PHILOSOPHICAL TRANSACTIONS —OF— **THE ROYAL SOCIETY** **A** | **MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES**

Directions in Molecular-Ion Spectroscopy

W. H. Wing

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Directions in molecular-ion spectroscopy

By W. H. Wing

Department of Physics, University of Arizona, Tucson, Arizona 85721, *U.S.A.*

Molecular ions, once regarded as little more than curiosities, are now recognized as major (even dominant) chemical agents in extraterrestrial and terrestrial environments in which ionization occurs. Spectroscopic analysis offers the most comprehensive means of understanding their structure and following their behaviour. The field of charged-molecule spectroscopy is quite young but is growing rapidly. Some reasons for the rapid growth, particularly interesting situations involving molecular ions, and possibilities and problems for the future of the field are briefly discussed.

State of the field

It is very satisfying for one who has been working for many years with those curiosities known as molecular ions to be able to attend a meeting devoted to that genus exclusively. Although the discipline of molecular spectroscopy is many decades old, interest in charged molecules has arisen much more recently. The rapid growth of the field is dramatically highlighted by comparing two comprehensive compilations of data, separated in time by about three decades, on diatomic molecules alone: Herzberg's volume (1950) and Huber & Herzberg's volume (1979) (table 1).

TABLE 1. NUMBERS OF KNOWN DIATOMIC MOLECULES

charge state...	0	+	−	2+	2−
1950	332	29	—	—	—
1979	786	141	40	6	—

In those 29 years, entries for neutral diatomics grew by a healthy 137 %, from 332 to 786 molecules. Cations, although less numerous, showed nearly a five-fold increase, from 29 to 141 entries. Although no anions were known at all in 1950, 40 had been found by 1979. Even six entries of doubly charged cations appeared, nearly all based on theoretical work; no entries were made for doubly charged anions. The extent and quality of the data increased dramatically as well. And dramatic growth occurred also in the data for polyatomic neutral and charged molecules.

Among the most remarkable features of this explosion of knowledge is the way in which it has given substance to heretofore shadowy concepts in bulk chemistry. The hydronium ion H_3O^+, for example, was introduced to many of us in our first course in chemistry almost as a fictive device, to explain solubility and pH. Now molecular-ion spectroscopists have successfully isolated it *in vacuo*, have learned how to manipulate it, and have examined its inner workings in enormous detail; in short, they have made it very real indeed.

Since 1979 the growth in the field of molecular-ion spectroscopy has continued, as the very existence of this Discussion Meeting demonstrates. I dare say that a substantial proportion of the species that will be discussed here today and tomorrow were spectroscopically unknown in

10-2

1979. We are fortunate that many of those whose efforts have developed molecular-ion spectroscopy as a distinct subdiscipline are present. We may expect, therefore, a very stimulating two days.

Why, then, has all this activity taken place? What makes molecular ions so interesting? And what problems and opportunities may the field face in its future development? I should like to introduce our subject by offering very briefly some answers, of necessity incomplete and biased by my own interests, to these three questions.

THE TECHNOLOGY

The most direct reason for the rapid growth is surely the many advances in spectroscopic technology. Ion traps, ion beams, jet-expansion beams, cooled discharges, and other sources especially tailored to the controlled production of molecular ions have been extensively developed. Exotic varieties of lasers and other intense coherent sources in the infrared through to the submillimetre electromagnetic spectrum have become routine pieces of laboratory apparatus. Passive instruments such as the Fourier-transform and scanning Fabry–Perot interferometers have become reliable tools as well. Low-cost computers to control the equipment, take the data, and perform the analyses clutter laboratory benches. And major improvements in radiation detector sensitivity and spectral range have been made. With these new tools have come many ingenious methods for exploiting them, several of which we will hear about in the lectures to follow. The importance of advanced technology to molecular-ion spectroscopy can perhaps best be judged from the observation that the spectra of most neutral molecules were first detected by traditional grating or prism spectrometers, whereas those of most molecular ions were only found once less conventional methods could be applied.

SOME INTERESTING CASES

What makes the field interesting is perhaps the most important question of the three. To the scientist–explorer, the first answer must be that it stirs the imagination. The simplest molecule of all, H_2^+, is a molecular ion. Its special role in the development of quantum theory is well known. The Schrödinger partial differential equation for its electronic motion is one of those few that can be separated into ordinary differential equations, and thus solved analytically, as was first done in 1927 (Burrau 1927).

The first molecule was also a molecular ion, as was the second molecule. Imagine the epoch at which the promordial nuclei have recently condensed and the radiation temperature is still several thousands of kelvins. The young Universe is a plasma sea composed mainly of photons, electrons, protons (H^+), and α-particles (He^{2+}). As expansion proceeds and the plasma cools, first He^+, then neutral He, then neutral H condense out (Lepp & Schull 1984). Once He appears, a burst of HeH^+ is formed from He and H^+ by radiative association and inverse rotational predissociation (Roberge & Dalgarno 1982). The rate is relatively small, however, at about 10^{-20} cm^2 s^{-1}. When H appears, a much larger burst of H_2^+ is formed by radiative association of H and H^+ (rate about 10^{-16} cm^2 s^{-1}).

The rest of the reason that any field is interesting must be the connections it makes, and the insight it has to offer, to other subjects. Let us briefly continue to follow, then, some connections molecular ions have to the other large-scale processes in the Universe.

When H_2^+ appears, chemistry begins (Dalgarno & Lepp 1987). Reactions with He produce more HeH^+, and those with H produce H_2. The H_2 destroys the primordial molecular ions, creating others, and a complex matrix of reactions ensues. The dominant processes become similar to those we see in the interstellar medium today.

This molecular-ion-driven chemistry strongly affected early molecular-cloud cooling and linkage to large-scale magnetic fields. Hence it affected the causal chain that begins with gravitational collapse rates and leads through the sizes of stars formed to the onset of nucleo-synthesis and the abundances of nuclides. It may have affected the scale of galaxy formation as well. In later, gentler times, molecular-ion catalysts strongly drive the rich chemistry of those clouds in which complex organic molecules are created (van Dishoeck & Black 1986). Did life originate in such a place? One need not speculate to realize how different our life would be today had not these several early manifestations of our subject presented themselves.

The special feature of molecular ions that gives the genus its very identity and positions them so importantly in processes such as these is, of course, the net non-zero charge. The charge interacts strongly with both nearby matter and the electromagnetic radiation field. At such long distances that a neutral molecule would ignore its neighbours, a molecular ion still polarizes surrounding material and thus, like any charged particle, tries to stick to whatever it encounters. At short distances it becomes a reactive chemical substance, and tends to transform whatever it sticks to. Thus molecular ions will dominate the chemistry of any medium in which they are formed in sufficient numbers, and the concentrations required are surprisingly small.

The ubiquitous earthly example of such a medium is surely an electrolyte. Every one of us is the possessor of such a substance; in fact, it is safe to assume that we all have several of them with us today. Although electrolytes have long been the province of the wet-laboratory methods of inorganic chemistry, the recent contributions of molecular-ion spectroscopy in elucidating structural geometry, molecular binding energies, and reaction channels have been substantial. I have already alluded to the hydronium ion and its role in electrolytes (and pedagogy). There is a curious irony here: the strong interactions of a molecular ion with its surroundings in condensed matter blur and distort the fine details of its spectrum. Nevertheless, without the ability to examine those details at the high resolution of gas-phase spectroscopy, much of our understanding of molecular structure would be lost. Thus there need be no tension between gas-phase and condensed-matter research, as sometimes exists. On the contrary, they go hand in hand.

For many of us here, space environments such as interstellar clouds, cometary atmospheres, and planetary outer atmospheres are the pre-eminent stages upon which molecular-ion processes play. Yet they also form copiously in plasma environments of possibly lesser inspirational value but certainly greater economic value to humanity: in flames and other combustion environments, in electrical discharges, and in controlled nuclear-fusion plasmas. Laser-based atomic spectroscopy is becoming a very useful tool for probing these environments, especially in understanding combustion processes. Because of the much higher complexity of the spectra, molecular-ion spectroscopy of these regions is less fully developed. But it seems likely to play an increasing role in the future.

The list of special molecular ions and their distinctive roles is long indeed. Yet one final addition may be of interest because of its novelty. The muonic hydrogen molecular ion is an exotic molecule whose valence electron has been replaced by a muon, which is some 200 times

more massive. The shorter de Broglie wavelength of this heavier lepton binds the molecule so closely together that, in its deuterated forms, the nuclei can actually undergo fusion. The muon is then released, and can repeat the process 150 or more times, as a kind of nuclear catalyst. The process was first noticed in cosmic muon collisions with photographic emulsions in the 1940s (Lattes *et al.* 1947) and quickly explained (Frank 1947; Sakharov 1948). It was re-discovered a decade later in bubble-chamber reactions by Alvarez and collaborators (1957). Recently, the discovery of a resonance in the reaction forming the deuterium–tritium isotope of this molecule (Thomsen 1987) has raised the possibility that it might be developed into a practical source of fusion power. Interest has revived, and an active international research community has developed.

Problems and opportunities

Now very briefly to the third question: what may the future hold for molecular-ion spectroscopy, and what problems must we overcome? The speakers at this Meeting will answer the question with respect to their own topics in much more detail and with much greater precision than I could hope to, but perhaps a few speculative suggestions will not be out of place.

When a field is young, and new vistas have just opened themselves to us, we may happily explore them for nothing more than the pleasure that activity gives us. As the subject matures, however, the bridges that we can build from it to other knowledge become more and more necessary. Therefore we must ask what information those bridges require for their sturdiest construction. The single most critical bridge is that between experiment and underlying theory. It must be buttressed whenever possible.

One question that will become increasingly important in the future is how best to characterize reactions in which molecular ions participate. This is not entirely a spectroscopic question; yet spectroscopy is such a wonderful tool that it can unquestionably be of great service. An unmet need of theoretical astrophysicists, for example, is for the details of dissociative electron recombination reactions with polyatomic ions such as H_3O^+ and H_3^+. Data for other species are needed as well, and the need can only increase as our understanding of interstellar cloud composition grows.

In a very different domain, molecules have yet to take their place in the repertory of systems that can be used to test fundamental physical laws. One unique advantage that they possess for this purpose is that they hold two or more atomic nuclei in permanent close proximity. Surprisingly little is known about the fringes of nuclear force fields: high-speed nuclear collisions are simply too blunt an instrument to perform the delicate probing that is required. Suggestions have been made, for example, of van-der-Waals-like long-range nuclear forces resulting from exchanges of two or more massless particles such as gluons, very much as the ordinary van der Waals force between molecules can be viewed as arising from the exchange of pairs of photons (Feinberg & Sucher 1979; Coon 1986). Yukawa-like long-range forces may arise from exchange of massive particles, and significant forces may also arise from short-range modifications of the gravitational interaction. At present, however, the existence of all is purely speculative. It is interesting to note that the present best upper bound for the strengths of long-range forces that might arise from the exchange of up to four massless gluons, the so-called tensor long-range forces, comes from the agreement between theory and experiment for the hyperfine structure of the hydrogen molecule (Feinberg & Sucher 1979). Suitably designed experiments on the

hydrogen molecular ion might provide a more stringent limit still, because of this molecule's simpler theoretical structure problem.

A broad difficulty in the interpretation of molecular spectroscopic data that is particularly keenly felt for certain small molecular ions is that the ability of theoretical quantum chemistry to predict has fallen far behind the ability of experimental spectroscopy to measure. This is surely the reason for the dearth of molecular experiments among tests of fundamental laws, despite their undeniable advantages, such as high spectroscopic Q.

It has become popular to believe that computational simulation of a phenomenon is essentially equivalent to studying the phenomenon itself. And indeed that is sometimes true, as we see from the recent dramatic shortening of product design cycles in many industries. In molecular physics as well, very substantial achievements have been made, particularly in the simulation of the overall geometry and structure of relatively complex organic molecules such as drugs. But on the whole, what is possible computationally still falls far short of what is required, and the gap with experiment is not closing. At the state of the art in molecular modelling, results for some situations can be achieved only by replacing quantum mechanics entirely by classical statistical-mechanical treatments whose connections to the physics can be remote at best (Beveridge & Jorgensen 1986). When quantum mechanics or indeed any dynamical theory is used, it is often severely limited. It was little more than a decade ago that internal motions were even recognized as an important feature of the structure of large molecules (Karplus 1986). Treatments of small molecules, although generally quantum-mechanical, have also been significantly unrealistic until recently. Of the hundreds of theoretical treatments of the hydrogen molecular ion from 1927 until 1976, when vibration–rotation spectra were observed (Wing *et al.* 1976), only a tiny handful went beyond the clamped-nucleus Born–Oppenheimer approximation, or considered corrections due to special relativity or vacuum polarization. Although this situation has been much improved, most other molecules are still treated at the Born–Oppenheimer level today, for the reason that their greatest source of computational error is the non-relativistic multielectron problem. Fresh theoretical approaches are badly needed.

Every major laboratory and every physical-chemistry journal contains reams of spectroscopic data that could not have been produced by present-day computer modelling, even though basic molecular quantum theory has been understood and accepted as valid for 60 years. The opportunities for improved analysis and insight seem considerable. Yet most experimentalists, for lack of something better, simply fit their results to a Dunham-like expansion about equilibrium (or do no analysis at all) and go to the next molecule. Although computer power and availability seemingly double every year or two, few theorists have yet attempted to match, or even approach, spectroscopic accuracy except for one-electron and two-electron molecules. Fewer still are attempting to solve structure and dynamics problems in the régimes of high excitation, far from equilibrium, where chaotic motion may exist (Berblinger *et al.* 1987), and yet where important reaction processess often occur.

A part of the problem is no doubt the tradition among many scientifically advanced nations of under-supporting theorists. Part may also be the natural time lag between the dissemination of a new technology and the achievement of practical results using it. Yet there may be important quantum theoretical problems that remain uncomputable in principle, by present methods at least, despite any foreseeable advance in computer technology, because their solution time will still exceed the lifetime of the computer, or the research grant, or the

researcher, or the Universe, or some other natural barrier. May some seemingly finite problem, such as à truly first-principles solution of the Schrödinger problem for a single diatomic molecule composed of heavy atoms, be of such scope?

END AND BEGINNING

The answers to such questions are far from clear. Yet it is a sign of the progress of our field, I believe, that it is beginning to make sense to ask them. What does seem clear is that major advances will require new ideas for how and what to compute, how and what to measure and, most importantly, what to do with the results. The best last words on this subject seem to have been said by the numerical analyst R. W. Hamming (1973): 'The purpose of computing is insight, not numbers.' This applies, of course, to measurement as well.

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