International Journal of Mass Spectrometry xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Fifty years of ion and neutral thermochemistry by mass spectrometry

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ARTICLE INFO

Article history:
Received 13 March 2014
Received in revised form 17 April 2014
Accepted 19 April 2014
Available online xxx

Keywords:
Appearance energy
Association
Collision-induced dissociation
Electron affinity
Equilibrium
Ionization energy
Photodissociation

ABSTRACT

Originating with the appearance potentials for "positive rays", the ability of mass spectrometry to obtain quantitative information about the energetics of both ions and neutrals has evolved dramatically. About 50 years ago, many of the techniques that are now common place were first implemented, the interim has seen significant advances in both instrumentation and analysis tools. In this review, a short historical perspective of mass spectrometric approaches to ion and neutral thermochemistry is provided. Included are determinations of ionization and appearance energies, electron affinities, and dissociation energies. The latter are explored via techniques utilizing metastable decomposition, visible and VUV photodissociation, infrared photodissociation, collision-induced dissociation, and electron-induced dissociations, as well as applications of equilibrium methods and association processes. Although many of these techniques focus on ion thermochemistry, the ability to measure the thermodynamics of neutrals via mass spectrometric approaches is also highlighted.

1. Introduction

Early experiments found that the appearance of "positive rays" was strongly influenced by the electric potential used to accelerate the electrons forming them. (Positive rays were ionized atoms and molecules [1], as first identified by Goldstein in 1886 [2]. Wien found that they were positively charged and much more massive than electrons, as demonstrated by deflection in a magnetic field [3].) This observation leads naturally to the realization that quantitative thermodynamic information might be obtained from mass spectrometric experiments. Indeed, early measurements determined that the minimum potential needed to create positive rays (by ionizing the gas) varied with the gas identity. This minimum potential equals the ionization energy, although the earliest such experiments generally did not include identification of the mass of the species. When mass characterization was included, the cationic species formed by ionization of molecular species near the threshold was generally found to be the intact molecule. At higher accelerating potentials, these molecular species were found to fragment. Measurements of such appearance energies rapidly expanded the thermochemical database for ions. F.H. Field and J.L. Franklin published one of the first compilations of such thermodynamic information in 1957 [4]. Subsequent versions include "Gas-phase Ion and Neutral Thermochemistry" (or "GIANT Tables") [5], proton affinity evaluations [6], and now the NIST Webbook [7] [2014 (#2844 2014), (retrieved March 6, 2014), (retrieved March 6, 2014) #2844], which contains regularly updated and evaluated thermodynamic information on ions and neutrals. Since these early days, increasingly sophisticated tools, many of which are covered thoroughly in an excellent review elsewhere [8], have been employed to examine the thermodynamics of ions and their neutrals. Here, we briefly recount historical aspects of the development of many of these experimental methods over the past 50 years or so.

Any account of ion thermochemistry must include the conventions for treating the enthalpy of the electron. Most thermodynamicists (including this author) use the "electron convention", where the enthalpy and free energy of formation of the electron are zero at all temperatures, as for any element. This convention allows the enthalpies and free energies of formation for all substances to change little with temperature. (It is also useful to recall that enthalpies and free energies are equal at zero K, but deviate somewhat at higher temperatures because of the contribution of entropy.) Many mass spectrometrists prefer the "ion convention", where the enthalpy of formation of the electron is assigned to equal its heat capacity. Generally, the heat capacity of the electron is assumed to follow Boltzmann statistics (5RT/2 or 6.197 kJ/mol at 298 K. A more correct treatment uses Fermi–Dirac statistics (3.145 kJ/mol at 298 K) [9,10]. Because the enthalpies of formation of ions at nonzero temperatures vary with the convention adopted, this must be specified in careful work.

2. Ionization and appearance energies

As noted in the introduction, ionization energies were the first thermodynamic data obtained concerning ions. The earliest

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http://dx.doi.org/10.1016/j.ijms.2014.04.005

determinations generally involved electron ionization, such that the minimum accelerating potential needed to induce ionization of a gas by electrons was measured. Hence, "ionization potential" was the term used originally, but as other means (e.g., photons) can be used to ionize gases, the preferred term is ionization energy (IE). The process involved is shown in reaction (1), where the enthalpy of reaction simply equals the IE.

$$AB + e^-(h\nu) \rightarrow AB^+ + 2e^-(e^-) \quad \Delta_r H = \text{IE} \qquad (1)$$

(This reaction also makes clear why ion enthalpies of formation depend on the convention used for the electron enthalpy.) The threshold laws for electron and photon ionization differ, as shown by Wigner [11]. For photoionization, the onset is a step function, whereas the probability of electron ionization increases linearly with electron energy exceeding the threshold. Because of the sharp rise associated with photoionization, more precise thresholds can generally be obtained, as demonstrated nicely for atomic species. Photoionization of molecular species was not accomplished until the middle of the 20th century and originally did not include mass selection. For example, the photoionization of NO showed steps in the photoionization yield that corresponded to the vibrational levels of NO^+ [12]. In this favorable case, the low IE of NO meant that ionization of other species present did not occur, hence no mass resolution was needed. For electron ionization, which was easier to implement experimentally, early developments included using electron monochromators to narrow the width of the electron energy distributions (to 50–70 meV) that lead to lower resolution in the IE onset. Less rigorous "quasi-monoenergetic" methods [13], such as retarding potential difference and energy distribution difference methods, were also developed.

When mass spectrometers were added to the instruments used to measure ion yields, the formation of molecular fragments (rather than the intact molecular ion) could now be observed. Using the same approaches as for IE measurements, appearance energies (AEs, originally "appearance potentials") of fragment ions could be determined. Here the enthalpy of reaction is that shown in reaction (2).

$$AB + e^-(h\nu) \rightarrow A^+ + B + 2e^-(e^-) \quad \Delta_r H = \text{AE} \qquad (2)$$

In 1958, photoionization sources were first coupled with mass selection [14]. A couple of years later, the use of a He discharge lamp as a monochromatic light source was employed for VUV photoelectron spectroscopy [15,16] in which the kinetic energies of the ejected electrons were first measured. The year 1967 saw the first measurement of threshold photoelectrons [17], as well as the first coincidence measurements of photoelectrons and photoions (PEPICO) [18]. Several threshold types of measurements have enhanced the resolution of such studies even further [19] and include threshold photoelectron spectroscopy (TPES), which is also known as ZEKE spectroscopy (zero kinetic energy electrons) [20,21], pulsed field ionization (PFI) [22], and threshold PEPICO (TPEPICO) experiments. An example of the dramatic improvement in resolution (and hence information) is shown in Fig. 1 for the ionization of benzene [23]. This compares results from regular photoelectron spectroscopy (PES) and photoionization studies (showing the vibrational steps alluded to above for NO) with PFI results. Comparison of the top and bottom spectra shows an enhancement in the resolution of about an order of magnitude (linewidths of ~10 and ~1 meV, respectively). (Some of the resolution enhancement is also attributable to the use of a supersonic expansion. The direct effects of this are better quantified for the case of benzene by Long et al. [24], who found linewidths in their photoelectron spectra of 6–10 meV for an effusive source and 3–5 meV for a supersonic expansion.) More recently, free electron (synchrotron) light sources have greatly expanded the range of systems studied by extending the photon range and intensity [19,25,26].

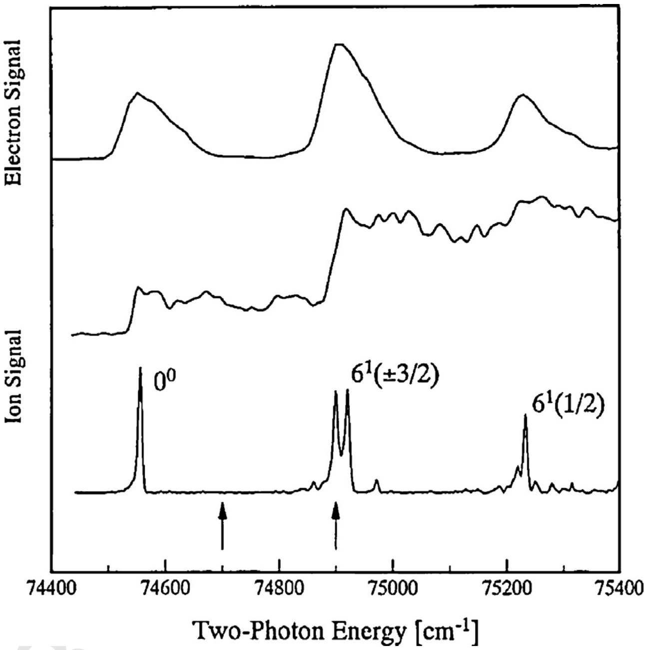

Fig. 1. Spectra for ionization of benzene using time-of-flight photoelectron spectroscopy (top), photoionization efficiency (middle), and zero electron kinetic energy photoelectron spectroscopy (bottom). Labels mark the origin 0–0 transition and two vibrational states of the ion.

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The methods described above provide many of the available IE and AE values, but additional approaches are valuable in unusual circumstances. Notably, this includes cases where Franck–Condon (FC) factors make it difficult to observe the adiabatic IE. Classic examples include NO_2 and CH_4, which greatly distort upon ionization. In such cases, accurate IEs (although less precise than spectroscopic) can be obtained using charge transfer reactions, which can be conducted as equilibrium, bracketing, or threshold measurements [27,28], see below. The NO_2 case is exemplary. Here, the bent NO_2 molecule distorts to linearity upon ionization ($NO_2{}^+$ is isoelectronic with CO_2). Hence, PES exhibits no intensity at the adiabatic IE and adiabatic IE values ranging from about 9.8 to 12.3 eV had been reported, with a couple of spectroscopic results indicating a value near 9.6 eV but a chemical reaction indicating a lower limit of 9.685 eV (as reviewed in Ref. [28]). At the time, the most definitive measurement in the literature had been performed by Grant and coworkers who used multiple photon processes to overcome the FC restrictions, and obtain a very high precision IE [29]. Here, two photons (of different color) were used to resonantly excite NO_2 to a linear Rydberg state, which was then photoionized with a third photon. Their onset was 9.586 ± 0.002 eV, although it was possible that this value could have corresponded to an excited vibrational state of $NO_2{}^+$, which would have shifted the true adiabatic IE down by 0.076 eV. In our laboratory, we examined the kinetic energy dependence of several charge transfer reactions with both NO_2 and $NO_2{}^+$. The most definitive result was the observation that charge transfer with Zn^+ was endothermic by 0.21 ± 0.03 eV, indicating $\text{IE}(NO_2) = 9.60 \pm 0.03$ eV [28,30]. In this case, the FC restrictions are overcome because nuclear motion is an intrinsic part of this endothermic charge transfer reaction, hence relaxation of the structure of the NO_2 upon ionization occurs naturally during the course of the reaction. The agreement between our result and the very precise value from Grant and coworkers verifies that this is the correct adiabatic IE.

Please cite this article in press as: P.B. Armentrout, Int. J. Mass Spectrom. (2014), http://dx.doi.org/10.1016/j.ijms.2014.04.005