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Review

Cesium cation affinities and basicities

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Dedicated to the memory of Sharon Lias for her remarkable contribution to the field of ion thermochemistry.

Abstract

This review focuses on the quantitative data related to cesium cation interaction with neutral or negatively charged ligands. The techniques used for measuring the cesium cation affinity (enthalpies, CCA), and cesium cation basicities (Gibbs free energies, CCB) are briefly described. The quantum chemical calculations methods that were specifically designed for the determination of cesium cation adduct structures and the energetic aspects of the interaction are discussed. The experimental results, obtained essentially from mass spectrometry techniques, and complemented by thermochemical data, are tabulated and commented. In particular, the correlations between cesium cation affinities and lithium cation affinities for the various kinds of ligands (rare gases, polyatomic neutral molecules, among them aromatic compounds and negative ions) serve as a basis for the interpretation of the diverse electrostatic modes of interaction. A brief account of some recent analytical applications of ion/molecule reactions with Cs^+, as well as other cationization approaches by Cs^+, is given.

Keywords: Cesium; Alkali metal ions; Adduct formation; Cation affinity; Thermochemistry; Cationization

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1. Introduction

Cesium is the largest alkali metal possessing a stable isotope, ^{133}Cs, in addition to the 11 radioisotopes that are of anthropogenic origin. Among them, the most hazardous are ^{134}Cs (half-life ∼2 years) and ^{137}Cs (half-life ∼30 years). These cesium radioisotopes were dispersed in our environment between 1945 and 1980 by atmospheric nuclear weapon tests, and, in 1986, after the Chernobyl accident [1–4]. The interaction between the cesium cation and neutral or anionic functions is involved in many processes, such as the special bonding of Cs^+ in water cluster [5], the effect of the chemical environment on the ^{133}Cs NMR chemical shift [6–9], the chiral recognition in solution and in the gas phase [10], quantitation in analytical mass spectrometry [11], the clarification of the electrospray ionization (ESI) process [12,13] and the selective Cs^+ adducts formation by crown ethers in ESI [14] or by others chelating molecules [15], the cesium retention by some mushrooms species [16–18], the mechanism of which is still under debate, the pectin treatment against radiocesium intake [19,20], the extraction of radiocesium from nuclear fuel or nuclear wastes [21–27] or the role of humic acid in radiocesium distribution in soils [28,29], to cite a few.

In fact, our interest in the formation of cesium cation adducts with organic acids [30–32] was prompted by the need for a better description of the influence of soil organic matter and humic substances [33] (principally humic and fulvic acids, respectively, HA and FA) on cesium cation transport in soils, and the high bioavailability of cesium in organic soils [34]. These acids bear a number of polar oxygenated groups, such as hydroxyl and carboxyl [35–37]. Models of metal binding to HA and FA hypothesize that cation interactions should occur mostly via these acidic functions [28,37–39]. An important step in the direction of modeling the interaction of cesium with soil organic matter is believed to be the determination of the intrinsic (in vacuo, without counter ion) structural and energetic aspects of Cs^+ adducts with simple organic functionalities.

For that reason, we examined the literature reporting on the experimental Cs^+ gas-phase affinities, CCA, or basicities, CCB, defined, respectively, as the enthalpy, or Gibbs free energy, of the dissociation process (L = neutral or anionic ligand):

$$[LCs]^+ \rightarrow L + Cs^+ \qquad (1)$$

Metal ions are prone to add several ligands, leading to a class of larger adducts often called clusters. Each step in Cs^+ cluster formation may be characterized by a thermochemical value for the process (1′):

$$[L_nCs]^+ \rightarrow L + [L_{n-1}Cs]^+ \qquad (1')$$

The $[L_nCs]^+$ cluster may contain different types of ligands.

In an early work by Kebarle and co-workers, the enthalpy and entropy of adduct formation with water molecules was determined [40,41], and there was no additional data in the 1977 and 2000 Kebarle reviews [42,43]. In 1986, Keesee and Castleman published an extensive compilation on the thermochemistry of gas-phase ion/molecule association and clustering [44], containing a few Cs^+ cation affinities.

More recently, Fujii examined the literature (surveyed up to the end of 1997, except in a few cases) on the alkali metal ion/molecule association reactions and their applications to mass spectrometry [45]. This review describes the principal experimental methods, and reports experimental as well as theoretical enthalpies of adduct formation, but it appears that data on Cs^+ were rather scarce, even at the end of the 20th century. In 2000, Rodgers and Armentrout gave a detailed account of their extensive measurements of ion/ligands bond energies using threshold collision induced dissociation [46], but at that time, only a few data related to the cesium cation were reported by this group. In a broad account of the thermochemistry of organometallic systems, Operti and Rabezzana collected metal cation/neutral organic ligands bond dissociation energies published between 1996 and 2003 [47], including a significant number of CCA and CCB. Finally, an updated source of data for the reaction between Cs^+ and neutral molecules can be found in the famous "WebBook" (National Institute of Standard and Technology, NIST), and other tables to which the late Sharon Lias contributed so much [48].

In the present review, we report our analysis of the literature on quantitative data related to the cesium interaction with neutral or negatively charged ligand, mostly dealing with the simple reaction (1), and in some case with the more complex clustering (1′). In addition to the experimental data, the methods of quantum chemical calculations applied to structural and energetic aspects of Cs^+ adducts were evaluated. In fact, most of the experimental papers on gas-phase thermochemistry made use of ab initio or density functional theory (DFT) calculations. Considering the size of the element cesium, the problem of an appropriate treatment of its wave functions is worth a specific part dedicated to theoretical calculations of Cs^+ affinities, which follows the description of the experimental techniques.

2. Experimental techniques and sources of cesium cation affinities and basicities

Ervin has reviewed recently the experimental techniques relevant to gas-phase ion thermochemistry [49], and Operti and Rabezzana described those pertaining to the determination of metal ion/ligand binding energies [47]. The experimental approaches that have been used for the determination of Cs^+ adduct thermochemistry are rather diverse, and the typical methods are given a brief description in the following.

2.1. High pressure mass spectrometry (HPMS)

Historically, HPMS was largely applied to the determination of bonding energetics in adducts (or clusters) of alkali metal ions with simple molecules, although Cs^+ was not studied extensively [40,41,50–52]. The HPMS technique consists in reacting ions with neutral molecules in the presence of a bath gas – or buffer gas – at pressures in the 10^2–10^3 Pa range. At such pressures, adduct ions are thermalized through termolecular collisions. In the case of metal cations M^+, the process leads frequently to the sequential formation of clusters of general formula $[L_nM]^+$. The alkali metal ions were produced by thermionic emission from a filament coated with an appropriate melt of alkali oxide, or carbonate, with silica and alumina, producing ideally a β-eucryptite aluminosilicate [53]. The equilibrium constants for reactions (1) and (1′) can be obtained from the ions abundances and the partial pressure of the neutral ligand. The equilibrium constant is determined at several temperatures, and a Van't Hoff plot leads to the corresponding enthalpy and entropy. A few data concerning Cs^+ were determined by Kebarle and co-workers [40,41]. Using a similar approach, enthalpies of Cs^+ clustering were also determined using variable temperature drift tube (DT) experiments, providing additional data on rate constants and ion mobility [54]. Banic and Iribarne designed a technique similar to HPMS [55], although working at higher pressures (between 0.06 and 1 atm, 1 atm = 101325 Pa), for measuring equilibrium constants, in particular for the formation of Cs^+ "mixed clusters" with H_2O, SO_2 and CO_2. The originality of this approach was the implementation of an atmospheric pressure ion source based on ion evaporation from a solution, in fact the ancestor of the atmospheric pressure electrospray ionization (ESI). More recently, Kebarle and co-workers used also an ESI source and a variable temperature high-pressure chamber to study the thermochemistry of ion hydration [56–58].

2.2. Collision-induced dissociation threshold (CIDT)

During the last decade, one of the most fruitful methods for the determination of alkali metal cation/ligand bond dissociation energies was CIDT, also called "threshold CID" (TCID) [46,59–61]. In this technique, the CID measurements are performed under carefully controlled conditions, in particular the pressure of the collision gas and the kinetic energy of the ion beam, for a better definition of the internal energy of the dissociating ions. The first description of the CIDT mass spectrometer was given by Ervin and Armentrout [46a], and a Fe^+ ion source was fitted later on [46b]. Metal ions were generated by argon ion sputtering from a continuous direct-current discharge. The first application of these instrument and source to an alkali ion appeared in 1994 [46c]. The alkali metal ions may be generated from the pure alkali metal or a metal salt, for example, CsCl for generating Cs^+. Adducts are produced by three-body association with the ligand in the presence of helium, allowed to thermalize, then mass selected by a magnetic sector and decelerated to a given kinetic energy. The fragmentation of adducts (reactions (1) or (1′)) by collision with a rare gas (xenon in most cases) takes place in an octopole collision cell. The intensities of fragment ions are measured using a quadrupole mass filter and a Daly detector. The intensity versus collision energy plot is fitted to a model that leads to the dissociation energy at 0 K. Applying thermal corrections gives absolute bond dissociation enthalpies at 298 K, accurate to about ±5–15 kJ mol^{-1}, and eventually Gibbs energies after entropy calculations. Kebarle adapted a special source to a triple quadrupole instrument for CIDT measurements [61], and a commercial instrument was also directly used by Jurczak and co-workers for a quantitative study of the Cs^+/crown ethers bond dissociation [62]. In the same vein, the collision-induced dissociation of lasalocid and monensin A bound to alkali metal cations, including Cs^+, has been investigated using ESI and CID, and a qualitative order of binding affinity for the cations was proposed [63]. Noteworthy, the same authors [64] showed that qualitative orders of adduct *stabilities* (with reference to backbone fragmentation, as opposed to the simple metal cation loss) could be extracted from energy resolved CID experiments on a commercial triple quadrupole instrument.

2.3. Ligand exchange equilibrium measurements in trapping devices

Quadrupole ion traps (QIT) [65] or ion cyclotron resonance (ICR) mass spectrometers [66], have been used for the determination of Gibbs free energies (ΔG) of ligand exchange (relative basicity), as illustrated by reaction (2) in the case of Cs^+:

$$[L^1Cs]^+ + L^2 \leftrightarrows [L^2Cs]^+ + L^1 \tag{2}$$

Adducts are trapped in the presence of a known pressure of the ligands L^1 and L^2. When a steady state is observed, usually after a few seconds when working in the 10^{-5} to 10^{-4} Pa range, an equilibrium constant can be calculated from the pressure ratio of the ligands and the ratio of ion intensities. When this equilibrium state cannot be achieved, bracketing techniques may be used, i.e., limits can be placed on the affinity or basicity on the basis of fast or slow kinetics of cation exchange. Equilibrium and bracketing are comparison methods, and a pre-established basicity scale (reference scale) is necessary. To the best of our knowledge, equilibrium measurements involving Cs^+ have not been published, but an example of bracketing is for the determination of CCA of the crown ether dibenzo-18-crown-6 by bracketing by Fourier transform ICR [67], using absolute CCA values from CIDT as reference. Relative values, or qualitative ordering, were also obtained by the ligand exchange method using FT-ICR [68–70] or ion trap mass spectrometry [71].

2.4. Selected ion flow tube (SIFT)

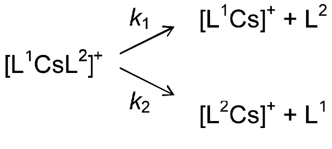
Bohme and co-workers have recently published a series of papers on the reactivity of transition-metal and main-group cations using the SIFT technique [72,73] coupled with an innovative inductively coupled plasma (ICP) ion source [74,75]. In flow tube techniques, the reacting ion is mixed with a fast stream of helium in which the neutral molecule is diluted, allowed to react and the charged product ion(s) are analyzed downstream.

The extent of reaction depends on the pressure of the neutral component and the speed of the helium flow, which determines the time of ion/molecule contact. SIFT is a technique essentially intended for kinetic studies, but when equilibrium can be reached, an accurate value of the Gibbs free energy for the cation attachment (at a single temperature) can be deduced. Some relevant data concerning Cs^+ were acquired with this original instrumentation [76–80].

2.5. Kinetic method

The kinetic method is probably one of the most utilized techniques for the determination of the relative proton and metal cation affinities, because of the ease of implementation using standard mass spectrometers [81,82]. Based on experimental and theoretical considerations, appraisals of the kinetic method were published in the last 10 years, including efforts in the direction of entropy determinations [82–89]. The kinetic method may be applied by using different types of mass spectrometers: sector, trapping (QIT and FTICR) and triple quadrupole instruments. When applied to the determination of CCA or CCB, the kinetic method consists in dissociating the cesium cation-bound dimer $[L^1CsL^2]^+$ [30,32]. In early studies, most cation-bound dimers were generated by fast atom bombardment, but currently electrospray ionization (ESI) is generally used for their production. After activation by collision, or by metastable decomposition in sector instruments, the dimer dissociates essentially into the fragments $[L^1Cs]^+$ and $[L^2Cs]^+$ (corresponding to respective bond breaking of Cs^+ with L^1 and L^2), as shown in Scheme 1.

The natural logarithm of the ratio of the two unimolecular rate constants $\ln(k_1/k_2)$, with (k_1/k_2) equal to the ratio of ion intensities, is related to the difference in CCA (or CCB) of L^1 and L^2, on the basis of the transition state theory and assumptions about the dissociation pathways [82–89]. For quantitative determinations, the method should be calibrated with known affinities or basicities. Chen and Cooks demonstrated an interesting application in relation to the determination of the heterolytic bond dissociation energy (HBDE) of alkali chlorides [90,91]. The dissociation of $[M_1ClM_2]^+$ (M_1, M_2 = alkali metal) gives $M_1Cl + M_2{}^+$, and $M_2Cl + M_1{}^+$ and the calibration is based on HBDE obtained through a thermodynamic cycle. On the basis of similar measurements on $[M_1XM_2]^+$ or $[X_1MX_2]^-$ (X = halogen), Wang and Cole validated electrostatic models of binding energies [92]. In the case of Cs^+, the determination of CCA or CCB by the kinetic method is impaired by the lack of suitable reference values [32]. This is the reason why most affinities were reported as relative values in the form of k_1/k_2 or $\ln(k_1/k_2)$ [93–97]. In this case, calculated values (ab initio, DFT) may be used as substitutes, as our groups did for calibrating the $\ln(k_1/k_2)$ values of the mixed clusters made up from cesium cations, carboxylate and nitrate ions [32].



Scheme 1.

2.6. Radiative association kinetics

The kinetics of complex formation, under the conditions of radiative relaxation (low-pressure radiative association kinetics), is linked to the strength of the bond being formed. Dunbar and co-workers demonstrated how to extract bond strengths from the corresponding rate constants [98–100]. Nevertheless, this method could not be applied to adduct formation of tribenzocyclotriyne and coronene with Cs^+ [101,102], because the reaction was too slow. Nicoll and Dearden analyzed by radiative association kinetics the complex formation of sandwich complexes between multidentate ligands (triglyme and crown ethers) and alkali metal cations, including Cs^+, to extract binding enthalpies for attachment of the second ligand [103]. Another work on radiative association of Cs^+ and 12-crown-4, which exhibits a significant association rate [104], does not report energetic data.

2.7. Blackbody infrared radiative dissociation (BIRD)

BIRD can be considered as the reverse process of radiative association. At very low pressure, trapped ions (essentially in an ICR cell) are slowly dissociated by the ambient blackbody radiation [105]. Although it may be anticipated that CCA or CCB could be determined this way, we did not found any such report, despite the mention of a Cs^+ loss in a study of cationized arginine derivatives [106].

2.8. Photodissociation

Photodissociation was used for the study of small cesium clusters $(Cs)_n{}^+$ [51,107–109]. The threshold for the photodissociation process, reaction (3) (n = 2, 3):

$$(Cs)_n{}^+ + h\nu \rightarrow (Cs)_{n-1} + Cs^+ \tag{3}$$

established a lower limit for the dissociation energy, i.e., the $(Cs)_n$–Cs^+ bond energy.

2.9. Ion mobility and scattering

Weak interaction potentials between the rare gases and Cs^+, as well as other alkali metal cations, have been documented [44] by modeling ion mobility [110] and ion beam scattering data [111]. Results are dependent on the interaction model used. Rajan and Gislason reported their results on Cs^+ mobility [111] with a comprehensive discussion of the earlier results.

2.10. Vaporization and lattice energies

Historically, thermochemical data on isolated (gas-phase) ions were obtained from thermodynamic cycles involving lattice energies, enthalpies of formation, ionization energies and/or electron affinities [112]. Conversely, enthalpies of formation and related data can be reached from the energetics of ion/molecule reaction. Such approach is particularly adapted to the study of non-volatile inorganic species, like salts and oxides.

Since we are interested in the interaction between anions and Cs^+ [30,32], we considered the available data that can be obtained from the heterolytic bond dissociation energy of the gaseous monomeric salt. At this step, we warn the reader regarding the different conventions related to ion thermochemistry. The difference lies in the treatment of the electron captured or liberated during ion formation. The electron may be treated either as an element (ideal gas, $\Delta_f H(e^-) = 0$, integrated heat capacity $H_T - H_0 = 5/2RT$, the so-called "electron convention") or as a species without any heat capacity [$\Delta_f H(e^-) = 0$, $H_T - H_0 = 0$ at all T, the so-called "ion convention") [48c,112]. At 298 K, the difference between the two conventions is 6.2 kJ mol^{-1} per electron. For example, the enthalpy of formation at 298.15 K of Cs^+ found in two reference compilations is 458.0 kJ mol^{-1} under the ion convention [48d], and 451.8 kJ mol^{-1} [48c] under the electron convention. A consistent use of any one of the two conventions leads to the same result in terms of reaction thermochemistry (when the electron is not implicated on either side of the reaction), as long as there is no mixing of both. The community of mass spectrometrists uses normally the ion convention. A complete description of the two conventions, and details of their origin and their consequences, is given in the Introduction to the WebBook [48a] and the early NIST data compilation of gas-phase ion and neutral thermochemistry ("GIANT table" [48c]). We recall also that the standard state pressure is 1 bar rather than 1 atm, making note, however, that such a change in the standard state has little effect on data, in regard to the usual level of precision. Scheme 2 illustrates how to estimate the enthalpy of heterolytic dissociation of cesium fluoride. By combining the enthalpy of vaporization $\Delta_{vap}H$ (or sublimation $\Delta_{sub}H$) of the salt with the enthalpies of formation $\Delta_f H$ of the solid salt and of the gaseous monatomic element, the metal ionization energy (IE) and the electron affinity (EA) of the halogen atom, the CCA of the fluoride anion is obtained.

Spectrometric data (EA, IE) on atoms and small molecules are in general rather accurate. It should be noticed that early data [113] made use of electron affinities deduced from lattice energies [112] and are therefore subject to larger errors. The thermochemical data suitable for the calculation of affinities (or basicities) using Hess's law, may be found already combined in thermodynamic tables, [48]. They are tabulated in the form of standard enthalpies (and Gibbs energies) of formation of the gaseous species of interest, for example, the gas-phases enthalpy of formation $\Delta_f H(g)$ of Cs^+, as well as of some inorganic anions and neutral partners, already evaluated through some particular part of the cycle shown in Scheme 2.

$$\begin{tikzcd}
{[CsF]_s} \arrow[r, "\text{from } \Delta_f H"] \arrow[d, "\Delta_{sub}H"'] & F_g \arrow[d, "EA"] & + & Cs_g \arrow[d, "IE"] \\
{[CsF]_g} \arrow[r, "\Delta H = CCA"] & F^-_g & + & Cs^+_g
\end{tikzcd}$$

Scheme 2.

The most challenging step of the thermodynamic cycle applied to inorganic, non-volatile compounds is the experimental determination of $\Delta_{vap}H$ or $\Delta_{sub}H$. For example, the vapors above alkali fluorides are mixtures of monomer, dimeric and even trimeric species, even at the high temperatures (about 700–2000 K) required for such measurements [114]. Assumptions about the vapor compositions should be made [113]. However, for the determination of the thermodynamic properties of cesium halides, this problem is less crucial, except for the fluoride that still dimerizes significantly [114,115]. Nevertheless, a significant discrepancy appears between a recent determination of the enthalpy of sublimation for CsI [116] and the older value [115]. In the case of sublimation of a salt containing a polyatomic anion, another source of error is decomposition at the elevated temperatures needed for vaporization [117]. These vaporization data were obtained mostly by high temperature mass spectrometry. This mass spectrometry technique was also used for the thermochemistry of reaction (4) [118]:

$$CsOH(s) + Cs^+(g) \leftrightarrows Cs_2OH^+(g) \tag{4}$$

These data were combined with ancillary enthalpies of formation, in order to obtain the proton affinity of cesium oxide and the CCA of cesium hydroxide [119], and to the enthalpy of formation of $Cs_2OH^+(g)$.

3. Theoretical calculations of Cs^+ affinities

Considering that our review focuses on experimental cesium cation affinities, we examined briefly the major features of relevant quantum calculations, with the aim to point out the optimal theoretical approaches. In the table of experimental data, references to the pertinent theoretical calculations are given, and the concerned reader may refer to the method used for a specific system.

Cesium cation affinities have been much less studied computationally as compared to affinities of earlier alkali metal cations. This is attributed to the scarcity of experimental data for comparison and validation of the computational models, and the small number of available basis sets: the EMSL Basis Set Library contains only 11 basis sets for cesium, while for potassium there is already 50 basis sets available [120,121]. Furthermore, cesium, as a sixth-period element, should exhibit quite strong relativistic effects, and the high number of electrons renders all-electron calculations quite time consuming. Therefore, most of the reported calculations on structures involving Cs^+ make use of effective core potentials (ECPs) [122,123], where core electrons are modeled by an appropriate function, and only valence electrons are treated explicitly, or for a better description, by adding also the next lower-shell electrons. If only valence electrons are treated explicitly, we are dealing with a "large-core" ECP, and if the outermost $(n - 1)$ shell is included in the treatment, the ECP is called "small-core". The relativistic ECPs directly incorporate the mass–velocity and one-electron Darwin effects into the potential and, hence, should approximately account for the dominant relativistic corrections that may contribute importantly to the description of heavier atoms. Using this approach, at least part of the relativistic effects will be also taken care of [124]. In the following, for brevity, we will designate by the acronym ECP, both the effective core potential and the corresponding standard basis set.

A number of cesium cation complexes with different ligands have been studied using a hybrid basis set suggested by Glendening and Feller. It consists of 6-31 + G* basis for oxygen and 6-31G* for hydrogen and carbon. Cesium is described by the relativistic small-core Hay-Wadt ECP with a split valence basis [125], which is augmented by an additional six-term d-type polarization function [126]. We will refer to that basis set as a Glendening–Feller basis. These authors calculated this way gas-phase binding energies and enthalpies for small $Cs^+(H_2O)_n$ clusters, with one to six water molecules [127], at the Hartree-Fock (HF) and second-order Møller-Plesset perturbation theory (MP2) level. The HF methodology was sufficient for describing smaller clusters ($n = 1–3$), while bigger clusters required correlated treatment at the MP2 level to compare favorably with the experimental values. Bigger basis sets (at least of triple zeta quality) led to much better description of the cesium cation polarizability and to better precision on the water–water distances [128]. Glendening also studied cesium cation-water clusters by using natural energy decomposition analysis [129]. Cesium complexes with up to six water molecules were also studied by Lee et al. [130], using the MP2 method with aug-cc-pVDZ basis on water and either Stuttgart–Dresden–Bonn relativistic small-core ECP [131] or Christiansen's relativistic small-core ECP [132] with additional polarization functions [126] on cesium. The first combination gave binding energies within experimental uncertainties, with errors smaller than 4.2 kJ mol^{-1} for clusters with one to three water molecules, and less that 18.0 kJ mol^{-1} for the four-water cluster. Hill et al. studied the Cs^+ complexation with up to four dimethylether (DME) ligands [133]. Calculations were carried out using both HF and MP2 methods combined with Glendening–Feller basis. The calculated bond dissociation energies were in good agreement (average deviation: 5 kJ mol^{-1}) with the experimental CIDT results of More et al. [134,135]. It was found that the $Cs^+(DME)_2$ complex is strongly bent, and that the $Cs^+(DME)_3$ complex is non-planar, with Cs^+ located 0.68 Å (1 Å = 0.1 nm) above the plane of the ether oxygen atoms. Similar studies of Cs^+ complexation with one or two 1,2-dimethoxyethane molecules, and with the 12-crown-4 macrocycle [136], were carried out by Hill et al. at the HF and MP2 levels. The calculated binding energies were divergent from the experimental ones by up to 58.6 kJ mol^{-1}. Higher-energy conformers of both Cs^+(12c4) and Cs^+(1,2-dimethoxyethane)$_n$, corresponding to adduct formation while retaining the structures of the most stable conformers of neutral ligands, were identified as possible causes for the discrepancy. The binding of the cesium cation (and other alkali metal cations) to another crown ether, 18-crown-6, was also studied by Glendening et al. [126] using the Glendening–Feller basis set. Calculated geometries compared favorably with the experimental ones, while the agreement between experimental and calculated binding energies was rather poor. Feller [137] studied the effect of aqueous microsolvation on the relative binding affinity of 18-crown-6 for the alkali metal cations. The corresponding binding energies were in much closer agreement with experimental aqueous phase values. Using the same methods, Hill and Feller [138] and More et al. [139] have studied the cesium cation binding (as well as other alkali cations) to 15-crown-5. Anderson et al. have investigated the binding of cesium cation to the dibenzo-18-crown-6 [67] with HF, MP2 and B3LYP methods and basis sets similar to that of Feller's group. Calculated binding energies were close to experimental ones, but still somewhat overestimated. Calix[4]arene-crowns-6 adduct formation with potassium and cesium ions were studied with HF/3-21G level calculations by Casnati et al. [140], leading to the conclusion that this level of theory was not able to predict the selectivity of the calixarene towards alkali metal ions. The origin of such discrepancy was due to the lack of solvent and counter-ions in the modeling.

The quantum chemical modeling of interactions between cesium and macrocyclic extractants (crown ethers, calixarenes) has received particular attention for their importance in the treatment of nuclear wastes. Golebiowski et al. reviewed the state of the art in quantum chemical calculations on alkali metal cations and calixarenes [141]. These authors developed the study of Cs^+ cation complexation and selectivity with calixarenes and crown ethers, using in particular hybrid quantum mechanics/molecular mechanics potentials, and solvation was included in their studies [142–144].

Burda et al. studied the interaction of cesium cation with guanine and adenine [145], using HF and MP2 methods, the Christiansen ECP [132] on cesium, and the 6-31G** basis set on the remaining atoms. The binding to guanine was found to be stronger than to adenine.

In addition to the most studied crown ethers and small biological molecules, the aromatic systems were considered for their interaction with alkali metal cations, from both the experimental and theoretical point of view. Streitwieser et al. have studied substituent effects in cesium derivatives of fluoro and chlorobenzenes [146] using Hay-Wadt [125] and Christiansen [132] ECPs on cesium, and 6-31 + G* basis set on the other atoms. The complexation between cesium cation and benzene [147a,b] was studied by Nicholas et al. [147a] using HF, MP2, SNWN and BP86 methods with Hay-Wadt ECP [125] on cesium, and 6-311G* basis set on other atoms. They gave evidence that SNWN and BP86 methods produce geometries in accordance with MP2, while the binding energies are by ∼20% too low. The distance between Cs^+ and the benzene centroid was calculated as 0.19 Å longer than at MP2 level. The geometries and binding enthalpies of Cs^+(benzene) complex were calculated by Feller et al. [147b] using MP2 and CCSD(T) methods with large customized basis sets up to quadruple zeta quality. The estimated binding energy at the complete basis set limit was still 10.9 kJ mol^{-1} too low compared to experiment [148]. Coletti and Re discussed very recently these somewhat poor to fair results [149], and proposed to improve them for rubidium and cesium by using an improved basis set superposition error-corrected geometry optimizations employing MP2 and MP4 levels of theory.

The determination of cation/ligand bond dissociation energies (BDE) by CIDT relies on a combination of experiments and modeling of adducts. Amunugama and Rodgers used Glendening–Feller basis with MP2 and B3LYP methods to investigate energetics and geometries of cesium (and other alkali metal) cation complexes with one or two molecules of toluene [150], fluorobenzene [151], aniline [152], phenol [153], anisole [154] and naphthalene [155]. The MP2 cesium cation/ligand BDEs (obtained at B3LYP optimized geometries and corrected for BSSE) were by 2–12 kJ mol^{-1} lower than experimental ones and the B3LYP ones were even lower.

Several studies were carried out with the catalysis for background. Sjöberg et al. studied the effect of cesium cation adsorption on the siloxane bond strength in silicate minerals [156] using B3LYP density functional theory with Hay-Wadt ECP [125] on cesium, and a 6-311G basis set for the other atoms. Ferrari et al. have studied interaction of Cs^+ and other alkali metal cations with carbon monoxide using HF, MP2, S-VWN, BLYP, B3LYP, QCISD and QCISD(T) methods with triple-zeta valence basis set proposed by Ahlrichs and co-workers [157] supplemented by a double set of polarization d functions on C and O atoms. Hay-Wadt ECP [125] (the s-valence part has been further decontracted in order to increase flexibility) was used for cesium. Good agreement was found between bond lengths calculated at MP2, BLYP, B3LYP and QCISD(T) levels. B3LYP provides bonding energies particularly close to those obtained by QCISD(T), followed by BLYP, whereas MP2 and S-VWN tend to overestimate the stability of the carbon-bonded adduct with respect to the oxygen-bonded adduct. Bonelli et al. have used the same basis sets as Ferrari et al. and the B3LYP method to study the interaction of cesium and other alkali metal cations with carbon dioxide [158], and acetylene and methylacetylene [159]. They found that the [O–C–O···Cs^+] adduct was linear, with a binding energy smaller by 4.6 kJ mol^{-1} than the experimental value reported in NIST [48]. A T-shaped bonding of cesium cation was obtained for acetylene and methylacetylene, with bonding energies of 20 and 28 kJ mol^{-1}, respectively. Ignaczak studied the cesium cation adsorption on the surface of copper and silver clusters [160] using B3LYP density functional with Hay-Wadt ECP [125], and reported that the cesium cation favors adsorption on the top position of metal (crystal face 100) surface.

Recent theoretical works were devoted to clusters, as in the case of $Cs^+(CH_3OH)_n$ by Cabaleiro-Lago and Rodriguez-Otero [161] using HF, MP2 and B3LYP methods with 6-31 + G* basis on methanol and Hay-Wadt ECP [125], augmented with polarization functions [126] on cesium. The calculations reproduce the frequency shifts in the O–H stretching mode in the Cs^+ clusters. Interaction energies in $Cs^+(CH_3OH)_n$ clusters calculated at HF and DFT level were close to each other in smaller clusters, while in larger ones, they were bigger by up to 43.5 kJ mol^{-1} by DFT, and the MP2 ones somewhat exceeded (by 0.4–23.4 kJ mol^{-1}) the DFT ones. Nguyen and Peslherbe have studied cesium cation microsolvation in acetonitrile clusters [162] using MP2 and CCSD(T) methods with Stuttgart–Dresden–Bonn quasi-relativistic ECP [131] with additional polarization functions on cesium [126], and 6-31G* and 6-311 + G* basis sets on the other atoms. MP2 binding energies were systematically too low (from −7.1 to −15.5 kJ mol^{-1}) while the CCSD(T) value was much closer to experiment (just 4.6 kJ mol^{-1} lower).

A linear structure was found for the complex acetone/Cs^+ studied by Song et al. [163], using MP2 calculations with aug-cc-pVDZ basis on acetone and Stuttgart–Dresden–Bonn quasi-relativistic ECP [131]. In an experimental study of the dissociation of mixed cation-bound dimer of unlabeled and perdeuterated acetone $(C_3H_6O)M(C_3D_6O)^+$ (M = alkali metal, H, Ag) for assessing the kinetic isotope effect, Schröder et al. [164] used B3LYP calculations with 6-31G(d) basis set on C, O and H and Hay-Wadt ECP [125] on cesium. They concluded that the discrepancies between experiments and calculations are possibly attributable to some unexpected limitation of the kinetic method with respect to the determination of kinetic isotope effects in metal-ligand binding.

In the context of biological molecules, Rozman [165] recently studied the gas-phase structures of Na^+ and Cs^+ adducts of leucine and isoleucine as well as the cation bound dimers, including the two possible tautomers of these amino acids (zwitterionic versus “charge-solvated”, i.e., without internal proton transfer). Geometries were optimized at the B3LYP/6-311++G** level and the cesiated structures studied at the B3LYP/LanL2DZ level. Rozman concluded that the kinetic method might not be reliable for structural determinations of the zwitterionic versus charge-solvated forms [165]. In a study of isoguanine tetrad and isoguanine pentad complexes with cesium cation, using the B3LYP functional, Christiansen ECPs [132] on cesium and DZVP basis on the other atoms, Meyer and Sühnel [166] showed that both complexes are non-planar, and that the pentad complex formation is preferred.

In the framework of the transport of cesium radioactive isotopes in the environment, Burk et al. studied interactions between cesium cation and small neutral analogs of humic substances [31] using the B3LYP functional with Stuttgart–Dresden–Bonn quasi-relativistic ECP [131] with additional polarization functions [126] on cesium and Dunning’s DZP basis set with polarization functions on other atoms. The calculated CCBs were in a range 22.6 kJ mol^{-1} (benzene) to 87.4 kJ mol^{-1} (3-aminoglutaric acid). In following studies, Maria et al. have studied cluster ions formed between cesium cation and anions of several organic acids [30,32] by using a similar calculation method with an additional set of diffuse functions on second row atoms for a better description of anionic species. Comparison with the few available experimental data indicated that calculated CCAs were on average 12.5 kJ mol^{-1} smaller than experimental ones. In one of these studies [32], CID experiments on clusters involving anions of dicarboxylic acids indicated the possibility of decarboxylation. This kind of reaction was investigated in a combined theory/experiment investigation, in which the decarboxylation pathways of alkali and alkaline earth diacetate anion were explored by Jacob et al. [167]. DFT calculations were used to provide insights into the structures and reactivity of organometallates. For the calculations, they used the B3LYP method with 6-31 + G* basis on C, O and H, and Hay-Wadt ECP [125] for cesium. They showed that organometallates could be formed by decarboxylation from group II metal acetates, while organoalkali species cannot be formed via this pathway.

Inorganic structures were also investigated, as, for example, their aromaticity in ion pairs with Cs^+. Li and Cheng have studied [168] the aromaticity of square planar N_4^{2-} in Cs_2N_4

using B3LYP functional with Hay-Wadt ECP [125] on cesium, and 6-311 + G* on nitrogen atoms. They gave evidence that Cs_2N_4 species may exist due to significant barriers to isomerization or dissociation. Similar studies on the aromaticity of As_5^- [169] and P_7^{3-} [170] anions in $CsAs_5$ and CsP_7^{2-} species were conducted by Xu and Jin using Stuttgart–Dresden–Bonn quasi-relativistic ECP and valence basis set on cesium and 6-311 + G* on arsenic and phosphorus. Other inorganic cesium systems salts were studied. Odde et al. [171] explored the dissociation of cesium hydroxide in the presence of up to four water molecules using B3LYP and MP2 methods with 6-311++G** basis on hydrogen and oxygen, and Christiansen ECPs [132] on cesium. Only three water molecules were required to form a stable dissociated complex. Structures, vibrational frequencies, infrared and Raman intensities of hexafluorophosphate anions complex with cesium cation was studied by Xuan et al. [172] using HF, MP2 and B3LYP calculations with Stuttgart–Dresden–Bonn quasi-relativistic ECP [131] or Hay-Wadt ECP [125] on cesium atom and 6-311 + G* for the other atoms. A tridentate coordination of the cation by PF_6^- was demonstrated to be the most stable structure in gas phase. Burk and Tamp have studied the gas-phase basicities of cesium oxide and hydroxide [119] using all available ECPs in the EMSL basis set exchange library [120,121] with and without additional polarization functions on cesium [126], and Dunnings DZP basis set without and with polarization and diffuse functions on the other atoms. The best agreement with experiment was obtained with Stuttgart–Dresden–Bonn quasi-relativistic [131] or Christiansen ECPs [132] with corresponding valence basis sets and with additional polarization functions on cesium and double-zeta plus polarization basis on the other elements. Very recently, Ali et al. [173] have studied neutral and positively charged pure cesium clusters, using MP2, CI, and nine different DFT methods with either 3-21G all-electron basis set or ECP due to Stevens et al. [174]. Based on the comparison with experimental data on Cs_2 and Cs_2^+ they concluded that the best results could be obtained with B3LYP/3-21G method.

4. Cesium cation binding energies

The compiled results [175–183] are listed in Tables 1–4, respectively, for CCAs and CCBs of neutral ligands, ligand exchange reactions on cesium cation, CCAs of negatively charged ligands and the interaction potentials between Cs^+ and the rare gases.

Thermochemical data for neutral ligands (Table 1), arranged by increasing complexity and size, are the most abundant. They were determined by a variety of techniques. We included data on simple systems corresponding to reaction (1), and also on multiply coordinated Cs^+, reaction (1′). The CCA value for CsOH was obtained from two different values of the proton affinity of Cs_2O, one in the WebBook, the other corrected by Burk and Tamp [119]. The latter authors commented that probably the sign of the enthalpy of reaction given in the original article [118] was inverted mistakenly. The relative CCAs and CCBs obtained by ligand exchange reaction, listed in Table 2, may be used in connection with data in Table 1 to obtain a few additional absolute values. Cesium cation affinities of negatively charged ligands in Table 3 were obtained from thermochemical cycle involving spectrometric and thermochemical data (see above) or by application of the Hess's law using tabulated enthalpies of formation. Uncertainties on these heterolytic bond dissociation enthalpies obtained from Hess's law are difficult to estimate. The enthalpy of sublimation of the salt is the main source of errors. As stated earlier, the complex composition of the gas phase requires many variables to be adjusted. Uncertainties in the range from a few kJ mol^{-1} up to 8.4 kJ mol^{-1} (2 kcal mol^{-1}) are cited for the alkali fluorides. The other sources of uncertainty come from the enthalpies of formation of the gaseous ions, but they are relatively minor. It should be noted that, in general, the reference thermodynamic tables [48] give the error bars only in a few cases.

Finally, Table 4 is devoted to rare gases, for which the very weak interactions with alkali metal cations are measured by specific techniques, such as ion mobility and scattering cross sections. The interactions are given in the form of interaction potentials rather than thermodynamic values. For a given system, when different sources of data are available, they sometimes differ widely, even when the same experimental technique was used.

Examination of the CCA and CCB data set reveals that the interaction between Cs^+ and neutral polyatomic ligands (Table 1) is relatively weak, probably one of the weakest ion/molecule interaction. Among the polyatomic molecules, carbon dioxide is the weakest base toward Cs^+ (CCA = 25.8 kJ mol^{-1}), whereas the strongest neutral ligand is the crown ether 18-crown-6 (CCA = 170 kJ mol^{-1}). For comparison, the sodium cation affinity for CO_2 is about 60 kJ mol^{-1} [184,185], and is 300 kJ mol^{-1} for 18-crown-6 [46]. The entropies of monoligand adduct formation LCs^+, inferred from published CCAs and CCBs at 298 K, are nearly constant, but are only available for monodentate ligands. This observation allows discussing CCA and CCB on the same basis. Intriguingly, some monosubstituted benzenes exhibit a higher value of the $T\Delta S$ term, and consequently low CCBs as compared to benzene. The sequences of affinity and basicity (CCA and CCB) of substituted benzenes are therefore dissimilar. This may be due to a significant structural change associated to the nature of the substituent, owing to the possibility of bonding on the aromatic electron cloud (π-bonding) or on the heteroatom non-bonding electrons (σ-bonding) [151–154]. Another reason could be that the interaction with the metal ion reduces the rotational flexibility of the substituent. For example, under the conditions of CIDT, when going from the anisole/Cs^+ adduct [154] to the phenol [153] and fluorobenzene [151] adducts, there is a shift from the predominant σ-bonding toward a larger participation of the π-bonding. These effects are worth mentioning from the standpoint of the cation/π interaction, and are further discussed below in the context of relationships between the Li^+ and the Cs^+ affinities.

The relatively large CCA and CCB values for acetonitrile are reminiscent of the high Li^+ cation basicities (LCBs) observed for compounds with a high dipole moment [186]: for the bonding energy of alkali metal cation with neutral organic molecules, the ion/dipole interaction is an important contribution. A general comparison of neutral ligands LCBs shows that they are

Table 1
Cesium cation affinities and basicities of neutral ligands

Ligands[a]	CCA[b]	CCB[b]	Techniques[c]	References to experimental work	References to quantum calculation
$(Cs)_1$	56.9		PD	[107]	[174]
	57.7		HL	[48]	
$(Cs_2)_1$	125.4		PD	[51]	[174]
$(CsOH)_1$	118.4[d]		HL	[48,118]	
	[197.7]				
$(CsI)_1(\mathbf{H_2O})_1$	47.3	22.3	HPMS	[56]	
$(H_2O)_1$	49.7 (4.2)	31.9 (12.8)	DT	[54]	[30,127,128,129,130]
	57.3	33.1	HPMS	[40]	
$(H_2O)_2$	47.4 (4.2)	26.8 (10.7)	DT	[54]	[127,128,129,130]
		25.1 (0.1)	HPMS	[55]	
	52.3	24.7	HPMS	[40]	
$(H_2O)_3$	40.8 (4.2)	20.1 (8.0)	DT	[54]	[127,128,129,130]
		20.2 (0.1)	HPMS	[55]	
	46.9	17.6	HPMS	[40]	
$(H_2O)_4$	44.4	12.6	HPMS	[40]	[127,128,129,130]
$(H_2O)(\mathbf{SO_2})$		17.8 (0.2)	HPMS	[55]	
$(H_2O)_2(\mathbf{SO_2})$		14.8 (0.2)	HPMS	[55]	
$(\mathbf{H_2O})_2(SO_2)$		22.2 (0.3)	HPMS	[55]	
$(H_2O)(\mathbf{CO_2})$		4.9 (0.1)	HPMS	[55]	
$(SO_2)_1$	45.4 (4.2)	21.9 (8.7)	DT	[54]	
		21.8 (0.1)	HPMS	[55]	
$(CO_2)_1$	25.8 (4.2)	8.0 (3.2)	DT	[54]	[30]
		10.0 (0.1)	HPMS	[55]	
		≥6.7 (1.3)	ICP/SIFT	[78]	
$(MeOH)_1$	64.4 [e]	38.1[e]	HPMS	[40,58]	
$(Acetonitrile)_1$	80.3 (0.4)	57.3 (0.4)	HPMS	[175]	[30,162]
$(Acetonitrile)_2$	69.9 (1.3)	42.7 (1.3)	HPMS	[175]	[162]
$(Acetonitrile)_3$	59.8 (0.4)	30.1 (0.8)	HPMS	[175]	[162]
$(Acetonitrile)_4$	50.6 (0.4)	16.8 (0.8)	HPMS	[175]	[162]
$(Acetonitrile)_5$	45.6 (1.3)	4.4 (2.1)	HPMS	[175]	[162]
$(Dimethylether)_1$	57 (5)		CIDT	[134]	[133]
	57 (5)[f]		CIDT	[46]	
$(Dimethylether)_2$	43 (6)		CIDT	[134]	[133]
	47 (6)[f]		CIDT	[46]	
$(Dimethylether)_3$	36 (9)		CIDT	[134]	[133]
	40 (9)[f]		CIDT	[46]	
$(1,2\text{-Dimethoxyethane})_1$	57 (5)		CIDT	[134]	[136]
	57 (5)[f]		CIDT	[46]	
$(1,2\text{-Dimethoxyethane})_2$	50 (7)		CIDT	[134]	[136]
	54 (7)[f]		CIDT	[46]	
$(Benzene)_1$	64.7 (4.9)	38.9 (7.7)	CIDT	[148]	[30,147,148,149]
	64.6 (4.8)[f]				
		36.0 (0.8)	ICP/SIFT	[80]	
$(Benzene)_2$	59.3 (8.0)	15.4 (12.1)	CIDT	[148]	[147,148,149]
	58.9 (7.7)[f]				
$(Toluene)_1$	64.9 (4.7)	30.4 (9.1)	CIDT	[150]	[30,150]
	64.0 (4.4)[f]				
$(Toluene)_2$	58.6 (4.2)	24.1 (14.1)	CIDT	[150]	[150]
	61.6 (4.0)[f]				
$(Aniline)_1$	70.8 (4.5)	42.6 (9.0)	CIDT	[152]	[30,152]
	69.3 (4.2)[f]				
$(Aniline)_2$	62.7 (3.5)	36.2 (14.2)	CIDT	[152]	[152]
	66.1 (3.3)[f]				

Table 1 (*Continued*)

Ligands[a]	CCA[b]	CCB[b]	Techniques[c]	References to experimental work	References to quantum calculation
$(\text{Phenol})_1$	66.2 (3.7) 65.3 (4.9)[f]	31.1 (8.5)	CIDT	[153]	[30,153]
$(\text{Phenol})_2$	57.5 (3.6) 60.4 (4.0)[f]	30.0 (14.1)	CIDT	[153]	[153]
$(\text{Anisole})_1$	66.6 (5.6) 66.4 (5.2)[f]	35.8 (10.2)	CIDT	[154]	[30,154]
$(\text{Anisole})_2$	57.9 (4.0) 61.5 (3.7)[f]	29.7 (15.4)	CIDT	[154]	[154]
$(\text{Fluorobenzene})_1$	50.5 (5.3) 50.2 (5.0)[f]	22.1 (8.4)	CIDT	[151]	[30,151]
$(\text{Fluorobenzene})_2$	40.9 (4.4) 44.6 (4.3) [f]	14.5 (14.5)	CIDT	[151]	[151]
$(\text{Naphthalene})_1$	69.6 (5.6) 69.3 (5.4)[f]	37.8 (10.2)	CIDT	[155]	[155]
$(\text{Naphthalene})_2$	61.4 (3.5) 65.1 (3.4)[f]	29.5 (15.3)	CIDT	[155]	[155]
$(\text{Indole})_1$	82.3 (2.9) 82.3 (2.9)[f]		CIDT	[176]	
$(\text{Indole})_2$	68.5 (2.9) 68.5 (2.9)[f]		CIDT	[176]	
$(\text{Triglyme})_2$	102 (10)		RAK	[103]	
$(\text{12-Crown4})_1$	86 (9) 85 (9)[f]		CIDT CIDT	[67,103,134] [46]	[136]
$(\text{15-Crown-5})_1$	101 (6) 100 (6)[f]		CIDT CIDT	[67,103] [46]	[138]
$(\text{18-Crown-6})_1$	170 (9) 168 (9)[f]		CIDT CIDT	[67,103] [46]	[126]
$(\text{Dibenzo-18-crown-6})_1$	136 (35)		Bracketing	[67]	[67]

[a] Ligand(s) involved in the Cs^+ adduct; when two different ligands are involved, the one lost during the dissociation is indicated in bold.

[b] Cesium cation affinities (CCA, enthalpies) and cesium cation basicities (CCB, Gibbs free energies) values in kJ mol^{-1}; Temperature was stated to be 298 K in most works, and 300 K or 295–296 K in fewer cases; When available, enthalpies at 0 K are given below the 298 K value, footnote f; Uncertainties listed between brackets.

[c] Techniques; CIDT: collision induced dissociation threshold, DT: diffusion tube, HL: Hess law using enthalpies of formation of relevant species [48], HPMS: high pressure mass spectrometry, ICP/SIFT: inductively coupled plasma/selected-ion flow tube, PD: photodissociation, RAK: radiative association kinetics.

[d] Calculated from data in ref. [118] and ancillary thermodynamic data [48]. The value between square bracket made use of the proton affinity of Cs_2O reported in ref [48]; this value appears to be in error [119].

[e] Values obtained from the HPMS data for H_2O and the ligand exchange reaction with H_2O in Table 2.

[f] Values at 0 K.

Table 2
Thermochemical data on ligand exchange reaction on cesium cation, determined by HPMS

Exchange reaction	$-\Delta G^\circ$ $[-\Delta H^\circ]$[a]	Reference
$Cs^+(H_2O)_2 + SO_2 \leftrightarrows Cs^+(H_2O)(SO_2) + H_2O$	7.16 (0.04)	[55]
$Cs^+(H_2O)_3 + SO_2 \leftrightarrows Cs^+(H_2O)_2(SO_2) + H_2O$	5.4 (0.2)	[55]
$Cs^+(H_2O)(CO_2) + H_2O \leftrightarrows Cs^+(H_2O)_2 + CO_2$	20.2 (0.2)	[55]
$Cs^+(H_2O)(CO_2) + SO_2 \leftrightarrows Cs^+(H_2O)(SO_2) + CO_2$	13 (0.2)	[55]
$Cs^+(CO_2) + SO_2 \leftrightarrows Cs^+(SO_2) + CO_2$	11.8 (0.1)	[55]
$Cs^+(CO_2) + H_2O \leftrightarrows Cs^+(H_2O) + CO_2$	24.2 (1.2)	[55]
$Cs^+(SO_2) + H_2O \leftrightarrows Cs^+(H_2O) + SO_2$	12.4 (1.2)	[55]
$Cs^+(H_2O) + CH_3OH \leftrightarrows Cs^+(CH_3OH) + H_2O$	5.02 (0.42) [7.11 (0.84)]	[58]
$Cs^+(H_2O)_2 + CH_3OH \leftrightarrows Cs^+(H_2O)(CH_3OH) + H_2O$	5.86 (0.42) [5.86 (0.84)]	[58]
$Cs^+(H_2O)(CH_3OH) + CH_3OH \leftrightarrows Cs^+(CH_3OH)_2 + H_2O$	2.93 (0.42) [6.69 (0.84)]	[58]

[a] Gibbs free energies (when available, enthalpies given between square brackets) in kJ mol^{-1}, for the indicated reaction, at temperatures between 299 and 304 K; Uncertainties listed in brackets.

Table 3
Cesium cation affinities of negatively charged ligands obtained from thermochemical cycle or enthalpies of formation

Ligand	CCA[a]	Method[b]	Reference to initial work or to data tables	References to quantum calculations
F^-	535.6[c]	TC	[113]	[30]
	548.5	TC	[114]	
	541.8	HL	[30]	
	555.4	HL	[48]	
Cl^-	460.2[c]	TC	[113]	
	465.0	HL	[48]	
	474.5	TC	[91]	
Br^-	443.5[c]	TC	[113]	
	448.4	HL	[48]	
I^-	414.2[c]	TC	[113]	
	417.8	HL	[48]	
HO^-	574.2	HL	[48]	[30,119]
	574.7	HL	[30]	
CsO^-	580.8[d]	HL	[48,177]	
$NO_3{}^-$	517.5	HL	[48]	[30]
$BO_2{}^-$	425.5	HL	[48]	
$LuCl_4{}^-$	379.7[e]	HL	[48]	
$CsSO_4{}^-$	582.8	HL	[48]	

[a] Cesium cation affinities (enthalpies) at 298 K (or 0 K, footnote c); values in kJ mol^{-1}. For a discussion on uncertainties, see text.

[b] Method for estimating CCA; TC: thermochemical cycle, HL: Hess's law, using enthalpies of formation of relevant species [48].

[c] Enthalpies at 0 K.

[d] Value calculated from $\Delta_f H°(CsO^-) = 36{,}4$ kJ mol^{-1} obtained from the electron affinity of CsO, $EA(CsO) = 0.273 \pm 0.012$ eV [177] and $\Delta_f H°(CsO) = 62{,}76$ kJ mol^{-1}. The $\Delta_f H°(CsO^-)$ in the WebBook (3 ± 63 kJ/mol) is not consistent with the tabulated EA(CsO) and $\Delta_f H°(CsO)$.

[e] The main contribution to the uncertainty comes from the error on the enthalpy of formation of $LuCl_4{}^-$, estimated to be ±10 kJ mol^{-1} [218].

Table 4
Interaction potentials between rare gases and the cesium cation

Ligands	Interaction potential[a]	Techniques [b]	References
He	1.3[c]	IMob	[44]
	1.5 (0.15)	Scattering	[111,44]
	1.35[c]	IMob	[178,110,111]
Ne	2.7[c]	IMob	[110,44]
	2.3 (0.15)	Scattering	[111,44]
	2.6[c]	IMob	[179]
Ar	9.5[c]	IMob	[110,44]
	8.16[c]	IMob	[180,44]
	8.20[c]	IMob	[181,44]
	8.14[c]	IMob	[182,110,111]
	8.7 at 225 K	DT	[183,111]
	6.1 (0.15)	Scattering	[111,44]
Kr	12.8[c]	IMob	[110,44]
	11.7[c]	IMob	[180,110,44]
	11.4[c]	IMob	[181,44]
	9.7 (0.15)	Scattering	[111,44]
	11.7[c]	IMob	[182,110]
Xe	14.9[c]	IMob	[110,44]
	10.2[c]	IMob	[178,110,44]
	10.5[c]	IMob	[180,110,44]
	10.96[c]	IMob	[181,44]
	11.5[c]	Scattering	[111,44]
	10.2[c]	IMob	[178,110]
	10.4[c]	IMob	[182,110]

[a] Minimum in the potential energy curve extracted from ion mobility data or ion beam scattering. Uncertainties listed in bracket, when available.

[b] Techniques; DT: diffusion tube, IMob: ion mobility, Scattering: scattering cross sections.

[c] According to ref. [44], the uncertainties on these values are most probably in the range ±(2.1–6.3) kJ mol^{-1}.

about 2.5–4 times larger that CCBs. The variations in CCAs within the ether series (dimethylether, 1,2-dimethoxyethane and crown ethers) are also intriguing: they are different from what is observed for other alkali metal cations and at variance with ab initio calculations [134], and the established ideas of multiple ligation of the alkali ions by polyethers. The likely cause of these large discrepancies was attributed to the presence of multiple conformers (excited conformations) of the multidentate ligand complexes [134]. Anyway, the largest CCAs for organic ligands were observed for the crown ethers and triglyme. The other largest values for Cs_2 and CsOH were evaluated from literature data. When adding a second, third ... ligand to an adduct, the associated CCA ($n > 1$ in reaction (1′)) are steadily decreasing at each step, and entropies are increasing, both effects attributable to gradually weaker bonds.

Thermochemical data on ligand exchange reactions around the cesium cation center, reported in Table 2, correspond mainly to relative Gibbs energies, or relative CCBs. Within the combined errors, they agree with the difference in absolute CCBs in Table 1, for the few cases where comparison can be made. The exchange between water and methanol may be used to obtain the absolute CCA and CCB for methanol, as reported in Table 1. The CCAs for a few negative species are reported in Table 3. As compared to neutral ligands, the electrostatic interaction between Cs^+ and the negatively charged ligands generate a large increase in affinity. When going to cations with smaller ionic radii, the electrostatic interaction is expected to increase. For illustration, the smallest alkali metal cation Li^+ exhibits affinities for F^- and I^- of 755 and 565 kJ mol^{-1}, whereas the corresponding CCAs are, respectively, 536 and 412 kJ mol^{-1} [113]. The largest CCAs may be ascribed to a high charge in the anions. The sulfate anion in $CsSO_4{}^-$ and the oxide ion in CsO^- can be considered as existing essentially in the form of an ion pair with Cs^+ (formally $Cs^+SO_4{}^{2-}$ and Cs^+O^{2-}), and the larger negative charge of $SO_4{}^{2-}$ and O^{2-}, as compared to the other anions of the table (formally monocharged) leads to CCAs in the 580 kJ mol^{-1} range. The smallest CCA for a negative ligand is for $LuCl_4{}^-$ with a charge dispersed on four atoms.

At the lower end of Cs^+ interaction energy range are the rare gases (Table 4), with interaction potentials between 1.3 kJ mol^{-1} for helium, up to approximately 10–15 kJ mol^{-1} for xenon. Considering the electronic structure of the interacting species, the charge/induced dipole (polarization) should dominate the attractive potential energy, and indeed we observed a fair relationship with the polarizability of the rare gases [187], and the median literature value for each gas. In fact it is apparent that xenon does not follow this trend when the literature values around 10–11 kJ mol^{-1} are considered, that is, a value lower than for krypton. The value of 14.9 kJ mol^{-1} would better fit the polarizability correlation, and was retained in the following correlations. The examination of data for the other alkali cations [44,110,111] confirms that their interactions with xenon are always larger than for krypton. Considering the large discrepancies noted in the literature [111], and the strong dependence of the resultant potentials on the model used for analyzing the experimental results, we concluded that it was difficult to correlate the potentials for rare gases with CCAs, unless using an internally consistent set of data. Such sets were established by Takebe [110] or by Rajan and Gilason [111], who also reported literature data in their discussion.

The search of similarity models [188] and regularities among series of data are expected to lead to useful generalization, and help extracting the essential and fundamental components of interactions. Considering the availability of a large number of data, we chose the Li$^+$ affinity and basicity scales (respectively, LCA and LCB) for comparison. We estimated that the correlation of Cs$^+$ affinity and basicity scales with the corresponding LCA [40,44,48,113,134,148,150,151–155,175] and LCB [186] should give a handy summary and would illustrate the general trend in the data. The plot of all available data, common to CCA and LCA scales, is shown in Fig. 1.

Although there is some general trend (see figure caption), there is clearly some outliers. The most apparent deviations correspond to the crown ether 12-crown-4 and 1,2-dimethoxyethane. The problem of polyethers was already discussed above, but it is worth noting that the ab initio calculated CCAs [134] (MP2 level, respectively, 140 and 94 kJ mol^{-1}) would deviate much less from the correlation. The deviations in the CCA values for dimethoxyethane and 12-crown-4 from the theoretical values have been identified as a result of the existence of alternate isomers of the cesium complexes, see above. For these ligands, the LCA and CCA correspond to completely different structures, and do not fit the general trend.

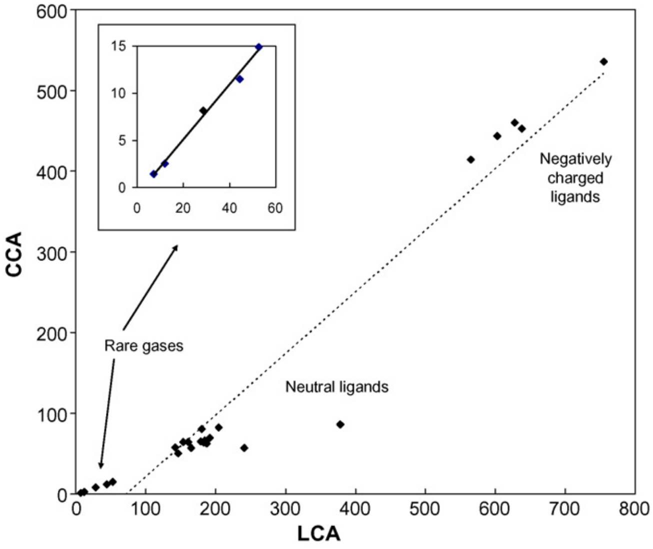


Fig. 1. Cesium cation affinities, for simple one-ligand adducts, plotted against the corresponding lithium cation affinities, in kJ mol^{-1} ($CCA = 0.763 \times LCA - 55.5$, N = number of points = 24; $r^2 = 0.937$). Note that the correlation is strongly influenced by the grouping of the data point at the two limits of the range. The insert correspond to the correlation of the rare gases potentials ($CCA = 0.290 \times LCA - 0.67$, $N = 5$; $r^2 = 0.993$). Most of the LCAs may be found in the WebBook [48a].

The rare gases appear to be well behaved, with a precise correlation equation between the interaction potentials, here taken as affinities. The slope value (smaller than 1) originates in the larger distance between Cs$^+$ and the atom than for Li$^+$. If we exclude the polyethers, the polyatomic neutral ligands are grouped as a small cloud. Within this series, there is also a trend, but no precise correlation. The most deviating points belong to the benzene series. We observed a similar scatter when Gibbs energies (basicities, LCBs versus CCBs) were plotted (not shown). Part of the scatter was attributed to the relatively large uncertainties on absolute CCAs and CCBs, and their small variations when limited to the aromatic series. Nevertheless, the identification of the factors that may be involved in this cation/π interaction is of current interest, since studies on aromatic systems were carried out because of the particular relevance of this interaction in biological systems [189,190]. If we disregard the effect of uncertainties on the scatter, two converging explanations may be proposed for such lack of precise fit between Li$^+$ and Cs$^+$ affinities. First, the calculated structures of the lithium cation adducts of substituted benzenes [191] exhibit significant differences from the cesium adducts [151–154], in term of the preferred σ- versus π-bonding. Rodgers and co-workers noted the predominance of the electrostatic interactions between the alkali metal cations and the aromatic molecules (ion/dipole, ion/quadrupole, ion/induced dipole), with respective distance (r) dependencies in r^{-2}, r^{-3} and r^{-4} [150–155]. With the large differences in charge-ligand distances for the Li$^+$ and Cs$^+$ adducts, and the structure differences, the lack of proportionality can be understood for the aromatic ligands. It is worth noting that the CCA correlations for aromatic ligands turned out to be better when going from Li$^+$ to Rb$^+$ affinities, and also with a slope gradually approaching 1, as seen in Fig. 2.

This observation is in agreement with the increasing similarity of the cations' size.

Returning to Fig. 1, at the high end of the interaction range are the negative ligands, in fact limited to the halogenides, and

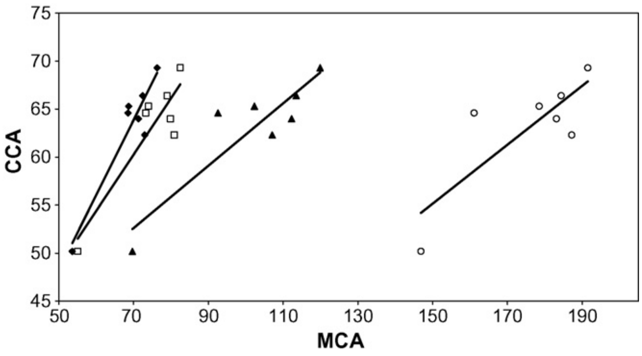


Fig. 2. Correlation of CCA with the other alkali metal cation affinities (MCAs) for aromatic molecules, in kJ mol^{-1}, for M = Li, Na, K, Rb. The regression equations for each M (lines from right to left) are: M = Li (○): $LCA = 0.307 \times CCA + 9.1$, $r^2 = 0.657$; M = Na (▲): $NaCA = 0.325 \times CCA + 29.9$, $r^2 = 0.807$; M = K (□): $KCA = 0.586 \times CCA + 19.2$, $r^2 = 0.814$; M = Rb (◆): $RbCA = 0.781 \times CCA + 9.2$, $r^2 = 0.879$.

BO_2^-. This series is well behaved (LCA = 0.625 CCA + 62.5; $N = 5$, $r^2 = 0.985$), but the slope is higher than for the neutral systems. From the large value of affinities, it is apparent that the attraction between the positive and negative charges, with a dependency in r^{-1}, dominates the interaction. If we postulate that one major effect governs the LCAs and CCAs of negative ions, it is natural to observe such a regularity. As regard to the value of the different slopes seen on the CCA versus LCA plot (Fig. 1), the smallest is for the rare gases, the intermediate value (but not precise) is for the polyatomic molecules (polyethers excluded, see above), and the largest (closest to one) is for the negative ions. This "family dependence" is interpreted in term of the electrostatic model of interaction: the strongest distance dependence for the rare gases (ion/induced dipole, r^{-4}) induces the smallest slope, and the largest slope corresponds to the weakest distance dependence (ion/ion, r^{-1}). An intermediate slope value might be predicted for neutral molecules corresponding to a blend of modes of interactions with intermediate distance dependencies, but as mentioned above, the correlations within this series was rather imprecise. This is most likely the result of the different modes of interaction of Li^+ and Cs^+ with polyatomic molecules. Finally, from our analysis of the trends in LCA and CCA, we conclude that the behaviors may differ significantly within the family of alkali metal cations. Even for the simplest molecules, a simple proportionality is not to be expected.

5. Analytical applications

The cesium cation is increasingly being used as a cationization agent. Although not recent, the strategy of using a metal cation to generate complexes amenable to ESI mass spectrometry (ESI MS) was labeled "coordination ion-spray MS" by Bayer et al. [192]. In that study, the Ag^+ cation was used to demonstrate the efficiency of this method, in particular for low polarity molecules, such as polycyclic aromatic hydrocarbons. This method was extended to other metal cations [193,194] and Cs^+ was widely used. A large number of recent examples involving cesium can be found in the literature. Some studies were carried out in order to study the behavior of the complexes formed, as, for instance, reported in refs. [62,195–197]. The broadening of this concept led to other kinds of studies. For example, Meakinen et al. [198] studied the conformational changes of tetraethyl resorcarene complexed with cesium, using ESI mass spectrometry. Kohtani et al. [199] carried out a study on metal–ion interactions with polyaniline peptides. Such peptides are known to form complexes with alkali metal cations, including cesium. Through ESI experiments, they highlighted the helical conformation stabilized by coordination of the metal ion to the C-terminus adopted by such peptides.

Host–guest complexation studies were also reported. Wu et al. studied the complexation of alkali metal cations with bis-crown ether by ESI MS [200]. Tarnowski et al. [201] tested several macrocyclic diamides as ligands for alkali metal ions including cesium. Jankowski et al. [202] monitored organic synthetic reactions on calixcrown-6 compounds, via cesium complexation, in ESI MS. The positively charged complex allowed monitoring of the reaction.

Some studies explored quantitative analysis by forming cesium adducts amenable to mass spectrometry. Rogatsky et al. [11] developed a sensitive method for the quantification of carbohydrates from human plasma using LC/MS/MS. The ability of cesium cations to form adduct ions $[M + Cs]^+$ with neutral carbohydrates was used for further analysis by ESI MS in positive mode. These experiments were carried out in the "multiple reaction monitoring" (MRM) mode to monitor the transition [M + 133] → [133]. According to the authors, the method developed is robust and highly sensitive for the quantification of carbohydrates in clinical research. Using the same concept, Kaiser et al. [203] developed a new method for the determination of cardiac glycosides using cesium adducts. The formation of cesium complexes of digoxin and digitoxin was studied through LC/MS experiments in the MRM mode leading to the formation of Cs^+ ions as main charged product in high yield. The measurement of Cs^+ ion led to the quantification of cardiac glycosides, with an improved specificity, while retaining accuracy and precision.

The use of cesium as a cationizing agent was extended to the study of polymers, as seen in some recent examples chosen from the literature. Bogan and Agnes [204] studied the cationization of polyethylene glycol with alkali metal cations including cesium, leading to the determination of the relative cation affinities. Jackson et al. [205] characterized poly(methylmethacrylate) and poly(butylmethacrylate) using ESI MS and alkali cations doping. They showed that the cation with greater ionic radii may yield the most useful structural information as the mass-to-charge ratio of the precursor ion increases. Among the data obtained on the analysis of biomolecules and polymers using Cs^+, are some studies with matrix-assisted laser desorption-ionization (MALDI) MS [206–210].

Lebrilla and co-workers examined the multiple cationization of acidic oligosaccharides by alkali metal ions [208]. The specific properties of Cs^+ (large size compared to Li^+ or Na^+) were critical in the adduct formation and the loss of acidic parts of the oligosaccharide adduct in the CID process. Schiller et al. used CsCl [209] as an auxiliary reagent for the analysis of phosphatidylcholine in MALDI/time of flight (TOF) mass spectrometry. Such compounds were cationized by the addition of inorganic ions. In biological samples, the presence of H^+, Na^+ and K^+ leads to a complex distribution of masses and a difficult peak assignment. The use of cesium, generating non-naturally occurring adducts easily identified due to the large shift in their mass-to-charge ratio, circumvented the problem of the mass spectra complexity. Kaufman and co-workers studied copolymers of methyl methacrylate (MMA) and butyl methacrylate (BMA) [207]. Interferences generated by metal cation, such as sodium and potassium led to difficult interpretation. The metal adducts overlapped the peaks from the copolymer. The use of cesium ions allowed the generation of ions with unambiguous m/z with respect to the ions from the copolymer. Laine et al. [210] investigated the systematic changes in fragmentation behavior of poly(methyl methacrylate). Such polymers were cationized with alkali metal cations, including cesium, in order to explore the influence of the cation size on the fragmentation behavior. It was shown that increasing the molecular weight of the poly(methyl methacrylate) required an increase in the size of the cation to improve the signal intensity. Among other application in analytical MS, we can cite mass calibration. The generation of high molecular weight cesium ion clusters by ESI MS was demonstrated and used for the calibration of a spectrometer [211], in the negative mode, up to $m/z = 6000$. Konig and Fales [212] report the calibration of a spectrometer up to $m/z = 10{,}000$ using cesium clusters generated from cesium salt of tridecafluoroheptanoic acid.

Another important application of cesium in analytical mass spectrometry is the so called "cation mass spectrometer" (CMS) developed by Wirtz and co-workers [213–217] who devised a new ionization technique for secondary ion mass spectrometry (SIMS). SIMS suffers from a limitation due to matrix effects, because the ionization of a specified element is strongly dependent on the composition of the surrounding material. The CMS method circumvents the matrix effect by detecting MCs^+ clusters, and additionally $MCs_2{}^+$ in the case of electronegative elements. Such clusters are generated by the combination of a secondary neutral M^0 species with a resputtered cesium cation in the region near the sample surface. The ion formation is decoupled from the emission process of the neutral species (M^0). As compared to classical SIMS, the ionization probability in CMS mode exhibits a much-reduced dependence on matrix composition. This drastically decreased the matrix effects and opened the way toward a convenient mode of quantitative analysis by SIMS.

6. Conclusion

As stated in the introduction of this review, the migration and dissemination of cesium in soils is of environmental concern. Despite this, there are relatively few quantitative data on the intrinsic interaction between Cs^+ and organic matter, in particular small molecules or anions that may be used for modeling organic functions.

The quantum calculations on relatively simple systems appear to be of fair to good precision from the point of view of energetics. These theoretical approaches may help the experimentalists, by tracing the flaws in data, and eventually expanding the cesium affinity/basicity scales. These Cs^+ scales constitute Lewis basicity scales distinct from the other cation scales, as shown in particular by the lack of precise correlation with the lithium affinity/basicity scales. Nevertheless, the number and variety of ligands need to be expanded.

A better understanding of the cation/π interaction was obtained by examining affinities of substituted benzenes toward the series of alkali metal cations, and particularly by the comparison of the scales pertaining to the most dissimilar cations, Li^+ and Cs^+. The systems that can be compared at this moment are still limited by the paucity of CCA values. An improved knowledge of the cesium cation interaction with model systems may benefit the modeling of various aspects of cesium retention and migration in soils and radioprotection. In the field of analytical mass spectrometry, we expect that the applications of cationization by Cs^+ will be further developed, in synergy with the knowledge of the coordinating properties of the cesium cation.

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Appendix A. Supplementary data

Supplementary data containing the full title of the cited references associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2007.03.004.

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