

Characterization of the Triple Ion $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^- \cdot (\text{CH}_3)_4\text{N}^+]$ in the Gas Phase

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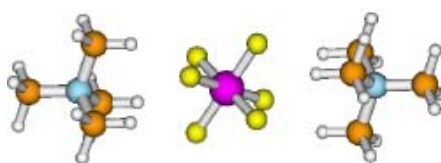
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Abstract: The triple ion $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^- \cdot (\text{CH}_3)_4\text{N}^+]$, generated by electrospray ionization of tetramethylammonium hexafluorophosphate, is characterized by collision-induced dissociation and infrared spectroscopy of the mass-selected gaseous ion in the range from 1000 to 2000 cm^{-1} . Quantum chemical calculations are used to elucidate the structures and energetics of the triple ion and its subunits and for the assignment of the infrared frequencies. The infrared bands observed in the gas-phase match quite closely with those of the bulk substance, suggesting that for this particular kind of ion associate the structural differences between the gas phase and the condensed state are almost negligible.

Keywords: ab initio calculations – infrared spectroscopy - ion pairing - mass spectrometry - tetramethylammonium

1. Introduction

Cation-anion interactions in solution are the result of a subtle balance between two essential forces: the Coulomb attraction, leading to ion association, and attractive interactions of the ions with solvent molecules, which favor dissociation of the solute ions. In addition, entropic effects come into play, leading to a positive correlation between concentration and ion association for a given dissolved salt. The balance between the ion-ion and ion-solvent interactions can be influenced both by the choice of

solvent and solute. On one side, there are solvents with large dielectric constants, such as water, which generally dissolve ions well. On the other hand, salt ions tend to strongly associate in organic solvents with low dielectric constants. All these interactions are strongly ion specific. An empirical law of matching water affinities states that the more similar in hydration free energies the two ions are, the stronger is the cation-anion pairing [1,2]. This leads to preferential association of small-small and larger-large over small-large ion pairs. While this rule is physically well justified and works well for monovalent ions in water, it is not directly applicable to polyvalent ions or solvents with low dielectric constants, in which ion association tends to be stronger [3,4].

An extreme situation is the gas phase, where solvent effects are turned off and only ion-ion interactions are present. In comparison to association of ions in solution, model studies of ion pairing in the gas phase also suffer from two additional features in that (i) cation-anion recombination leads to neutral species which are much more difficult to detect and (ii) compounds existing as ion pairs in the bulk usually do not evaporate intact and rather undergo decomposition, e.g. the gaseous phase in the sublimation of NH_4Cl is a mixture of NH_3 and HCl . With the advent of electrospray ionization, many new opportunities for ion chemistry were opened, yet 1:1 ion pairs still escape detection, when mass spectrometric techniques are used, simply due to the lack of a net charge. In this context, we note some recent studies of ionic liquids, which have been shown to indeed evaporate as intact ion pairs [5-11].

As model systems for ion pairing and because of their pertinent role as phase-transfer catalysts, tetraalkylammonium salts, $[\text{R}_4\text{N}^+ \cdot \text{X}^-]$, have received considerable attention. Of particular interest is the differential behavior of these compounds in aqueous and non-aqueous solvents [12], therefore, their hydration shells have been studied experimentally in the condensed [13-16] and gaseous phase [17,18], by molecular dynamic simulations [19-22], and in various solvents [23-25]. At high dilutions, tetraalkylammonium salts are completely dissociated in solution. At elevated concentrations, however, the cation and anions can recombine ("ion pairing" [4]) to give neutral contact ion-pairs (CIP), i.e. $[\text{R}_4\text{N}^+ \cdot \text{X}^-]$, or triple ions (TI [26]), i.e. the overall cationic species $[\text{R}_4\text{N}^+ \cdot \text{X}^- \cdot \text{R}_4\text{N}^+]$ and the corresponding anion $[\text{X}^- \cdot \text{R}_4\text{N}^+ \cdot \text{X}^-]$. Similarly, ion pairs of higher order are conceivable, such as cluster ions of the type $[(\text{UO}_2)_m(\text{X})_{2m-1}(\text{H}_2\text{O})_n]^+$ with $m = 1 - 5$ and $n = 0 - 4$ reported recently [27].

Tetramethylammonium hexafluorophosphate, $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^-]$, is further noteworthy with respect to a variety of electrochemical measurements, in which it is used as a common conducting salt. In this particular context we found accidentally that upon electrospray ionization (ESI) this salt forms a surprisingly abundant triple ion of the type $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^- \cdot (\text{CH}_3)_4\text{N}^+]$, a net monocation with m/z 293. Upon first sight, the formation of this particular TI was somewhat surprising because tetraalkylammonium ions as well as hexafluorophosphate do not offer any specific binding sites. Here,

we describe the characterization of the structure and energetics of these species by means of collision experiments, infrared spectra, and quantum chemical calculations.

2. Experimental and computational methods

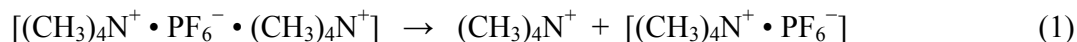
Measurements were performed with a Finnigan LCQ Classic ion-trap mass spectrometer (IT-MS) which has been described elsewhere [28] by electrospray ionization of dilute methanolic solutions of tetramethylammonium hexafluorophosphate. In brief, the LCQ bears a conventional ESI source consisting of the spray unit (typical flow rate 5 $\mu\text{l}/\text{min.}$, typical spray voltage 5 kV) with nitrogen as a sheath gas, followed by a heated transfer capillary (kept at 200 $^{\circ}\text{C}$), a first set of lenses which determines the soft- or hardness of ionization by variation of the degree of collisional activation in the medium-pressure regime [29-31], two transfer octopoles, and a Paul ion-trap with ca. 10^{-5} mbar helium for ion storage and manipulation, including a variety of MS^n experiments [32]. For detection, the ions are ejected from the trap to an electron multiplier; we note that for effectively trapping the relatively light $(\text{CH}_3)_4\text{N}^+$ cation, the q_z value of the ion trap was reduced from the standard value of 0.25 to 0.20. Low-energy CID was performed by application of an excitation AC voltage to the end caps of the trap to induce collisions of the isolated ions with the helium buffer gas for a period of 20 ms for which we have recently introduced a simple linear conversion factor for the extraction of approximate appearance energies (AEs) based on comparisons with reference molecules of known bond strengths [33,34]. We note that the agreement between the AE derived experimentally and the theoretical predictions (see below) can be regarded as an additional proof for the suitability of the conversion factor also for parent- and fragment ions with significant mass differences (i.e. m/z 74 versus 293).

In addition, gas-phase infrared spectra of the mass-selected triple ion $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^- \cdot (\text{CH}_3)_4\text{N}^+]$ were recorded with a Bruker Esquire 3000 IT-MS [35-37] mounted to a beamline of the free electron laser at CLIO (Centre Laser Infrarouge Orsay, France). The ions of interest were generated by ESI from methanolic solution as described above and transferred into the ion trap. After mass selection, infrared multi-photon dissociation was induced by admittance of two pulses of IR-laser light (about 1 W each) to the ion trap, resulting in a total trapping time of about 0.4 second. In the 45 MeV range in which CLIO was operated in these experiments, the IR light covers a spectral range from about 1000 to 1800 cm^{-1} . Note that in this kind of action spectra, the assumption that the amount of ion fragmentation is proportional to the IR absorbance is not always justified due to the multiphotonic nature of IRMPD and the major weight is therefore put on the peak positions, rather than the peak heights in the IRMPD spectra [38].

Ab initio calculations [39] were performed at the MP2 level of theory with the aug-cc-pVDZ basis set [40]. The minimum geometries were obtained from ab initio optimization and further checked by frequency analysis at the same level of theory and same basis set. Harmonic frequency analysis was also used to obtain thermochemical data. All calculations refer to the gaseous state in that additional solvation, aggregation etc. is deliberately not included, in order to match the present experimental conditions.

3. Results and Discussion

Electrospray ionization (ESI) of a dilute methanolic solution of $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^-]$ under mild ionization conditions gives rise to the monomeric cation $(\text{CH}_3)_4\text{N}^+$, m/z 74, and a cluster at m/z 293 which, based upon the ion mass, the precursor used, and the isotope pattern, is assigned to the triple ion $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^- \cdot (\text{CH}_3)_4\text{N}^+]$. Upon collisional-induced dissociation (CID) of mass-selected $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^- \cdot (\text{CH}_3)_4\text{N}^+]$, the cationic subunit $(\text{CH}_3)_4\text{N}^+$, m/z 74, is observed as exclusive fragment, which indicates dissociation of the triple ion according to reaction (1).



The result of energy-dependent CID spectra of mass-selected $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^- \cdot (\text{CH}_3)_4\text{N}^+]$ is shown in Figure 1. Quantitative analysis of the threshold behavior [33,34] provides a phenomenological appearance energy of $AE(1) = (136 \pm 14) \text{ kJ mol}^{-1}$ for the occurrence of reaction (1).

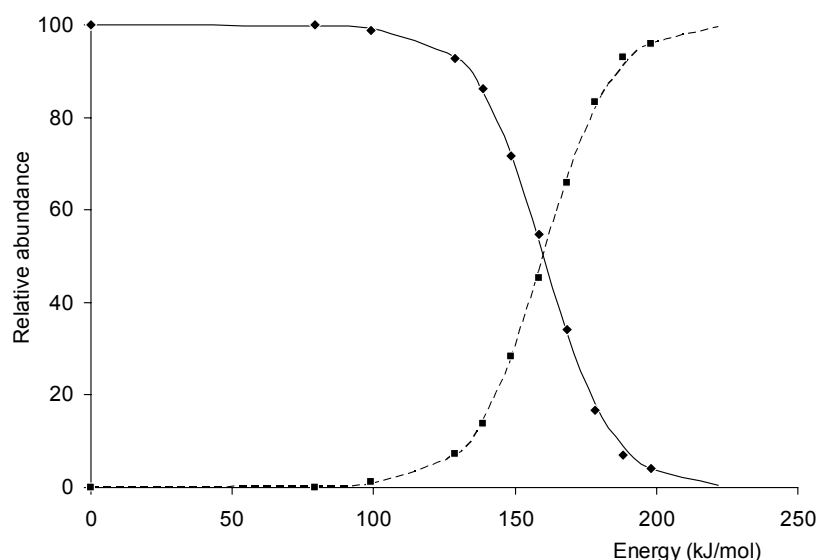


Figure 1. Breakdown diagram obtained for the CID of mass-selected $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^- \cdot (\text{CH}_3)_4\text{N}^+]$ (◆) to exclusively yield the cationic fragment $(\text{CH}_3)_4\text{N}^+$ (■) as a function of the collision energy (converted to kJ mol^{-1}).

In reaction (1), we assume formation of the ion pair $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^-]$ as the neutral fragment, as also suggested by the quantum chemical calculations reported below. A chemically feasible alternative with regard to the neutral product would involve a substitution concomitant with the formation of fluoromethane (reaction 2), i.e. the usual reaction occurring upon thermolysis of tetraalkylammonium salts. According to our computational studies the corresponding reaction products are 240 kJ mol^{-1} higher in energy than $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^-]$. Despite the entropic advantage of reaction (2) in comparison to reaction (1), i.e. formation of four products in (2) versus only two in (1), the fragmentation via (2) is hence considered unlikely.

Table 1. Calculated MP2/aug-cc-pVDZ energetics (kJ mol^{-1}) for ion-pair formation in the gas phase.

	ΔE	$\Delta_r H_{298\text{K}}$	$\Delta_r G_{298\text{K}}$	BSSE
$(\text{CH}_3)_4\text{N}^+ + \text{PF}_6^- \rightarrow [(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^-]$	-354.2	-348.1	-301.0	20.7
$(\text{CH}_3)_4\text{N}^+ + [(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^-] \rightarrow [(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^- \cdot (\text{CH}_3)_4\text{N}^+]$	-147.9	-141.5	-99.2	19.7
$2 (\text{CH}_3)_4\text{N}^+ + \text{PF}_6^- \rightarrow [(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^- \cdot (\text{CH}_3)_4\text{N}^+]$	-502.1	-489.6	-400.2	39.1

In order to achieve more direct insight into the structure of the gaseous triple ion, ab initio calculations have been performed. The free tetramethylammonium ion has a tetrahedral symmetry and PF_6^- is octahedral, as expected (Figure 2). Upon approaching the two ions, one face of the $(\text{CH}_3)_4\text{N}^+$ ion points towards one face of the PF_6^- octahedron with one C–H bond of each of the three approaching methyl groups oriented almost perfectly parallel to the P–N axis.

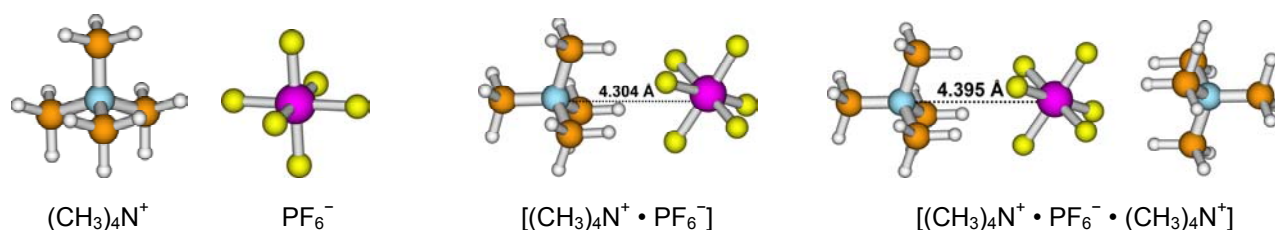


Figure 2. Optimized structures of the free components $(\text{CH}_3)_4\text{N}^+$ and PF_6^- , the neutral ion pair $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^-]$, and the triple ion $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^- \cdot (\text{CH}_3)_4\text{N}^+]$ (selected bond lengths given in Å).

Next, the computed IR spectra are presented (Figure 3), in which all frequencies are scaled by a factor 0.98 which is chosen to match the computed modes with the intense band at 1492 cm^{-1} in the IR spectrum of the solid compound [41]; the magnitude of the scaling factor also is in agreement with the recommendations of Radom and coworkers for the theoretical method applied [42]. With regard to the respective stretching modes of the C–H bonds, an increase in the splitting between the symmetric and asymmetric stretches (3048 and 3168 cm^{-1} in free $(\text{CH}_3)_4\text{N}^+$ versus 3036 and 3180 cm^{-1} in the ion pair) reflects the interactions between $(\text{CH}_3)_4\text{N}^+$ and PF_6^- in the complex (see central structure in Figure 2).

The orientation of the methyl groups relative to the three closest fluorine atoms of PF_6^- is staggered due to steric interactions [43]. The binding energy of the neutral ion pair at 298 K amounts to 348 kJ mol^{-1} . As expected, the approach of another $(\text{CH}_3)_4\text{N}^+$ cation to this entity occurs from the opposite side in an almost identical manner. Further, the interplay of Coulomb attraction and repulsion leads to an increased distance of the subunits, i.e. $r_{\text{P-N}} = 4.304 \text{ \AA}$ in the neutral ion pair $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^-]$ compared to $r_{\text{P-N}} = 4.395 \text{ \AA}$ in the triple ion $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^- \cdot (\text{CH}_3)_4\text{N}^+]$. The binding energy of the second ammonium ion to the neutral ion pair is computed as 142 kJ mol^{-1} at 298 K, which is consistent with the value of $(136 \pm 14) \text{ kJ mol}^{-1}$ derived from the energy-variable collision experiments (Figure 1).

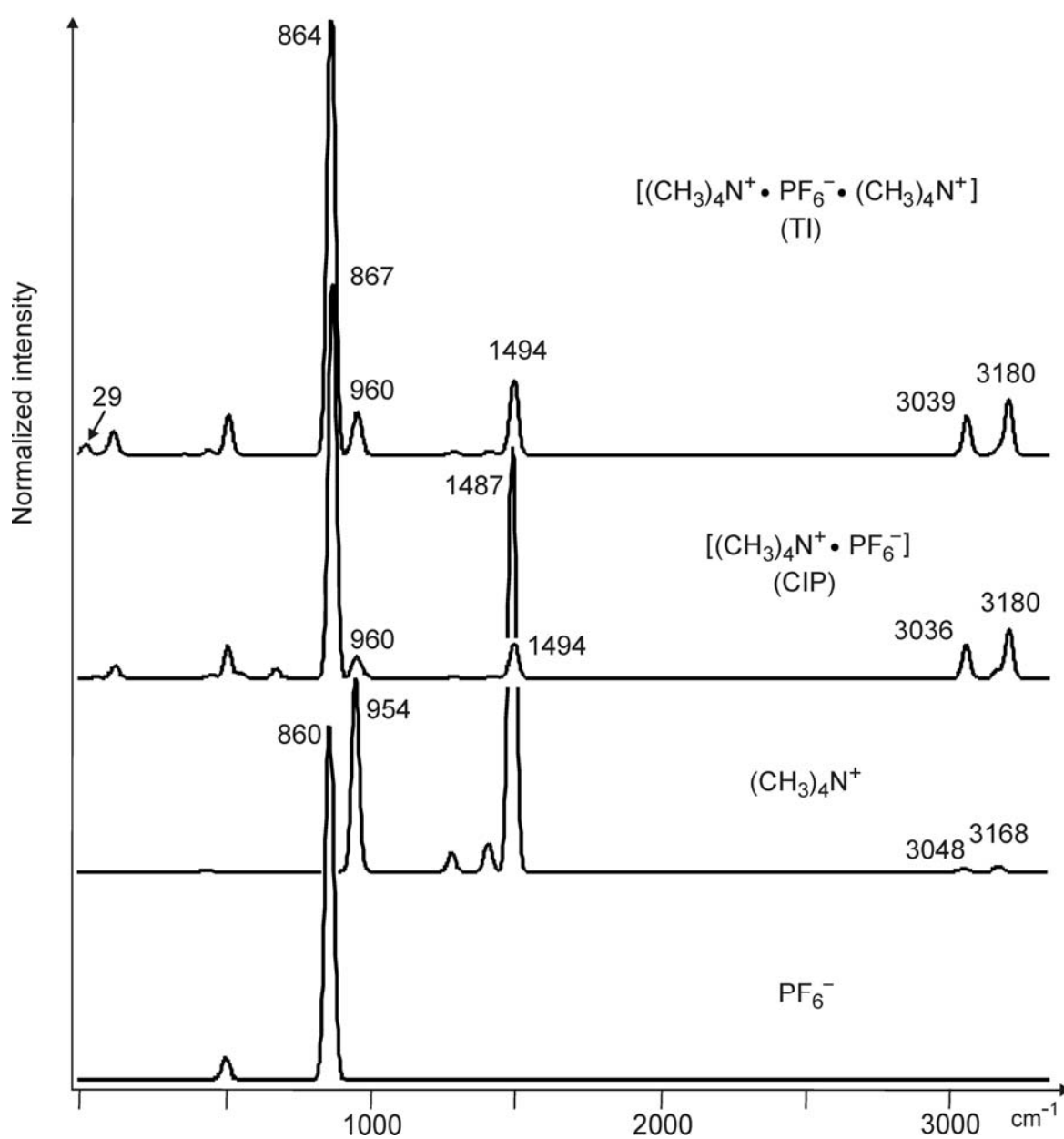


Figure 3. Computed IR spectra of the triple ion $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^- \cdot (\text{CH}_3)_4\text{N}^+]$, the contact ion pair $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^-]$ and the free ions $(\text{CH}_3)_4\text{N}^+$ and PF_6^- (a uniform scaling factor of 0.98 was applied).

To further probe the structure of the triple ion, we recorded its infrared multiphoton dissociation (IRMPD [44,45]) spectrum at the CLIO facility in the range between 1000 and 2000 cm^{-1} . Upon IRMPD of mass-selected $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^- \cdot (\text{CH}_3)_4\text{N}^+]$, the cation $(\text{CH}_3)_4\text{N}^+$ is observed as exclusive ionic fragment. The spectrum obtained (Figure 4) is rather simple which is consistent with the high symmetry of the computed structure (Figure 2). The two bands observed in this spectral range are a strong adsorption at $(1499 \pm 7) \text{ cm}^{-1}$ and a weaker peak located at $(1442 \pm 7) \text{ cm}^{-1}$, where the values given and their errors are the averages derived from four independent IRMPD spectra. The computed positions of these respective modes are 1489 cm^{-1} and 1466 cm^{-1} with an intensity ratio of 94 : 6, which is in reasonable agreement with the IRMPD results. Note that as far as intensities are concerned, the multiphotonic nature of the IRMPD experiments as an action spectroscopy requiring photodissociation causes a discrimination of the weaker IR modes [38]. Irrespective of this particular shortcoming, the lack of the reasonably intense band at about 960 cm^{-1} in the experimental spectrum is ascribed to a mere experimental artifact in which the IR laser was tuned for the range from 1000 to 2000 cm^{-1} and its intensity drastically drops at the edges.

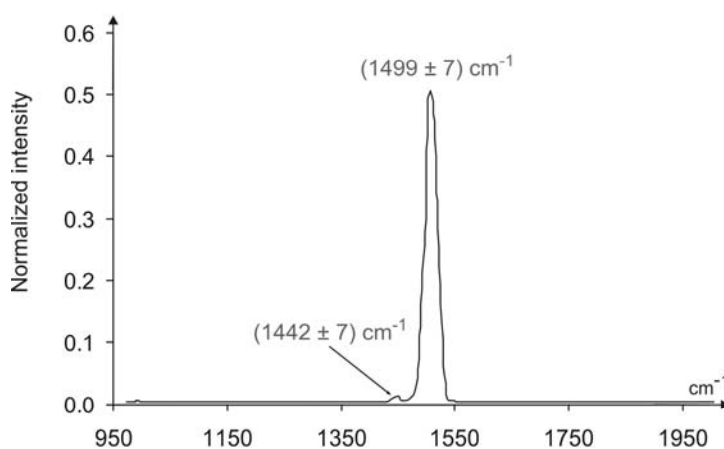


Figure 4. IRMPD spectrum of mass-selected $[(\text{CH}_3)_4\text{N}^+ \cdot \text{PF}_6^- \cdot (\text{CH}_3)_4\text{N}^+]$ (m/z 293) in the range from 1000 to 2000 cm^{-1} .

It is instructive to compare these gas-phase data with the IR spectrum of the bulk compound [41]. In the investigated range, the only significant bands are noted at 1415 cm^{-1} (m) and 1492 cm^{-1} (vs) which is in very good agreement with respect to the intense band near 1492 cm^{-1} , for which the gas phase data give a position of 1499 cm^{-1} , whereas the less intense band at 1415 cm^{-1} is somewhat blue-shifted in the IRMPD spectrum and even more so in theory (1466 cm^{-1}), which might indicate particularly pronounced anharmonicity of this mode. Last but not least, it is interesting to note that the deviation

from the 180° geometry of the triple ion is associated with a low-frequency bending mode of only 29 cm⁻¹. In analogy to a proposal of Yañez and coworkers for the LiP₄⁺ cation [46], the triple ion may thus have some characteristics of a planetary system in its dynamic behavior in that the two ammonium ions can easily and in concerted motion "orbit" around the central hexafluorophosphate.

4. Conclusions

The triple ion [(CH₃)₄N⁺ • PF₆⁻ • (CH₃)₄N⁺] was generated by ESI-MS of tetramethylammonium hexafluorophosphate and investigated by CID and IR spectroscopy, and ab initio calculations. Both experiment and calculations show that it has a binding energy of ~140 kJ mol⁻¹ with respect to the loss of the neutral ion pair [(CH₃)₄N⁺ • PF₆⁻] concomitant with free (CH₃)₄N⁺ as the ionic species. In the spectral range studied experimentally (1000 - 2000 cm⁻¹), the mass-selected ion exhibits only two bands at 1442 and 1499 cm⁻¹. Calculations assign these bands as bending modes within the methyl groups of the tetramethylammonium moieties. Interestingly, the gas-phase IR data match closely to those of the bulk substance (1415 and 1492 cm⁻¹), indicating that solvation as well as aggregation have only small effects on the positions of these bands and, consequently, the geometry of this triple ion. Furthermore, the observation of a triple ion of two tetraalkylammonium ions even with a counteranion as weakly coordinating as PF₆⁻ underlines the importance of ion pairing in the absence of polar environments.

Acknowledgement. This work was supported by the Czech Academy of Sciences (Z40550506), the European Research Council (AdG HORIZOMS), the Grant Agency of the Czech Republic (203/08/0114 and 203/08/1487), the Ministry of Education of the Czech Republic (MSM0021620857, RP MSMT 14/63, and LC512), and the Ministry of Science, Education, and Sport of Croatia (098-0982933-2920). DS and LD thank the assistance of the entire team of CLIO for support in the IRMPD measurements (project IC 013-09). JH thanks the International Max-Planck Research School for support.

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