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Mass Spectrometry

Volume 6

A Specialist Periodical Report

Mass Spectrometry

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Mass Spectrometry

Volume 6

Foreword

Had J. J. Thomson been alive today he would have surely marvelled at the development in ion chemistry that has taken place since his initial observations on the behaviour of ions in magnetic and electric fields. Even those early pioneers Aston, Bainbridge, Dempster, Herzog, Mattauch, and Nier amongst others could scarcely have foreseen the developments in instrumentation which have occurred to such an extent that the mass spectrometer, usually with its attached computerized data system, can be operated routinely in analytical laboratories interested only in the results it gives and not in the underlying principles. Thus, some chapters of this Specialist Periodical Report are more concerned with the extraordinary ability of the mass spectrometer to yield molecular structural information and analytical identification and estimation of compounds available only in very small quantities. On the other hand, the successors of those early pioneers are making enormous strides in the understanding of ion chemistry, and the remainder of the chapters is given over to descriptions of these advances.

This dichotomy in outlook of the Reports together with the limited space available means that their usefulness will vary from reader to reader. However, it is hoped that the balance is reasonable for the majority. As introduced earlier, and continued in this volume, there are some short, authoritative accounts of developments in specialized areas. Ion mobilities and secondary ions are two such fields which have increasing practical importance in areas other than mass spectrometry alone. Somewhat more esoteric is the article on the effects of electromagnetic radiation on ions by which their structures can be probed. Along with the chapter on the theory and energetics of mass spectrometry these articles provide a strong American contribution to Volume 6 in the guise of Tomas Baer, Robert Dunbar, Alan Krauss, Victor Krohn, and Larry Viehland.

The international flavour of this series is enhanced by our regular Australian contribution from John Bowie and his colleagues. It is hoped to extend this international aspect of the Reporters to the series along with a continuation of the specialized topics. From this viewpoint the very helpful, objective criticisms and suggestions of reviewers are greatly appreciated.

Amongst our new contributors we welcome Ian Howe and Richard Cragg, who have taken over from stalwarts William Bentley and Trevor Spalding. Sadly, Volume 6 will see the last of contributions from Francis Mellon and Andrew McCormick, and it is not out of place to record how indebted we are to them for their efforts. Other new contributors, Donald Sedgwick and Leslie Martin, make a welcome appearance and have already given the old topics they took on a new, fresher aspect by the inclusion of microprocessor technology and pharmacokinetics, respectively.

As I seem so far to have mentioned every contributor bar an old acquaintance, David Games, it seems only right to recognize his continued exertions. David, your manuscripts may be always or nearly always last to arrive on my desk but they are never least – many thanks.

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Finally, my whole-hearted thanks to the editorial office of The Royal Society of Chemistry for making my task much easier than it would be without them.

R. A. W. JOHNSTONE

Contents

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1

Theory and Energetics of Mass Spectrometry

BY T. BAER

1 Introduction

A review of the theory and energetics in mass spectrometry is a formidable task because the field is so broad. Consistent with the theory and energetics chapters of previous volumes, I have tried to limit the review to those aspects of the literature during the past two years which are relevant to the fundamental understanding of ion dynamics. Particular emphasis has been given to those developments which will help us in our ultimate quest, the ability to predict qualitatively or quantitatively the behaviour of energized ions.

2 Ion Thermochemistry

As dynamical experiments and theories are becoming more sophisticated and precise, the need for accurate thermochemical data on molecules, ions, and fragments continues to grow. During the past few years the experimental effort has been supported by numerous calculations, most of which are of the *ab initio* type. With the advent of readily available high-level programs, numerous groups are now performing calculations. In combination with good experimental information, these results are of great value in extending our chemical knowledge because accompanying the calculated energy is an assumed structure. Although some of the theoretical work will be treated under a separate subheading, a large portion of it will be mixed in with the review of experimental results.

Molecular Orbital Calculations.—*Ab initio* calculations have decreased in cost to such an extent that few calculations are now being done with semiempirical programs. This is also partly as a result of the fact that the semiempirical programs are usually parametrized to do one job well, but at the expense of their predictive ability for other properties.

The most commonly used *ab initio* program is the STO-3G (Slater-type orbitals with 3 gaussian functions). This uses a minimal, split-valence set of basis functions. The split valence means that two basis functions are used for each valence atomic orbital. More sophisticated basis sets are ones belonging to the K-LMG family, in which K is the number of gaussians used to describe the inner-shell s-type functions, L is the number of gaussians for the s- and p-type valence functions, and M is the number of gaussians for the outer sp-type functions. A commonly used basis set has been the 4-31G[1] which is available through the

Quantum Chemistry Program Exchange (QCPE) of the University of Indiana. This and the other K-LMG programs have been developed by Pople and his co-workers.[1]

Some new K-LMG programs have been developed and are, or will soon be, available through the QCPE. Two of these are ones which use the 6-21G and 3-21G basis sets.[2] Either of these is claimed to be as good as the 4-31G or the PFPB 4-21G basis set.[3] The K-21G split-valence basis sets are definitely superior to the STO-3G minimal basis set. Equilibrium geometries are about as good as those of the 4-31G but superior with regard to the description of the bond angles involving heteroatoms. Vibrational frequencies are also equal to, or better than, those of the 4-31G. Similarly, electric dipole moments are better with either the 6- or the 3-21G than with the 4-31G. Happily, because the 3-21G has fewer primitive gaussian functions it is faster than the 4-31G set. It appears to be inferior to the 4-31G only in the calculation of reaction energies. Comparisons for over 20 molecules are given.[2]

Halgren *et al.*[4] have compared the speed and accuracy of a number of semiempirical and *ab initio* programs for calculations of various properties. The overall effectiveness *versus* speed curve is shown in Figure 1. This paper also

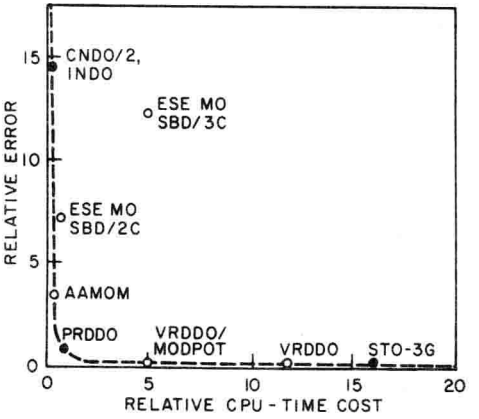

Figure 1 *Relative error versus relative CPU-time cost for the SCF methods discussed. The dashed line represents rel. error × rel. cost − 1, or unit cost efficiency*
(Reproduced with permission from *J. Am. Chem. Soc.*, 1978, **100**, 6595)

introduces a new semiempirical program, the PRDDO (partial retention of diatomic differential overlap). It is 16 times faster than one of the simplest *ab initio* programs, the STO-3G, yet it agrees very well with this program in relative energies, atomic charges, and dipole moments. In a follow-up to this paper, Dewar and Ford[5] have added their MNDO[6] program to this comparison. They

[1] R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724.
[2] J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939.
[3] P. Pulay, G. Fogarasi, F. Pang, and J. E. Boggs, *J. Am. Chem. Soc.*, 1979, **101**, 2550.
[4] T. A. Halgren, D. A. Kleier, J. H. Hall, L. D. Brown, and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1978, **100**, 6595.
[5] M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, 1979, **101**, 5558.
[6] M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1979, **101**, 4989.

compared seven MO methods by listing the root mean square (r.m.s.) error of the energy, ionization energy (Koopmans' theory), and dipole moment with respect to experimental results. These are listed in Table 1 and should serve as a guide to experimentalists. Although impressive, the calculations must be used with care. Furthermore it is doubtful that single configuration calculations will reach experimental accuracies of say 1 kJ mol^{-1}. For such precision elaborate configuration interaction (CI) calculations must be carried out. These are still the domain of the theoreticians.

Table 1 *Summary of r.m.s. error for molecular orbital methods relative to experiment**

Method	ΔE/kJ mol^{-1}	ΔIE/eV	$\Delta\mu$/D
CNDO/2	705	4.40	2.24
PRDDO	136	1.06	0.98
STO-3G	126	1.14	0.80
MBS	123	1.10	0.89
4-31G	59	0.57	0.41
Double Zeta	53	0.55	0.37
MNDO	45	1.01	0.83

* The r.m.s. errors are based on results from 23 molecules. Table taken from ref. 5.

The most studied molecular ion during the past two years has been CN^+. No less than four separate investigations were reported dealing primarily with the identity of the ground state. As with the isoelectronic C_2, the two states $^1\Sigma^+$ and $^3\Pi$ are very close in energy. Wu[7] did an SCF calculation and concluded that the $^3\Pi$ is lower in energy by 0.33 eV. The fact that this was a single configuration calculation makes it somewhat suspect. Yet Ha[8] using CI also found that the $^3\Pi$ is lower than the $^1\Sigma^+$ state by 0.41 eV. Murrell *et al.*[9] would not commit themselves, stating that the two states are extremely close. This caution is certainly justified because Hirst[10] using the ATMOL SCF calculation with CI found that either state could be made the ground state depending on the number of configurations used. Yet the bond distances are quite different (1.20 Å and 1.28 Å). Other diatomics studied[11] are the mixed alkali metals and alkali salts such as NaK^+, $NaRb^+$, $NaCs^+$, KBr^+, KCs^+, $RbCs^+$, Na_2^+, K_2^+, Rb_2^+, and Cs_2^+. A number of stable excited electronic states were found.

Often the most stable structure for an ion is not the same as the most stable neutral structure. These situations are sometimes difficult to establish experimentally, but they are quite amenable to calculations. In fact the calculation of energies of isomers is one of the most fruitful uses of MO calculations. Murrell and Derzi[12] have concluded that, although HCN is 0.5 eV more stable than HNC, in the ionic form HNC^+ is more stable than HCN^+ by 0.9 eV, and that the

[7] A. A. Wu, *Chem. Phys. Lett.*, 1978, **59**, 457.
[8] T. K. Ha, *Chem. Phys. Lett.*, 1979, **66**, 317.
[9] J. N. Murrell, A. Al-Derzi, and J. Tennyson, *Mol. Phys.*, 1979, **38**, 1755.
[10] D. M. Hirst, *Chem. Phys. Lett.*, 1979, **65**, 181.
[11] A. Valance, *J. Chem. Phys.*, 1978, **69**, 355.
[12] J. N. Murrell and A. Al-Derzi, *J. Chem. Soc., Faraday Trans.* 2, 1980, **76**, 319.

activation for HCN^+ going to HNC^+ is about 0.45 eV. These results are based on an *ab initio* SCF calculation in which the basis functions consisted of contracted gaussians augmented by polarization functions. Another study[13] of HCN^+ addressed the problem of the $\tilde{A}$ and $\tilde{B}$ states and, in particular, the slow predissociation rate at 20.3 eV which results in sharp vibrational structure in the spectra from photoelectron spectroscopy (PES).

The isomers HNO^+ and NOH^+ have been investigated,[14,15] and in both cases HNO^+ was found to be more stable. Bruna and Marian[14] using the MRD-CI (multi-reference double-excitation) program developed by Buenker *et al.*[16] found the energy difference only about 12 kJ mol^{-1}. Both ions are bent; the angle in HNO^+ is 131° while in NOH^+ it is 124°. The other SCF study with CI found the energy difference to be 54 kJ mol^{-1} and the angles 126° and 116°, respectively.[15]

The MRD-CI program was also used[17] to calculate the relative stability of the HCS^+–CSH^+ system. HCS^+ was found more stable by 465 kJ mol^{-1}. In a follow-up to this study, CNDO/2 investigation of the same isomers found an energy difference of 520 kJ mol^{-1}.[18] Yet another study with the MRD-CI program was the calculation[19] of the low-lying states of NH_2^+. A rather strange result is that two states, the linear $^3\Sigma_g^-$ and the bent $^3B_1$ (150°), are candidates for the ground state. They differ in energy by only 330 cm^{-1} while the barrier is about 900 cm^{-1}. The reaction $N^+ + H^2 \rightarrow NH^+ + H$ was also investigated with CI by calculating triplet states of NH_2^+ which might correlate with the dissociation products.[20] In a study similarly relevant to dynamics, Hansoul *et al.*[21] investigated the higher-lying states of HCN^+ by CI. They found that the third state ($\tilde{B}$) at 19 eV cannot be assigned to the removal of a single 4σ electron. Instead at least two configurations, one of which is a two-electron excitation, are involved. On the basis of the experimentally observed H^+ onset the authors conclude that the $\tilde{B}$ state is strongly coupled with the $\tilde{A}$ state.

One of the most remarkable predictions comes from an INDO calculation on N_2O^+. The neutral N_2O is linear as is also the $^2\Pi$ state of the ion, which is thought to be the ground state. Yet Barber *et al.*[22] have found that for a bent state (N—N—O angle of 61.1°) the $^2A''$ is 306 kJ mol^{-1} more stable than the $^2\Pi$ state. The barrier is 220 kJ mol^{-1} which would explain why no experimental evidence for such a low-lying state of N_2O^+ has been reported. In view of these calculations it would be extremely interesting to carry out *ab initio* CI calculations and to determine onsets of N_2O^+ fragments from the dissociation of molecular ions containing N_2O. The $^4A''$ state of N_2O^+ has been carefully studied by Hopper[23] who found that it is stable but has an energy considerably above the linear $^2\Pi$ state.

[13] D. M. Hirst, *Mol. Phys.*, 1979, **38**, 2017.
[14] P. J. Bruna and C. M. Marian, *Chem. Phys.*, 1979, **37**, 425.
[15] A. D. McLean, G. H. Loew, and D. S. Berkowitz, *Mol. Phys.*, 1978, **36**, 1359.
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[23] D. G. Hopper, *J. Am. Chem. Soc.*, 1978, **100**, 1019.

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