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Application of In^+ ions in ion attachment mass spectrometry

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Abstract

Theoretical and experimental understanding and evaluation of In^+ as a new type of attachment ions for ion attachment mass spectrometry was carried out. In order to establish the affinities of molecular species to these group III B metal ions, theoretical studies using ab initio molecular orbital techniques were made. The experimental study was done by using a quadrupole mass spectrometer fitted with an ion–molecule reaction chamber. In particular, a study of the gas phase ion chemistry of In^+, generated by thermionic emission, with acetone and benzene molecules is reported. This study demonstrated that, as a new attachment ion, In^+ is as useful as Li^+ reported earlier, providing an indication of the many advantages afforded by alkali metal ions. (Int J Mass Spectrom 198 (2000) 15–21) © 2000 Elsevier Science B.V.

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1. Introduction

Ion attachment mass spectrometry (MS) [1] is a technique where a sample is ionized by a primary ion in an ion–molecule reaction. In general, it has the advantage of being a soft ionization technique; the sample ion is, therefore, less likely to fragment and greater information about the intact sample molecule may be obtained. An added advantage of this technique is that direct determination of unstable, intermediary, and reactive species is possible. Sensitivity is high because of the ion–molecule reactions.

Studies on the ion chemistry of various metal ions with various classes of molecules have been done in several laboratories [2–7]. Alkali ions, especially Li^+ ions, have been mainly utilized as primary ions since they can be readily generated by thermionic emission. Staley and Beauchamp [6] have been pioneers in this area. Studies involving affinities of alkali ions have also been reported [7].

With recent developments in Li^+ ion attachment mass spectrometry instrumentation [1a, 1b, 1c], we have shown in previous studies that the newly developed method is especially suitable for detecting free radicals [1d, 1e] in microwave (mw) plasma. This is because the neutral radicals in the plasma are cationized by Li^+ in the reaction chamber before being sampled by the quadrupole mass spectrometer (QMS). Ion attachment mass spectrometry can be also applied to product analysis in plasma studies, particularly for detection of unfamiliar neutral species as well as hydrocarbon polymer radicals that are generated in quite complex ways [1f].

Because of these advantages, its popularity for analytical applications is likely to increase. However,

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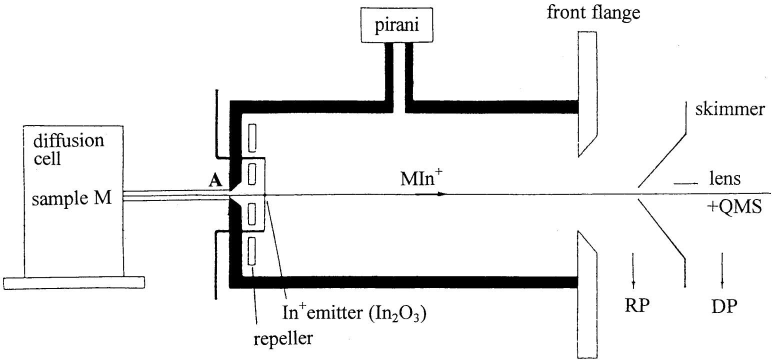

Fig. 1. Schematic of the In^+ ion reactor/mass spectrometer system. The diffusion cell is connected to the reactor allowing the sample through aperture A.

to date, the choice of primary ions has remained remarkably limited and future developments in the area call for exploring the utility of a wider range of primary ions.

In atoms in the ground state $^3P_{1/2}$ have the electronic configurations Kr $5s^25p^1$. The ionization potentials (IP) of In are 5.8 eV. This value is low enough to permit the use of surface ionization techniques to generate ions in sufficient quantities for mass-spectrometric studies. In their ground-state electronic configurations, their ions resemble alkali ions in the valence shell and can assume *sp* hybridization in compounds. However, the use of group III B metal ions as primary species for ion attachment MS has not been previously explored.

Almost nothing was previously known about In^+ cation adducts of organics or the nature of their bonding. These ions may behave characteristically in terms of interaction with organics, but they cannot be accessed experimentally. In this sense, *ab initio* molecular orbital (MO) calculations help by providing important insight into factors such as binding energies, charge distributions, geometrical distortions, and the intrinsic interactions between a compound and these ions [8–10].

We report here a study of: (1) efficient emitters of group III B metal ions (Al, Ga, In); (2) theoretical determination of In^+ affinities of some molecular species; (3) ion adduct mass spectra obtained by using In^+ ions as a primary species in ion attachment MS; and (4) features of group III B In^+ metal ion attachment to the molecular species. We discuss the significance of our results with reference to those obtained from some other related Li^+ studies [11,12].

Our objective is to give some guide to the possibility of using In metal ions as primary ions, which will be essential in the future development of more sensitive detection with the ion attachment/mass spectrometry technique.

2. Experimental

2.1. Apparatus

The apparatus used (Fig. 1) in this study was a modified QP-1000 series quadrupole mass spectrometer manufactured by Shimadzu, Inc., Japan which was essentially the same as used previously in this laboratory for studies of Li^+ ion attachment mass spectrometry [1a]. Briefly, the combined sample inlet system/ion attachment reactor/mass spectrometer was constructed to detect and assign the target species (M) by mass analyzing an ion adduct formation.

Primary ions from a thermionic source are produced in the reactor chamber where ion attachment to the species M takes place. The ionized adducts travel through the chamber with the aid of a small electric field provided by a 6 V potential drop across the chamber. They are focused by a final lens element onto a quadrupole mass spectrometer for detection and mass analysis.

We studied acetone and benzene drawn into the reaction chamber through aperture A. Sample concentrations were prepared by the method of passing a carrier gas over a permeation tube of either acetone or benzene (Gastec, Tokyo) enclosed in the diffusion cell (in a stainless steel housing) [13].

2.2. Emitters of primary ions

Al_2O_3, Ga_2O_3, and In_2O_3 in fine powder form (purity 99.99%, Wako Chemicals, Tokyo) were used as the thermionic materials [14–16]. The oxides were mixed with distilled water to form a slurry. An Ir wire of 0.127 mm in diameter was wound into a filament in the form of a 5 mm long helix of about three turns with an internal diameter of 2 mm. The entire filament was dipped into the slurry to achieve the desired coating. The coated filament was placed in the reaction chamber, which was then evacuated. A current of 1.2 A through the filament was sufficient to produce an ion emission current of 10^{-6} A. For the first several hours of operation, emission of the contaminants Na^+ and K^+ may be significant. These subsequently decreased to less than 1% of the total emission. Variations of total ion-emission current and ion purity with the surface temperature of the filament and over time were studied using the quadrupole mass spectrometer.

2.3. Calculations

Standard ab initio MO and density functional theory (DFT) calculations were carried out by using the "GAUSSIAN 94" software package [17] on an NEC SX-4 supercomputer. We calculated the binding energies of In^+ and Li^+ with the target molecules based on the second order Møller-Plesset perturbation theory (MP2) and Becke's three parameter hybrid method with Perdew/Wang 91 (B3PW91) optimized structures.

For carbon, hydrogen, oxygen, and lithium atoms, standard double-zeta plus polarization (DZ + P) basis sets were used. For heavy atoms such as indium, relativistic effects may not be negligible. Hence, for In, we employed the relativistically corrected effective core potential (ECP) with the triple-zeta plus polarization (TZ + P) basis set [18]. In all the energies we present in this article, the effect of zero point energies and the enthalpy correction as −RT have been neglected since both corrections were expected to be trivial.

It is well known that the larger basis sets with diffuse functions and basis set superposition error (BSSE) correction are important for the accurate affinity calculations especially at the MP2 level of theory. But even at the present level of theory, we believe that our calculations may give a reasonably good prediction. It is especially true in the DFT calculations [19,20] since the influence of BSSE and the size of the basis set in DFT calculations are negligible.

3. Results and discussion

3.1. Efficient emitters

The choice of an appropriate primary ion is governed by several considerations: (1) the metal atom must have a low IP so that ion production will be abundant; (2) the primary ion should have a high affinity with the target molecules; (3) low temperature is preferable for efficient attachment; and (4) the purity of the ion emission is important. With these considerations in mind, Al^+, Ga^+, and In^+ were investigated for use as alternative primary ions in ion attachment mass spectrometry.

Ir filaments were coated with oxides of group III B metals (Al_2O_3, Ga_2O_3, and In_2O_3) to form thermionic emitters of purely ground state Al^+, Ga^+, and In^+ ions. The characteristics of Al^+, Ga^+, and In^+ ion emissions, such as the dependence of ion purity and abundance on temperature, together with their stability over time, were studied.

A detailed study of Al^+ ions was ruled out because the Al_2O_3-coated emitter produced Al^+ ions of high abundance only when heated above 2000 °C. A filament temperature of above 2000 °C is not preferred for efficient attachment under the present experimental setup.

Table 1
Binding energies (affinities, kcal/mol) and distance *R* (Å)[a], calculated at the MP2 and DFT levels for complexes of In^+ together with those of Li^+

	MP2		B3PW91	
Complex	Affinity	R	Affinity	R
H_2O–In^+	23.3	2.428	25.2	2.402
H_2O–Li^+ [b]	32.8	1.886	37.3	1.871
$(CH_3)_2CO$–In^+	29.1	2.288	33.1	2.249
$(CH_3)_2CO$–Li^+ [c]	43.6	1.807	46.5	1.786
C_6H_6–In^+	27.0	2.617	27.2	2.626
C_6H_6–Li^+ [d]	40.6	1.906	39.1	1.900
CH_4–In^+	3.34	3.066	4.42	3.021
CH_4–Li^+	11.2	2.196	12.3	2.195
CH_3–In^+	12.1	2.311	18.0	2.307
CH_3–Li^+	13.8	2.232	14.9	2.342
C_2H_3–In^+	19.7	2.143	23.0	2.246
C_2H_3–Li^+	22.4	2.263	22.0	2.238
C_2H_5–In^+	15.4	2.525	20.0	2.456
C_2H_5–Li^+	18.7	2.287	20.3	2.265

[a] Bond length (angstrom) between metal ion and the target species.
[b] Experimental value: 34.0 kcal/mol.
[c] Experimental value: 44.5 kcal/mol.
[d] Experimental value: 37.9 kcal/mol.

The Ga_2O_3-coated filament began to emit a high total ion-emission current around 1400 °C, but the current decreased to a small value after 1–2 h, showing that almost all the Ga_2O_3 compound had evaporated from the filament. This was perhaps caused by the volatile nature of Ga_2O_3 with the heated Ir filament. Practically, the Ga_2O_3 was found unsuitable as a source of primary ions.

A very stable In^+ ion-emission current could be obtained throughout at least a whole week of heating with the emitter temperature at around 1500 °C. This is a much lower temperature than that at which Al^+ ions could be obtained. The purity of In^+ ions increased to 95% after 1 day of aging. Therefore, further investigations were made for In^+ only.

3.2. Theoretical considerations (geometry and energies)

The aim of this study was to establish the In^+ affinity of some organics. Since there are no previous calculations or experimental values available, we calculated the binding energies (affinities) of In^+ with the target molecules based on optimized structures. The target molecules included H_2O, $(CH_3)_2CO$, C_6H_6, CH_4, CH_3, C_2H_3, and C_2H_5. The results are summarized in Table 1. The study allows prediction and represents our first step in establishing In^+ ion attachment mass spectrometry.

For comparison, we also calculated the Li^+ ion affinity of these species—the results are in good agreement with experimental values available from the literature [21] and theoretical values at various levels [22–24]. The calculated Li^+ ion affinities were within only 2.6 kcal/mol of the experimental values. A summary is shown also in Table 1.

In order to determine the most stable structure, we carried out an optimization at the MP2 and DFT levels of theory using the CDZ + P with ECP and TZ + P basis set on some possible stable isomers. It was found that the symmetry of the most stable structure obtained for In^+ ion complexes was exactly the same as that previously found for Li^+ complexes [25,26].

The distances between the metal ion and ligand organics (denoted as R) are also listed in Table 1, since the predominant interaction of the ion complex is believed to be electrostatic.

With regards to the In^+ affinity of organics that

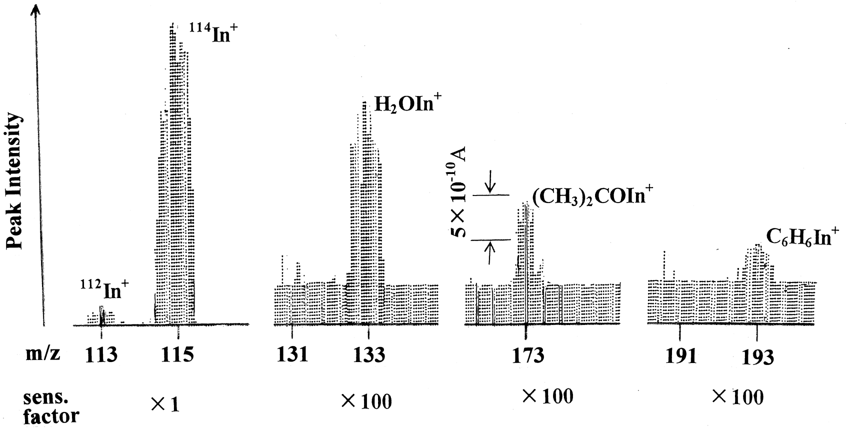

Fig. 2. The partial mass spectra of In^+ ion adducts obtained from acetone and benzene samples, showing $(CH_3)_2CO–In^+$ (*m/z* 173) and $C_6H_6–In^+$ (*m/z* 193). Samples were introduced through the diffusion cell at rates of 2.6×10^{-10} and 1.1×10^{-10} g/s, respectively.

have not been obtained experimentally, the following remarks can be drawn from this theoretical study of seven In^+ adducts.

(1) The In^+ affinities of the closed-shell molecules were calculated at the MP2 and B3PW91 levels. The values of In^+ affinity presently calculated were weaker than those calculated for the Li^+ affinity. However, the values, except that for CH_4, are still large enough for them to attach to In^+ ions, since compounds whose Li^+ affinities are larger than ~10 kcal/mol are detected even if they are present in a small abundance under our experimental conditions for Li^+ ion attachment mass spectrometry [1j]. Hence the In^+ adducts of these species should be observable mass spectrometrically if experimental techniques are devised to permit attachment reactions in the gas phase.

(2) Regarding the open-shell molecule systems of CH_3, C_2H_3, and C_2H_5, the binding energies of $CH_3–In^+$, $C_2H_3–In^+$, and $C_2H_5–In^+$ were calculated to be 12.1 (18.0), 19.7 (23.0), and 15.4 (20.0) kcal/mol, respectively, again at the MP2 (B3PW91) level. Comparison clearly shows that, in contrast to the closed-shell molecules, the In^+ affinity of these radicals is almost as strong as the Li^+ affinity. Because $C_2H_3–Li^+$ and $C_2H_5–Li^+$ could be observed [1e] with our ion attachment mass spectrometric system, we can reasonably predict that the In^+ complexes should also be easily detected when these species are present.

(3) For the closed-shell species, the agreement between MP2 and B3PW91 value is reasonable. In contrast, there are large discrepancies between these levels for the affinities and bond lengths of the metalated radicals. Further, In^+ binds the radicals stronger than Li^+ at the B3PW91 but weaker at the MP2.

3.3. *In^+ adduct mass spectra*

The In^+ mass spectra were taken in the partial scan mode for a mixture of acetone and benzene compounds in N_2 gas. The sample gas was introduced directly to the reactor at a flow rate of 5 mL/min. Only the quasimolecular species, In^+ complexes, were found to be present, demonstrating that In^+ ion attachment mass spectrometry always provides single ion species.

Fig. 2 shows four partial mass spectra over the *m/z* regions 113–117, 131–135, 172–176, and 191–195, where the primary ions, In^+, H_2O-In^+, $(CH_3)_2CO$-In^+, and C_6H_6-In^+ were monitored. The acetone sample was introduced at a rate of 2.6×10^{-10} g/s from the permeation tube at 25 °C, whereas the benzene sample at the rate of 1.1×10^{-10} g/s. Measurement of the acetone adduct ion yielded a value of

1.1×10^{-9} A, which is the output of the ion multiplier with the gain at 5×10^4. This current corresponds to 2.2×10^{-14} A (1.4×10^5 ions/s). Thus, the sensitivity is 8.5×10^{-5} A/(g/s).

Taking the actual noise level of the system as the ultimate limitation on the minimum detectable sample size, we can estimate the minimum detectable amount (mda). The mda was calculated to be 2.3×10^{-11} g/s on the assumption that the capability of the ion detection system in the present mode, at a signal-to-noise ratio of 3, was around 2×10^{-15} A. No attempt was made in the present study to improve the ultimate sensitivity of In^+ ion attachment mass spectrometry. By employing more efficient ion production, it is likely that the sensitivity could be extended.

Studies on Li^+ have been reported [1a] and provide an interesting comparison. The sensitivity when using Li^+ as the primary ion is 5.8×10^{-4} A/(g/s) for acetone, which is calculated from the output current with the multiplier gain at 2×10^3. Comparison indicates that sensitivity demonstrated for In^+ is actually worse [8.5×10^{-5} A/(g/s)], confirming the previous estimate of the MO calculation; the In^+ affinity of acetone is smaller than the Li^+ affinity. The emission intensity of In^+ ions is approximately 1/3 that of Li^+ ions, which may be related to the slightly higher IP of In. This emission property is another reason which may partially explain the poorer sensitivity of In^+ ion attachment mass spectrometry when compared with the corresponding Li^+ ion system.

3.4. Concluding remarks

The In^+ reactor/quadrupole mass spectrometer setup was successfully used for the understanding and evaluation of a new class of attachment ions utilizing ions of the group III B metal, In. An In^+ emitter of an Ir filament coated with In_2O_3 was satisfactory for this purpose.

Analysis by In^+ ion attachment mass spectrometry showed only the quasimolecular ions formed by In^+ ion attachment and indicated the capability for measurements at levels of 2.3×10^{-11} g/s for acetone. The linear dynamic range for the measurements is ultimately limited by the finite abundance of the primary ion emission. It might be interesting to compare the present results with quantitative experimental work on complexes of Ag^+ and Cd^+ [27].

Our experimental results validated calculations performed before the experiments. MO calculations revealed smaller affinity values in In^+ ion attachment than in Li^+ ion attachment, which predicts poorer sensitivity in In^+ ion attachment mass spectrometry. This drawback may be overcome by using ions of another group III B metal, Ga. Preliminary theoretical study indicates that a wider range of compounds have sufficient Ga^+ binding energies to be detectable at concentrations as low as Li^+ ions can provide. It should be noted, however, that this system would best be accomplished after a practically efficient Ga^+ emitter has been found.

MO calculations indicate also that C_2H_3 and C_2H_5 radicals have In^+ affinities as large as their Li^+ affinities. We can reasonably predict that these radicals will be detected with In^+ ions as easily as with Li^+ ions. Therefore, the present method appears to have advantages over the established Li^+ ion attachment mass spectrometry, since the former can detect the radical species among the complex gaseous samples more specifically (selectively) than the latter.

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