860 93 870 93 880 93 890 93 900 93 910 93 920

Exp. Sim.
position of 194 cm⁻¹ measured with respect to 00⁺ (see Table 4). This peak is assigned as the ν₂ = 1 → ν₂⁺ = 1 hot band transition. Here we assume that the intensity for the ν₁ = 1 → ν₁⁺ = 0 photoionization transition is too low to be observed due to the signal-to-noise limitation. We note that the FCF calculations predict the intensity for the formation of BCl₃⁺(X 2B₂) in ν₂⁺ = 1 is higher than that in ν₂⁺ = 1 from BCl₃[X 1A₁; νᵣ(e) = 1]. The weak vibrational bands at 94 037, 94 206, 94 367, 94 516, 94 662 and 94 824 cm⁻¹, which have the corresponding energies of 146, 315, 476, 625, 771 and 933 cm⁻¹ above the IE(BCl₃), are tentatively assigned to the transitions BCl₃[X 1A₁; νᵣ(e) = 1] → BCl₃⁺(X 2B₂, ν₂⁺ = 2, 3, 4, 5, 6 and 7), respectively. By using the ν₂⁺ vibrational level positions determined based on the strong vibrational progression, we have obtained predictions for the ν₂⁺ vibrational level positions of the weak (hot-band) vibrational progression (see values in parentheses of Table 4). The discrepancies between the corresponding predictions and observed band positions are ≤ 12 cm⁻¹. The weak PFI-PE vibrational band at 93 976 cm⁻¹ [85 cm⁻¹ above the IE(BCl₃)] is assigned to ν₁ = 1 → ν₁⁺ = 2. Taking into account the ν₁ frequency, the transition energy for ν₁ = 1 → ν₁⁺ = 2 is 328 cm⁻¹.

### B. PFI-PEPICO TOF measurements of BCl₃

Selected PFI-PEPICO TOF spectra measured at VUV energies of 12.4983, 12.4835, 12.4704, 12.4310 and 12.4113 eV are depicted in Fig. 4. These spectra have been background subtracted using procedures described in previous studies. These spectra reveal two TOF peaks at 43.0 and 51.5 μs, corresponding to the formation of BCl₂⁺ and BCl₃⁺, respectively. The TOF peaks are broadened resulting from contributions of the isotopomers of BCl₃. As the photon energy is increased from 12.4113 to 12.4983 eV, the intensity of the BCl₃⁺ parent ion was found to decrease compared to that of the BCl₂⁺ daughter ion. Assuming that all the thermal rotational and vibrational energies are available for dissociation, we expect to observe daughter BCl₂⁺ ions at energies below the 0 K AE for process (1) because of the Boltzmann distribution of rovibrational excitations. At a photon energy of 12.4835 eV, only a small residual parent ion peak is observed in the TOF spectrum. The parent ion peak is found to completely disappear at the photon energy of 12.4983 eV, indicating that the 0 K AE(BCl₂⁺) from BCl₃ is lower than this energy.

The procedures used in the breakdown curves (Fig. 5) for BCl₃⁺ and BCl₂⁺ involve measurements of the photon energy dependence of the relative intensities for BCl₃⁺ [I(BCl₃⁺)] and BCl₂⁺ [I(BCl₂⁺)], which are obtained by their respective TOF peak areas observed in the PFI-PEPICO TOF spectra. The fractional abundances of BCl₃⁺ and BCl₂⁺ are defined as I(BCl₃⁺)/I(BCl₂⁺) and I(BCl₂⁺)/I(BCl₃⁺), respectively. Fig. 5 depicts the breakdown diagrams derived from the PFI-PEPICO TOF measurements. The breakdown diagram basically consists of the fractional abundances for the parent BCl₃⁺ ion (open squares) and the daughter BCl₂⁺ ion (open circles) plotted as a function of photon energy (hν) in eV. Error bars due to counting statistics are about the size of individual data points shown in Fig. 5.

The breakdown diagram of Fig. 5 has also been simulated using a procedure described previously. 44 In the ideal situation with a 0 K gas sample, the breakdown curve for the parent

<table>
<thead>
<tr>
<th>IE(BCl₃)/eV</th>
<th>AE(BCl₂⁺)/eV</th>
<th>ΔHᵣ⁰/kcal mol⁻¹</th>
<th>BCl₂⁺</th>
<th>BCl₃⁺</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Experimental</th>
<th>11.6410 ± 0.0003</th>
<th>12.495 ± 0.002</th>
<th>163.4 ± 0.5</th>
<th>−96.08 ± 0.5</th>
<th>172.36 ± 0.5</th>
<th>0.854 ± 0.002</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.60 ± 0.02</td>
<td>12.30 ± 0.02</td>
<td>159 ± 0.7</td>
<td>11.64 ± 0.02</td>
<td>11.62</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Theoretical: 11.606 ± 0.0003 12.486 ± 0.002 161.6 ± 0.5 −97.7 ± 0.5 170.0 ± 0.5 0.880 ± 0.0002

* The values in bold fonts are recommended values. Ref. 17. ΔHᵣ⁰ value, ref. 17. Ref. 3. Ref. 2. Ref. 3. Ref. 1. CCSD(T,Full)/CBS calculations with high-level corrections.
In order to obtain a prediction for the 0 K AE for reaction (1), we have performed CCSD(T, Full)/CBS calculations with high-level corrections on the total energies for BCl$_3$, BCl$_3^+$, BCl$_2$, BCl$_2^+$, and Cl (see Table 1). After taking into account of the high-level corrections (ΔE$_{2PVE}$ + ΔE$_{CV}$ + ΔE$_{ER}$ + ΔE$_{SO}$), the CCSD(T, Full)/CBS calculation yields an AE value of 12.486 eV for reaction (1), which is in excellent agreement with the experimental AE of 12.495 ± 0.002 eV. The CCSD(T, Full)/CBS calculations also yield a value of 7.383 eV for the IE(BCl$_3$).

C. Thermochemistry of the BCl$_2$/BCl$_3$ and BCl$_3$/BCl$_3^+$ system

Table 6 lists the IE values for BCl$_3$, 0 K AE(BCl$_3^+$) for process (1), 0 K heat of formation (ΔH$_{0}$) values for BCl$_3^+$, BCl$_3$, and BCl$_2^+$, and D$_0$ value for Cl$_2$B$^-$–Cl obtained from the literature and those determined in the present study. The values in bold are obtained in the present study. Using the 0 K AE(BCl$_3^+$) = 12.495 ± 0.002 eV for process (1) and the IE(BCl$_3$) = 11.6410 ± 0.0002 eV, we have determined the D$_0$(Cl$_2$B$^-$–Cl) = 0.854 ± 0.002 eV. The 0 K bond dissociation energy for the neutral, i.e., D$_0$(Cl$_2$B–Cl), is known poorly. Using the CCSD(T, Full)/CBS predictions for the IE(BCl$_3$) = 7.383 eV and 0 K AE(BCl$_3^+$) = 12.486 eV, we obtained a prediction of D$_0$(Cl$_2$B–Cl) = 5.103 eV. It is interesting to observe the significant decrease of more than 4 eV in bond energy from the neutral to the ion. The low D$_0$(Cl$_2$B$^-$–Cl) is consistent with the formation of the very stable linear BCl$_3^+$ ion. Since the IE(BCl$_3$) is a measure between the energy of BCl$_2$ and that of BCl$_3^+$, the very stable BCl$_3^+$ is also consistent with a low IE(BCl$_3$) value.

The ΔH$_{0}$(BCl$_3$) = −96.08 ± 0.5 kcal mol$^{-1}$ and ΔH$_{0}$ (Cl) = 28.90 ± 0.001 kcal mol$^{-1}$ are well known. A0

In order to obtain a prediction for the 0 K AE of BCl$_3$ to BCl$_2$ and Cl, we calculated the density of vibrational states using the Beyer-Swinehart direct count algorithm. No efforts were made to analyze the cold components of the parent and daughter ion signal because the ion observed TOF peaks are broadened by the unresolved mass distributions of the BCl$_3^+$ and BCl$_3^-$ isotopomers. The overall fits to the breakdown data derived from the PFI-PEPICO TOF measurements are shown as solid lines in Fig. 5. The simulation also takes into account the uniform coincidence background of 3%, which results from the dispersion of prompt electrons into the dark gap of the synchronotron period. The simulation yields a value of 12.486 eV for the 0 K AE of reaction (1).

We have demonstrated previously in PFI-PEPICO TOF experiments that the disappearance energy for the parent ion is an intrinsic feature for identifying the 0 K AE of the dissociation process. If the coincidence measurement has a constant coincidence background as is observed in the present case, the breakdown curve should exhibit a break at the 0 K AE (see the break marked by arrow in Fig. 5). The 0 K AE(BCl$_3^+$) = 12.495 ± 0.002 eV determined based on this break is unambiguous and does not depend on the statistical simulation. Nevertheless, the agreement observed between the 0 K AE(BCl$_3^+$) value of 12.495 ± 0.002 eV and the value of 12.496 eV obtained by the statistical simulation gives a physical interpretation for the observed break in the breakdown diagram. The assigned error limit of ±0.002 eV has taken into account the uncertainty due to the VUV energy calibration.

V. Conclusions

The structure of BCl$_3^+$ (X) and the bond dissociation energy for Cl$_2$B$^-$–Cl have been investigated using VUV laser and synchronotron based PFI methods, together with ab initio calculations performed at the CCSD(T, Full)/CBS level with high-level corrections. Both the experiment and theoretical calculations of this study show that the bending modes for BCl$_3^+$ (X) are strongly excited upon photoionization of BCl$_3$, supporting the conclusion of a C$_{2v}$ structure for the BCl$_3^+$ ground state.
This conclusion is contrary to the conclusion of the previous matrix isolation study and the prediction based on the density functional theory calculation. The present theoretical study also accounts for the perturbed structures observed in the PFIPE spectrum at energies 800–1900 cm⁻¹ above the IE(BCl₃). The assignment of the PFIPE spectrum for BCl₃ gives the adiabatic IE(BCl₃) = 93.891 ± 2 cm⁻¹ (11.64±0.0003 eV). Furthermore, we have determined a highly precise value of 12.495 ± 0.002 eV for the 0 K AE of process (1). These IE(BCl₃) and 0 K AE(BCl₂⁻) values have allowed the determination of the D₀(Cl₂B⁻Cl) = 0.854 ± 0.002 eV, ΔH₀₂₃ (BCl₃) = 172.36 ± 0.5 kcal mol⁻¹ and ΔH₀₃ (BCl₂⁻) = 163.4 ± 0.5 kcal mol⁻¹ with higher precision.

Acknowledgements

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