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Concluding remarks for advances in ion spectroscopy Faraday Discussion

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Because the Introductory Lecture of this Faraday Discussion emphasized the recent history and exciting developments in the fields of experimental methods and applications of gaseous ion spectroscopy, these Concluding Remarks are, by design, directed somewhat more toward the roles played by theory. In discussing both the experimental and theoretical studies of gaseous ions, it is important to recognize and appreciate the delicate balance workers in the field are pursuing in terms of methodological/tool development and applications to current-day pressing problems in chemistry, physics, materials science, and biology. Without both components of modern research in this field, progress will not be efficient. Substantial discussion is included about the reductive approach that is commonly used to attempt to connect studies of ions in the gas phase (*i.e.*, as isolated species) with properties of these ions as they exist in nature. Issues of how small a model system can be, to what extent surroundings/solvation can be addressed, and how our experimental or theoretical tools might limit us are all discussed in some detail. The current ability of theory to assist in the interpretation of experimental spectral data on gaseous ions is discussed, as are several of the most pressing limitations of theory on this front. Finally, the author offers his thoughts about what advances/improvements in theory are needed and the outlook for when they might be expected, and urges the experimental community to remain in close contact with theory groups developing new methods so that progress can be optimized.

1. Introduction

I want to begin by talking a bit about why the scientists taking part in this Faraday Discussion (FD) do what they do and how they view the roles of their research within the big picture of chemical science. In the article (DOI: 10.1039/c9fd00030e) accompanying Mark Johnson's Introductory Lecture, we see the following Section titles:

2. Ions and the chemistry of interstellar clouds

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3. Cool ions: supersonic jets, population labeling and laser-induced fluorescence (LIF)

4. Universal spectroscopy of cold ions: messenger tagging

5. Time-resolved photophysics and photochemistry

6. Cryogenic ion traps and the electrospray interface: meeting the challenges of biological macromolecules

7. The rise of ion mobility

Mark did an excellent job of tracing a *ca.* 60 or so year timeline of (mainly) experimental advances in how ions are generated in the gas phase, how they are cooled if needed, how mobility methods can sometimes be used to separate ions having the same mass-to-charge ratio, and how tagging techniques can be used to greatly enhance the range of applicability of infrared (IR) and electronic spectroscopies. His contrasting Claude Woods' pioneering 1975 microwave spectrum of CO^+ to the 1983 microwave-optical double resonance CO^+ spectrum from JILA illustrated how the kind of tool developments highlighted in this FD can qualitatively improve our view and understanding of ions even within a short timeframe.

In an excellent year-2010 review on the status of ion spectroscopy by two experts, Tom Baer and the late Rob Dunbar,[1] the Section titles again are focused on a wide range of spectroscopic tools, many of which have undergone tremendous growth and improvement in the past 10 years. Moreover, in the Program outline for this FD, two of the four Section titles, *Controlling internal degrees* and *Pushing resolution in frequency and time*, have clear emphases on improving experimental tools used to study ions using spectroscopic means.

In my Closing Remarks Lecture, I pointed out that it is natural and appropriate that cutting-edge physical chemistry research has a very strong focus on methods/tools development, although the expectation is that today's new methods will someday be in the hands of a much broader, and perhaps less technically skilled, range of scientists. We have seen such evolution in the field of nuclear magnetic resonance (now even used in a wide range of medical applications by technicians and physicians who need not know all the details of pulse sequences, relaxation times, chemical shifts and the like). Similar evolutions have taken place in solution-phase infrared (IR), Fourier-transform IR, surface-enhanced Raman spectroscopy (SERS), and fingerprint mass spectroscopic (MS) techniques (*e.g.*, as used in airport baggage screening).

Many of the new methods discussed in this FD are in early stages of development and testing and often require laboratory resources that are not widely available (*e.g.*, storage rings, free-electron laser light sources, specialized cooling and trapping devices) in most chemistry, physics, or biology research groups. As such, they are in use primarily within the hands of their primary developers, many of who contributed to this FD where we have heard or read about the following techniques: traveling wave ion mobility, IR-UV ion-dip, hole burning, He tagging, cryogenic ion traps, storage rings, magnetic bottles, free-electron lasers, FT-ICR, photo-electron angular distribution, photodissociation, action spectra, superfluid He nano-droplets, electron-transfer dissociation, double resonance spectroscopy, electron velocity map imaging, blackbody radiative dissociation, *ab initio* molecular dynamics, equations of motion, surface hopping, complex absorbing potential, metastable resonance states, and more.

However, based on the long track record of how physical chemistry method developments have been brought into broad if not routine use, there is every reason to anticipate that many of the exciting new methods talked about in this FD will follow in the footsteps of NMR, IR, SERS, and MS methods.

Theoretical chemistry's contributions to ion spectroscopy display a similar growth path, and I will have more to say about this later when I will try to shed some light on where this field is likely to evolve. For example, the methods that are currently routinely available within widely used software packages (*e.g.*, Gaussian, QChem, MOLPRO, *etc.*) are now being used with much success by a broad range of experimental and theoretical scientists in the field of ion spectroscopy. Gaussian and plane-wave basis sets, Hartree–Fock (HF), Møller–Plesset perturbation theory (MPPT), coupled cluster (CC) with perturbative treatment of triple excitations (CCSD(T)), density functional theory (DFT), and time-dependent DFT (TDDFT) are examples of such methods. In contrast, methods that are still under much development and which show great promise are largely being used by cutting-edge theory groups and by experimental scientists closely associated with theorists. The explicitly correlated methods and quantum Monte Carlo techniques are examples.

In summary, I think it fair to say that we experimental and theoretical scientists taking part in this FD are striving to advance the fundamental tools necessary to carry out spectroscopic studies on ions while also making use of both well established and (our) cutting edge methods to study interesting/important problems in chemical science (including atmospheric, astrochemical, biological, energy, materials, and other areas). This combination of developing and testing new methods while also carrying out studies of pressing chemical problems is, I believe, a healthy state of affairs for our discipline.

2. Physical chemistry's reductive approach and potential pitfalls

I believe it is useful to reflect on the content of the papers presented and discussed in this FD by considering the chemical problems to which the various tools are being applied. In addition to a few presentations focused on astrochemical or atmospheric science, I counted eight that treated biological molecules and eight that dealt with negatively charged ions. Because much of my scientific career[2] has involved studies of molecular anions, I was especially pleased by the latter.

The two areas in which there were eight presentations present special challenges and pitfalls that I now wish to discuss: (1) lessons we can learn and problems to be aware of when using (usually small) model systems to attempt to characterize larger (*e.g.*, biological) systems, and (2) the need for special techniques when dealing with certain commonly encountered states of molecular anions.

When faced with attempting to probe or describe the behaviour of a biological molecule or ion as it exists in nature, it is usually necessary for the physical chemist to use a smaller model system, at least in the initial phases of study. Moreover, the physical chemist often chooses to first examine the model system in the absence of the surroundings (*i.e.*, solvent, other ions, and other biological molecules) while planning to deal with such affects after the bare system has been adequately characterized. Two important issues arise when using such a reductive approach as I will attempt to illustrate using examples from my own research and from that of three of this FD's participants: (1) how small can the model system be while still adequately representing the behaviour of the full biological system of interest? And (2) how can one adequately "add in" the role of the surroundings once the isolated model system has been described?

a. Using gas-phase spectra to approximate condensed-phase situations

First, I would like to discuss the effects of "surroundings" on the spectroscopic properties of ions using results from X. B. Wang,[3] and from J. Verlet and D. Neumark,[4] who took part in this FD. In Fig. 1 we see a plot of the gas-phase vertical electron binding energies (determined by photodetachment) of several dicarboxylate dianions having varying numbers of methylene units separating the two negatively charged groups. Assuming that these species adopt quasi-linear structures in the gas phase (to minimize their internal Coulomb repulsion energy), one can estimate the distance (*r*) between the two –COO$^-$sites. Plotting the electron binding energies *vs.* 1/*r*, with *r* measured from the midpoints of each of the two oxygen atoms, one obtains a nearly linear graph as shown in Fig. 1 with a slope[5] of *ca.* 14.4 eV Å^{-1}. This slope is what one expects for the Coulomb repulsion of two unit charges separated by a distance *r* when *r* is measured in Å and the energy is stated in eV.

This value for the slope tells us that the intervening –(CH$_2$)$_n$– units produce essentially no screening of the Coulomb interaction between the two negatively

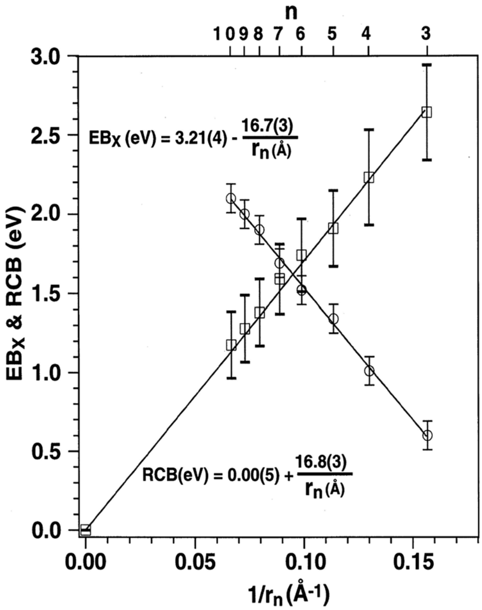

Fig. 1 Taken from ref. 3; shows a plot of the electron binding energy (EB) for $^-$OOC–(CH$_2$)$_n$–COO$^-$ dianions for *n* ranging from 3 to 10. Copyright (1998) by The American Physical Society.

charged sites. The electron binding energy of each site is simply reduced by the *unscreened* Coulomb repulsion from the other site. If there were dielectric screening consistent with the dielectric constant of saturated hydrocarbons (*i.e.*, $\varepsilon \approx 2$), the slope would be close to $14.4/\varepsilon$ (eV Å^{-1}) $= 7.2$, which it is not.

Although this observation might not be surprising to most of our FD participants, I think it is important because it emphasizes the point that dielectric-type screening (either high-frequency/optical or low-frequency/static) is a phenomenon that involves not only molecules/matter lying on a direct path between the two charges but also matter surrounding both charges in 3-dimensions. I'll have a bit more to say about this later.

In Fig. 2 we see plots of the vertical electron binding energy (VBE) for one excess electron bound to water clusters $(H_2O)_n^-$ having up to 200 water molecules taken from work by J. Verlet and D. Neumark.[4]

The three plots (I–III) are thought to arise from three distinct geometrical binding motifs that the water clusters adopt, with the curve labelled I belonging to the motif that connects to the bulk solvated electron in water. The VBEs are plotted *vs.* $n^{-1/3}$ because this parameter would reflect the radius of a solvation sphere if the water molecules surrounded the excess electron in such a manner.

There are two important lessons to derive from the Fig. 2 data of ref. 4. First, these data make it clear that one cannot expect to obtain solution-phase spectroscopic data (in this case electron binding energies) by carrying out experiments or calculations on small model systems containing only a few solvent molecules. Clearly, even with 200 water molecules, the VBE has not reached that of the fully solvated electron. Of course, by observing that the VBE data vary essentially linearly with $n^{-1/3}$ it is possible to extrapolate the $n \geq 20$ data to the bulk-solvation limit. However, in the absence of such an underlying theoretical model in terms of which to interpret how the number of solvent molecules affect the

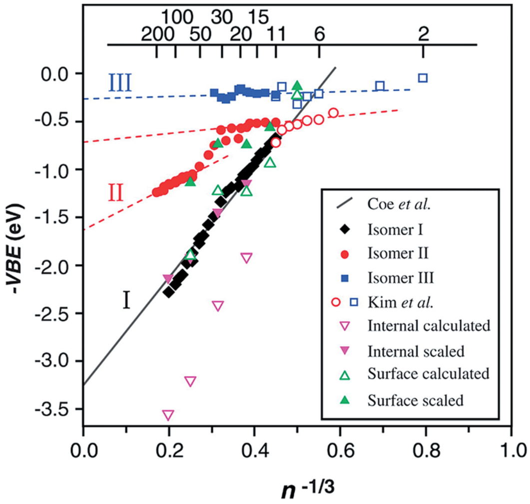

Fig. 2 The vertical electron binding energies, determined by photo-electron spectroscopy, for water cluster anions $(H_2O)_n^-$ for n ranging from 2 to *ca.* 200 plotted as functions of $n^{-1/3}$. From J. R. R. Verlet, A. E. Bragg, A. Kammrath, O. Cheshnovsky and D. M. Neumark, *Science*, 2005, **307**, 93–96. Reprinted with permission from AAAS.

spectroscopic signature, one should certainly not assume that studies carried out on "lightly solvated" model ions can be used to accurately describe the same ion in a full-solvation environment.

The second lesson to derive from the data for curve I of Fig. 2 relates to the so-called dielectric screening. As noted in ref. 4, the slope of curve I is consistent with a model in which the excess electron is confined within a spherical cavity surrounded by a spherical dielectric medium whose dielectric constant ε is close to the room-temperature static (low-frequency) dielectric constant of water ($\varepsilon = 78$). The derivation of such a model depends on assuming that the radius r of the (small) spherical volume ($4/3\pi r^3$) within which the excess electron is trapped is much less than the radius R of the larger spherical volume ($4/3\pi R^3 - 4/3\pi r^3$) containing the n water molecules. It is clear from Fig. 2 that the data only display the proper linear slope once n has reached *ca.* 20, again suggesting that one must be wary of using spectroscopic data on lightly solvated ions to approximate behaviour in solution.

b. How small can a model system be, can we really ignore solvation, and might our tools limit what we find?

Next, I would like to describe the history of my own group's research into how very-low energy electrons can cause strand breaks (*i.e.*, ruptures of covalent bonds) in DNA. This story provides several lessons that should be of much use to both experimental and theoretical scientists interested in ion spectroscopy.

In 2000, the research group of Leon Sanche published a ground-breaking paper[6] in which *E. coli* DNA that had been desiccated was bombarded by a beam of free electrons having a well-specified kinetic energy (KE). In Fig. 3 we see plots of the yields of strand breaks as functions of KE.

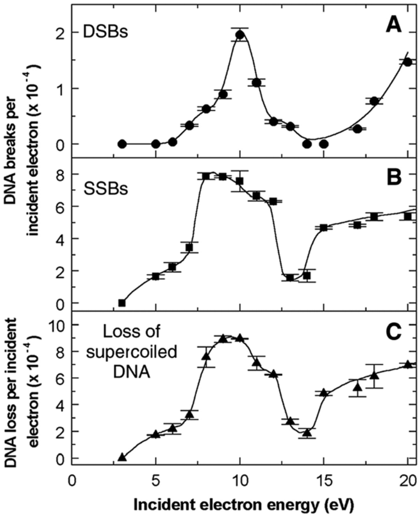

Fig. 3 Plots of single (SSB) and double (DSB) strand breaks in DNA as functions of the kinetic energy of electrons used to bombard the DNA sample (taken from ref. 6). From B. Boudaiffa, P. Cloutier, D. Hunting, M. A. Huels and L. Sanche, *Science*, 2000, **287** (5458), 1658. Reprinted with permission from AAAS.

In 1998, earlier workers had determined[7] at what kinetic energies free electrons would attach to the π* orbitals of DNA's four bases. Their electron transmission spectra (the signal is reported in so-called derivative mode) are shown in Fig. 4. In the spectra, the vertical lines are used to locate the KE values at which the attachment of the free electron into the base π* orbital has its peak value. Since these bases have several π* orbitals, there are several peaks in each of their ETS spectra.

Knowing of the results of ref. 7 and being aware that the workers of ref. 6 believed[8] the electron-attached states producing their strand breaks involved shake-up states of the anions (*e.g.*, states in which an electron is captured into a base π* orbital and another electron is excited from a π orbital into another π* orbital), we decided to explore the possibility that electrons with KEs lower than those studied in ref. 6 could also induce strand breaks in DNA. We also wanted to try to determine which covalent bonds are broken.

In 2002, we reported[9] the results of quantum chemistry calculations on a model system composed of a cytosine base-sugar-phosphate unit (*i.e.*, a nucleotide) with a *ca.* 1 eV electron attached to the cytosine's lowest-energy π* orbital. In this study and our later work, the phosphate unit was neutralized to simulate the year-2000 Sanche experiments' situation where counter cations neutralized the phosphate groups. We found that (i) the C–O bond connecting the deoxyribose (sugar) unit to the phosphate group could be cleaved if a barrier of *ca.* 12 kcal mol^{-1} could be surmounted, but (ii) that the rate of surmounting such a barrier would be too small to compete against the *ca.* $10^{14}\ \text{s}^{-1}$ autodetachment rate unless (iii) dielectric stabilization by the surrounding media renders the π*-attached anion stable rather than metastable. In subsequent publications,[10] we

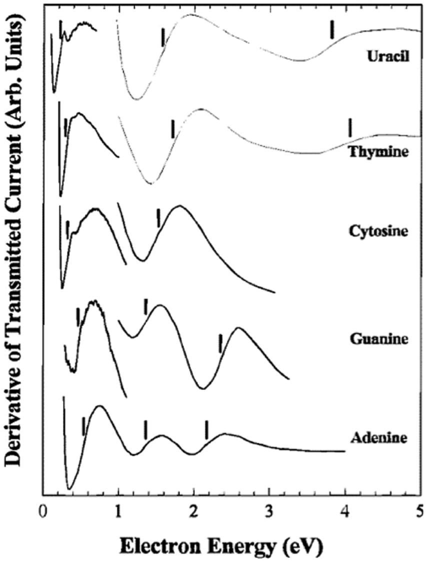

Fig. 4 Electron transmission spectra (ETS) of DNA's four bases and of uracil. Reprinted with permission from K. Aflatooni, G. A. Gallup and P. D. Burrow, *J. Phys. Chem. A*, 1998, **102**, 6205. Copyright (1998) American Chemical Society.

extended these studies to examine (i) the effects of base π stacking, (ii) the possibility of cleaving other bonds (base-sugar N–C bonds and base N–H bonds, in particular), and (iii) the effects of various dielectric stabilization strengths. The central findings were (i) that base π stacking did not interfere with the base-through-sugar-to-phosphate electron transfer mechanism, (ii) that base–sugar N–C bonds were the next most likely to be cleaved (*i.e.*, have the second lowest barrier to surmount), and (iii) that even screening by a dielectric medium having $\varepsilon \approx 2$ is sufficient to render the π*-attached anion stable with respect to autodetachment.

This was the first time that researchers had predicted the sugar–phosphate C–O bonds to be the most susceptible to cleavage under such conditions, and explained why (because of the large *ca.* 5 eV electron affinity of the phosphate unit) and how (*via* a through-bond electron transfer process).

In 2004, new experiments[11] from a joint Burrow and Sanche team re-examined the DNA strand break yields using electron beams of even lower KE than used in the year 2000 Sanche experiments. In Fig. 5 we see a plot of single strand break yield as a function of electron energy for $0 < \text{KE} < 5$ eV.

These findings appear to support our year 2002 prediction that electrons with kinetic energies as low as 1 eV can cause strand breaks, and it should be noted that peaks in the SSB yield shown in Fig. 5 appear (see Fig. 4) in the energy ranges at which the four DNA bases have their π* orbitals. However, for such low-energy electrons, it appears that double strand breaks are not created as is also shown in Fig. 5. In contrast, the electron-attached species formed at higher KE values produce both single and double strand breaks as shown in Fig. 3.

Between our prediction in 2002 that electrons with KEs much lower than those used in the original 2000 Sanche experiments could cleave bonds in DNA and 2006, there were several experimental studies of the effect of electrons that collide with DNA fragments. To illustrate, in 2004 the Märk group[12] determined that

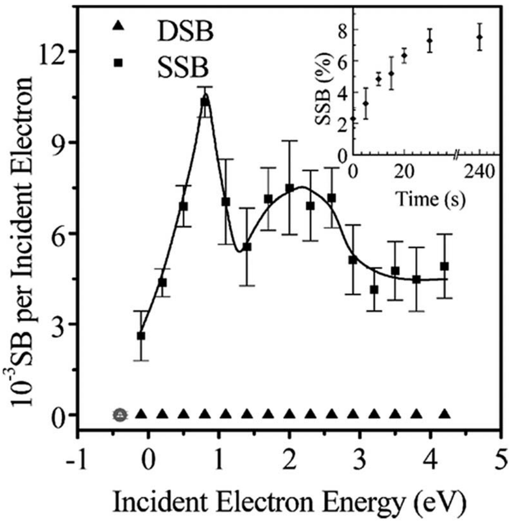

Fig. 5 Plots of the yields of DNA single and double strand breaks as functions of the electron kinetic energy. Copyright (2004) by The American Physical Society.

electrons having KE < 20 eV could fragment deoxyribose molecules and they showed what fragments would occur and with what abundances. Also in 2004, this same group[13] determined that electrons with KEs in the 5–10 eV range could fragment thymine or cytosine and they found that loss of an H atom to form a nitrogen-centered base anion took place for KE ≈ 2 eV. In 2006, the Illenberger group[14] studied what happens when electrons with KE < 15 eV collided with purine bases and found that at the lowest KE values the primary cleavage occurs at the base N–H bond again to form base N-centered anions.

Although the Burrow/Sanche findings described above validated our prediction that electrons with very low KEs could cause DNA strand breaks, it was not until 2005–2006 that experiments[15] showed evidence supporting our prediction that the sugar–phosphate C–O bonds would dominate the cleavage events with the sugar–base C–N bond cleavage taking second place. I will say more about these experiments later.

Having described the history of our involvement in the study of if and how electrons having very low (*e.g.*, 1–3 eV) KEs can break strong covalent bonds within DNA, I will now suggest to you what lessons we can learn from such studies. First, I think it fair to say that by limiting studies to electron–nucleobase interactions, the scientists could not uncover the most likely bond-cleavage events that took place in the condensed-media experiments[6] reported by Sanche in 2000. Most scientists working in the field thought correctly that base π^* orbitals were the most likely attachment sites for low-energy electrons, so it made sense consider bond cleavage within the bases, but to limit consideration to those events was a mistake. A similar statement could be made about the study of electron–ribose interactions and even about electron–nucleoside (*i.e.*, a base–sugar unit absent the terminal phosphate unit) interactions that were also carried out but that I need not discuss here. *So, these are good examples showing that the model system needs to contain the most essential building blocks if it is to have any chance to simulate the actual system under laboratory study*.

The second lesson that our DNA damage story provides has to do with limitations produced by the tools used to carry out the experiment or theoretical simulation. The early experiments[6] by Sanche employed an electron beam with KEs exceeding 3 eV, as did most if not all of the other experiments on electrons interacting with nucleobases, deoxyribose units, and other DNA fragments. This limitation to KE values mostly above the energies of the base π^* orbitals produced bond fragmentation outcomes derived largely from shake-up states of the electron-attached species. Only in 2006 when the Burrow/Sanche team used an electron source that generated KEs below 3 eV did experimental evidence appear that shape resonance π^*-attached states could also yield single strand breaks (with substantial yields). *So, by using experimental tools that did not generate electrons in the appropriate KE range, these early pioneering studies were not able to uncover the roles played by the shape resonance states, which, in turn, did not allow them to discover the importance of the sugar–phosphate C–O bond cleavage process*.

As mentioned above, in 2005 and 2006 experiments were carried out on single-strand CGTA and CGAT oligomers[15] in which electrons having KE > 4 eV were employed. In these experiments, it was possible to chemically analyze the products of the bond cleavage and it was discovered that sugar–phosphate C–O bond cleavage was the most common event but that sugar–base C–N bond cleavage also occurred but with lower yields. Although these findings appear to support our predictions about which bonds would be most likely to cleave, it should be noted that the KE values used are consistent with forming primarily (*i.e.*, at 4 eV, some shape resonance states might be created) shake up states. Thus, even as of 2019, there still do not exist definitive experiments demonstrating that electron attachment to form base π^* shape resonances primarily cleaves sugar–phosphate C–O bonds.

Before moving on to discuss the roles of theory in ion spectroscopy and the pitfalls that can occur on that front, it is important to return to the issue of solvation (*i.e.*, the effect of surrounding matter) to discuss the third lesson that our DNA story provides. In ref. 9 (see also ref. 10) we noted that the base π^*-attached shape resonances are expected to undergo autodetachment within *ca.* 10^{-14} s in the absence of solvent stabilization (*i.e.*, in the gas phase as isolated species). Having such a short lifetime, there would not be enough time for a nascent π^* anion to undergo base-through-sugar-to-phosphate electron transfer and subsequent sugar–phosphate C–O bond cleavage. However, by allowing for the high-frequency dielectric response of the surrounding (modelled using a continuum dielectric with $\varepsilon = 2$), we demonstrated that the π^* anion could be differentially stabilized relative to the neutral sufficiently to render it no longer susceptible to autodetachment. Because the year-2000 Sanche experiments were carried out on DNA specimens that were surrounded by other DNA molecules, proteins, and other components of the desiccated *E. coli* sample, describing the relaxation of the surroundings as the electron-attachment occurs and shortly thereafter using $\varepsilon = 2$ was reasonable. It would not have been appropriate to use a much higher dielectric constant (*e.g.*, $\varepsilon = 78$) since the electron attachment, electron transfer, and C–O bond rupture steps do not allow enough time for full solvent reorganization to take place; this would require *ca.* 10^{-12} s or longer.

These observations on solvation effects in our DNA study suggest that it might not be sufficient in gas-phase studies involving electrons impinging on nucleotides (or larger DNA fragments) to have only a few water molecules attached to model the kind of surroundings in experiments like the 2000 Sanche experiments. Depending on where the (few to several) solvent molecules attached to the nucleotide, they could stabilize electron-attached states with the electron on the base or moving through the sugar or in the region of the sugar–phosphate C–O σ^* orbital. However, I am sceptical that such micro-solvation could model the kind of $\varepsilon \approx 2$ dielectric stabilization that seems to be necessary to stabilize the entire nucleotide throughout the full electron attachment, electron transfer, and bond cleavage events. I might be wrong, but I caution workers to strive hard to make sure that any solvation covers the full route of the attached electron's migration from base to phosphate.

3. Theory's roles, issues, and future

I will now make several observations on the roles played by theory in ion spectroscopy and I will offer some opinions on where further advances are needed. First, I noticed in this FD that there were many questions from experimentalists about when DFT can be trusted, when it cannot, and what kinds of functionals to use. In a brief oral presentation at this FD, Sotiris Xantheas showed results on the errors (relative to coupled-cluster results) in binding energies for a wide size range of water clusters calculated using a variety of functionals within DFT. For many of the functionals, the errors grew essentially linearly with cluster size, while for other functionals, the errors varied much less with cluster size. It is well known that many DFT functionals do not offer a correct long-range (*i.e.*, when an electron is far from most of the system's electron density) description of the potential experienced by the electron whose motion the theory attempts to model. Some functionals attempt to mitigate these problems by mixing in terms that (approximately) remove the errors at large distances. However, even in 2019 the situation is still under active development as Sotiris' remarks were intended to demonstrate. Related to these problems with long-range errors, time-dependent DFT (TDDFT), which is used to compute electronic excitation energies, does not perform well for transitions that involve considerable charge transfer (*i.e.*, movement of electron density from one region to another). Again related to difficulties at long ranges, DFT has a difficult time describing dispersion (*i.e.*, van der Waals) interactions among spatially separated fragments (molecules or ions). Some functionals attempt to fix these problems by adding on to the DFT energy terms that vary as R^{-6} at large intermolecular distances. Other workers are attempting to invent new functionals that will more properly treat dispersion-like interactions, but the field remains under development.

On the positive side of the ledger, many functionals used in DFT calculations do reasonably well in predicting molecular geometries and harmonic vibrational frequencies. These positive attributes, combined with DFT's low computational cost, have made it very attractive and useful among the experimental physical chemistry community, and I don't expect this situation to change. In my opinion, it is wise for experimentalists who make use of DFT and TDDFT calculations to assist in interpreting their spectral data to stay in close contact with theoreticians who are active in these fields. I wish we could give definitive answers as to which functionals are best, how to best handle charge transfer issues, and how to include dispersion energies, but I can't at this time. Because there are many excellent theoretical groups working on them, DFT and TDDFT are likely to continue to undergo evolutionary improvements for several/many years to come, and I expect their use in interpreting vibrational and electronic spectra to remain popular and to become of even greater use.

In this FD we heard from several of the theoreticians that there are other theoretical tools that can provide more reliability and higher accuracy than DFT (for energies) and TDDFT (for excitation energies), and examples were given to support these claims. Of course, the question then is why don't we all just use these methods rather than DFT. In my opinion, the answer is that they are still more computationally costly than DFT and they are not yet as familiar and easy to use as the tools that appear in many widely accessible software packages. In a sense, their states of development are analogous to those of many of the cutting-edge experimental methods that we heard about at this FD. Although they might not quite yet be appropriate for use in the hands of non-experts, I strongly suggest that our experimental colleagues continue to dialog with the developers of these new tools and to collaborate on using these tools when possible (*i.e.*, on systems for which they are computationally feasible).

What are some of these higher-accuracy tools that I am talking about? I am not thinking of HF, MPPT, multi-configurational HF (MCHF), equations of motion coupled cluster (EOM-CC) methods,[16] or even coupled-cluster (CC) theory (including CCSD(T)). These are all well established methods, are widely available in several software packages, and are taught in our graduate-school curriculum. The methods that I have in mind include (i) explicitly correlated methods (in which functions that depend on the distances between pairs of electrons are used to form the electronic wave function), (ii) Monte Carlo methods that aim to solve the N-electron Schrödinger equation in imaginary time to generate the full N-electron wave function (two of this FD's participants, Anne McCoy (in treating nuclear motion issues) and Ken Jordan (in electronic structure issues) have considerable experience with these methods), and (iii) extensions of the EOM-CC technique that Anna Krylov discussed (DOI: 10.1039/c8fd00185e) in this FD to permit the study of metastable electronic states.

The explicitly correlated and Monte Carlo methods produce total electronic energies and thus would serve as competitors to DFT, HF, MPPT, MCHF, and CC theory once they become more practical to use on molecules and ions of broad interest. In a remark at this FD, Ken Jordan noted that workers have made great progress on extending CC theory to produce algorithms whose computational cost scales linearly with system size, which is an optimistic sign. To be of use in ion or molecule spectroscopy, these theories need to be advanced to allow one to also obtain derivatives of the electronic energy with respect to geometry. Such derivatives produce force constants and vibrational frequencies and are used in locating minima and transition states on energy surfaces. At present, reliable and computationally practical codes to obtain such geometrical derivatives for these methods are still under development (*i.e.*, not widely available). In addition, these theories need to be improved to allow them to be more feasibly applied to excited electronic states (*e.g.*, to carry out a CCSD(T) calculation on an excited state is not a straightforwardly automated procedure, and many excited states simply cannot be described with a single dominant/reference electronic configuration, which CC theory assumes) since there are times when one wants to determine properties (*e.g.*, dipole moments, polarizabilities, potential energy surface shapes, *etc.*) of excited states.

In terms of competition for TDDFT, I think the EOM-CC methods discussed in this FD discussion offer the best currently available option, and I believe such methods are ideally suited for interfacing with electronic spectroscopies (UV-Vis, photo-electron, and electron-scattering). Why? Because EOM-CC calculations generate electronic excitation energies (EEs), ionization potentials (IPs), and electron affinities (EAs), which are intensive quantities and are precisely what experiments measure. In contrast, DFT, HF, CC, MPPT, *etc.* produce total electronic energies, which are extensive quantities, which essentially no experiment measures.

Another important attribute of EOM-CC theory (and of TDDFT) is that it allows one to generate, in a single calculation, the energies of several (even many) excited (or electron-attached or electron-detached) states. Not only does this mean that one can probe a wide variety (*e.g.*, $\pi\pi^*$, $n\pi^*$, *etc.*) of states, but it means one can obtain energies of bound electron-attached states and electron-unbound states (including metastable states and states describing a free/continuum electron). As I will elaborate on later, these characteristics are especially useful for studying negative molecular ions.

Many workers have contributed to the development of so-called equations of motion (EOM) methods. In my early career, my group developed some of the fundaments of the theory,[17] especially with respect to computing EAs, when the reference wave function Ψ_N of the neutral molecule is assumed to be of the Møller–Plesset perturbation theory form and the equations $[H,O_k]\Psi_N = -\mathrm{EA}_k\Psi_N$ are solved through third-order for the (intensive) EAs. In these EOM equations, O_k is the operator that acts on Ψ_N to generate the k^{th} state $\Psi_{k,N+1}$ of the $(N + 1)$-electron system (*i.e.*, the anion). In EOM-CC, the same kind of equations are solved but Ψ_N is taken to be of the more accurate CC form. Moreover, the EOM-CC framework has been extended to allow one to compute, as intensive energy differences, EAs, IPs, EEs and more, as Anna Krylov discussed (DOI: 10.1039/c8fd00185e) in her FD presentation.

Several research groups have pioneered the modern development of EOM-CC, but I want to highlight Anna Krylov's involvement for two reasons. First, her group has done much to bring these tools into the mainstream by making them widely available within the QChem software package. Secondly, her group has extended the EOM framework to allow one to determine EAs for anionic states that are metastable (*i.e.*, have finite lifetimes) with respect to auto-detachment. They do this by using a so-called complex absorbing potential (CAP)[18] whose strength is determined by a scaling parameter λ. In this approach one obtains EOM-CC EA_k values that are complex and that depend on λ. One then varies λ until one finds a value at which the real and imaginary components of EA_k are stationary (*i.e.*, $\mathrm{dRe}(\mathrm{EA}_k)/\mathrm{d}\lambda = 0 = \mathrm{dIm}(\mathrm{EA}_k)/\mathrm{d}\lambda$). We see this procedure demonstrated in Fig. 6 of Krylov *et al.* (DOI: 10.1039/c8fd00185e). At such stationary points, the real part of EA_k gives the energy of the metastable state and the imaginary part gives one half the state's Heisenberg width Γ_k (inversely related to the lifetime).

There are other methods for finding metastable states in the continuum within which they exist. For example, the late Howard Taylor pioneered the so-called stabilization methods[19] for finding EA_k and Γ_k. In this approach, one uses a method for computing the energies E_k of several electron-attached states relative to the energy of the parent species and does so for a range of values of a parameter η that, for example, scales the radial extent of the more diffuse atomic orbital basis functions. Because one needs to compute the energies of several states, using a method such as EOM-CC is quite appropriate; at a more approximate level, one could use Koopmans' theorem and approximate the E_k in terms of HF orbital energies. However, it would not be appropriate to use DFT virtual orbital energies for this purpose as these have been shown to not produce reliable estimates for EAs. Ken Jordan and his co-workers have pioneered the use of EOM-CC methods within the stabilization approach and have applied this to treat several metastable anions.[1,20]

An example of such a so-called stabilization plot is shown in Fig. 6 where the energies of eight electron-attached states are plotted *vs.* a diffuse-orbital scaling factor.

At energies near $E = 0.5$ and $E = 1.6$, pairs of the electronic energies undergo avoided crossings. The relatively flat portions of the energy curves near $E = 0.5$ and near $E = 1.6$ give approximations to the energies of two metastable states. The curves that are steeply increasing as η increases approximate the energies of states of the parent molecule plus a free electron whose kinetic energy is given by those curves. Through the stabilization method's underlying equations, one can use the energies of pairs of E_k *vs.* η plots to determine the widths Γ_k of the metastable states (the widths depend strongly on the energy splitting with which pairs of energy curves avoid one another as they undergo avoided crossings).

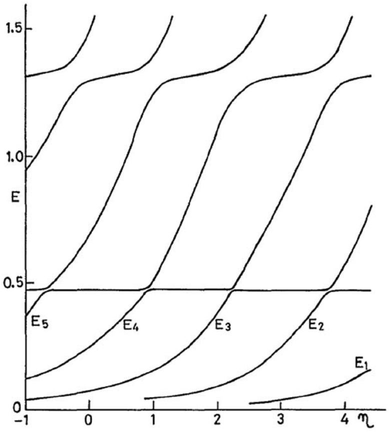

Fig. 6 A stabilization plot showing the energies of eight electronic states as functions of a scaling parameter that compresses (as η is increased) the radial extent of the diffuse basis functions.

In my mind, these methods for studying metastable states will soon be widely available in commonly used software packages and should be on the radar of experimental scientists who study such systems. The primary difficulties in bringing them to that status are (i) for the CAP method, the search for values of the parameter λ at which $\mathrm{dRe}(\mathrm{EA}_k)/\mathrm{d}\lambda = 0 = \mathrm{dIm}(\mathrm{EA}_k)/\mathrm{d}\lambda$ is not yet automated and straightforward, and (ii) for the stabilization method, the analytical formulas[21] used to extract the energies and half-widths from the pairs of E_k *vs.* η curves involve using so-called Padé approximants and subsequent complex variable analysis, and these components are not yet parts of widely used software packages. Nevertheless, I think both of these methods are things that experimentalists should become familiar with because soon they will be of much value to them.

Let me now use an example to illustrate some of the theoretical issues I have already discussed and a few more. In Fig. 7, we see qualitative depictions of energies as functions of some geometrical coordinate of a neutral molecule and its stable anion with a few low-energy vibrational levels of each labelled.

To carry out, for example, an EOM-CC calculation on this kind of system, one would have to: (i) first perform a CC-level calculation for the wave function of the neutral molecule; (ii) then use this as the so-called reference wave function for performing an EOM-CC calculation of EA_k values. The largest EA_k value would produce a data point on the blue curve shown in Fig. 7, while the initial CC-level calculation would give a point on the red curve. Doing this for a series of geometries would allow one to form the red and blue curves.

If the system had more than one bound electronic state, other *positive* EA_k values could be used to give data points on their respective energy curves. However, if the situation were as depicted in Fig. 7 (*i.e.*, with only one bound state for the anion), the remaining EA_k values from the EOM-CC calculation would be *negative* and could *not* be used to generate data points for any of the states of interest. If one were using an atomic orbital basis set containing several diffuse functions, many of these EA_k values would correspond to energies of the neutral

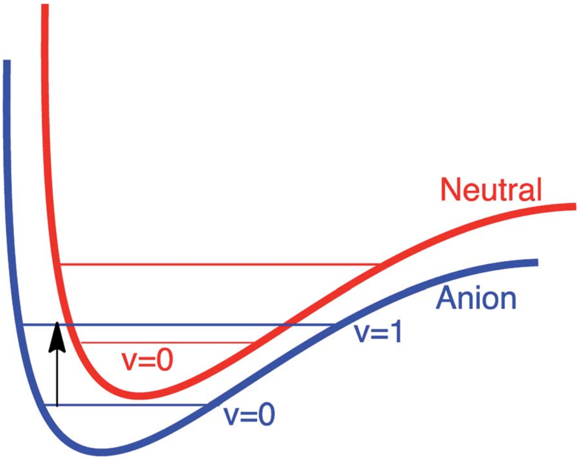

Fig. 7 Plots of the energies as functions of a geometrical coordinate of a neutral molecule and an electronically stable anion.

molecule plus a free electron with kinetic energy equal to $|\mathrm{EA}_k|$ (*e.g.*, as the energies lying below $E = 0.5$ in Fig. 6).

There are two more complications that might arise when carrying out the kind of calculations outlined above. First, the red curve might cross the blue curve (*i.e.*, the anion's energy surface might intersect that of the neutral molecule plus a free electron with zero kinetic energy). These kind of conical intersection situations require evaluation of matrix elements of the form $\langle \Psi_{N+1}|\nabla|\Psi_{N,\mathrm{KE}}\rangle$, where Ψ_{N+1} is the wave function of the anion and $\Psi_{N,\mathrm{KE}}$ is the wave function of the neutral molecule plus the outgoing electron having kinetic energy KE, and ∇ is the derivative along the internal geometry coordinate along which the red and blue surfaces intersect. These so-called non-adiabatic coupling matrix elements are available in several of the commonly used electronic structure codes, but they have not been implemented (yet) to permit the evaluation of the rates of surface hopping (from the blue to the red curve) in these programs. Such combined non-adiabatic multi-surface molecular dynamics calculations are presently in the realm of theoreticians specializing in such matters (*e.g.*, John Tully and Todd Martinez). I expect that many widely used software packages will soon contain modules that allow one to combine the electronic structure and molecular dynamics components of the kind of study I am discussing here.

Of special importance to ion spectroscopy is the second complication arising in cases qualitatively described in Fig. 7. Photons with energy at or above the energy of the black arrow could eject an electron from the anion. The spectral line shape and selection rules governing this kind of photo-detachment depend on squares of matrix elements of the form $\langle \Psi_{N+1}|E\cdot r|\Psi_{N,\mathrm{KE}}\rangle\langle \chi_{N+1,\nu}|\chi_{N,\nu'}\rangle$. Here Ψ_{N+1} is the electronic wave function of the (bound) anion and $\chi_{N+1,\nu}$ is it vibration/rotation wave function; $\Psi_{N,\mathrm{KE}}$ is the wave function of the neutral molecule plus an electron ejected with kinetic energy KE and $\chi_{N,\nu'}$ is the vibration/rotation wave function of the neutral molecule. These electric dipole matrix elements and the accompanying Franck–Condon integrals are, of course, well known to this FD audience, and their evaluations are possible in presently available software packages.

However, once the photon energy is increased to or above the energy of the black arrow in Fig. 7, the situation becomes complicated (and is not currently treated in any software package of which I am aware). The same (black arrow) photon that can induce an electric-dipole ejection of an electron (from the anion to the $\nu' = 0$ level of the neutral) can also excite the anion from $\nu = 0$ to $\nu = 1$. Then, this $\nu = 1$ anion can eject an electron to produce the $\nu' = 0$ state of the neutral plus an ejected electron by converting its excess vibrational energy into electronic energy.

The two pathways for ejecting electrons discussed above generate amplitudes of a combined excited-state wave function, and the two amplitudes can interfere in a way that produces somewhat unusual photo-electron line shapes. Mark Johnson and his colleague, John Tully, wrote a very nice paper[22] on these so-called Fano line shapes, which appear in Mark's experiments on small water cluster anions. In those experiments, an infrared photon at *ca.* 3350 cm^{-1} was energetic enough to directly photo-detach the excess electron, but this same photon could excite an O–H vibrational mode of the cluster anion and this vibrationally excited anion can "shake" the electron off *via* a non-adiabatic coupling process.

It turns out that the cross-section $\sigma(\varepsilon)$ for observing photo-detached electrons is given by the following formula: $\sigma(\varepsilon) = \sigma_\mathrm{a}\frac{(q+\varepsilon)^2}{1+\varepsilon^2} + \sigma_\mathrm{b}$.[23] Here, $\sigma_\mathrm{a} + \sigma_\mathrm{b}$ is the cross-section in the absence of the non-adiabatic electron ejection mechanism and is proportional to the square of $\langle \Psi_{N+1}|E\cdot r|\Psi_{N,\mathrm{KE}}\rangle\langle\chi_{N+1,1}|\chi_{N,0}\rangle$ for the case at hand. The factor $\frac{(q+\varepsilon)^2}{1+\varepsilon^2}$ depends on a dimensionless energy variable ε related to the photon energy E, the energy of the $\nu = 1$ anion $\langle \Psi_{N+1}\chi_{N+1,1}|H|\Psi_{N+1}\chi_{N+1,1}\rangle \equiv E_0$:

$$\varepsilon = (E - E_0)/\Gamma$$

and the width Γ of this level arising due to the non-adiabatic electron ejection process:

$$\Gamma = 2\pi|\langle \Psi_{N+1}\chi_{N+1,1}|H|\Psi_{N,\mathrm{KE}}\chi_{N,0}\rangle|^2.$$

The integral $\langle \Psi_{N+1}\chi_{N+1,1}|H|\Psi_{N,\mathrm{KE}}\chi_{N,0}\rangle \equiv H_\text{non-adiabatic}$ that enters into the expression for Γ describes the non-adiabatic coupling between the vibrationally excited anion and the $\nu = 0$ neutral-plus-free-electron state.

Depending on the value of the parameter q, these cross-sections can vary in a variety of ways with the photon energy (see, for example, Fig. 1 in ref. 23). Whenever $|E - E_0| \gg \Gamma$, the factor $\frac{(q+\varepsilon)^2}{1+\varepsilon^2}$ reduces to unity and the cross-section reduces to $\sigma_\mathrm{a} + \sigma_\mathrm{b}$.

In Fig. 8 we see an example from the paper by Mark Johnson and John Tully mentioned earlier, in which a negative value for q produces the unusual line shape features.

The q parameter reflects the amplitudes for the two electron-ejection processes and is approximately:

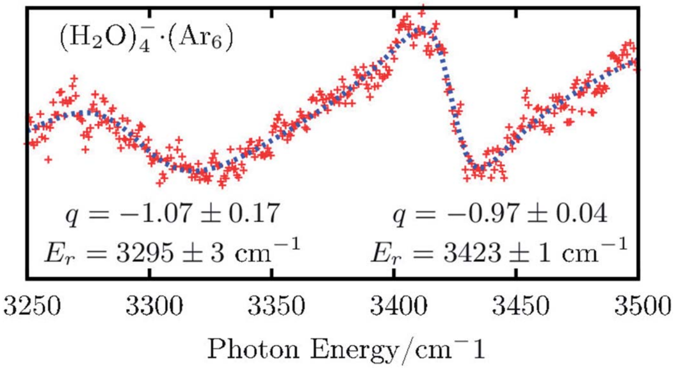

Fig. 8 Photo-electron count as a function of photon energy for water cluster anions absorbing infrared photons (from ref. 22). Reproduced from S. T. Edwards, M. A. Johnson and J. C. Tully, *J. Chem. Phys.*, 2012, **136**, 154305. With the permission of AIP Publishing.

$$q = \frac{\langle \Psi_{N+1}\chi_{N+1,0}|E\cdot r|\Phi\rangle}{\pi H_{\text{non-adiabatic}}\langle \Psi_{N+1}\chi_{N+1,0}|E\cdot r|\Psi_{N,\text{KE}}\chi_{N,0}\rangle}$$

where Φ is the hybrid wave function created by the photon absorption:

$$\Phi = \Psi_{N+1}\chi_{N+1,1} + P\int_0^\infty \mathrm{d}E' \frac{H_{\text{non-adiabatic}}\Psi_{N,\text{KE}'}}{\mathsf{E} - E'}\chi_{N,0}$$

The denominator in this expression for q is the amplitude for the direct ionization process (times π) multiplied by the non-adiabatic coupling matrix element, and contains the electric-dipole transition matrix element and the Franck–Condon overlap of the anion and neutral vibration/rotation functions.

The numerator contains the amplitude for photon-induced population of the $\nu = 1$ level of the anion

$$\langle \Psi_{N+1}\chi_{N+1,0}|E\cdot r|\Psi_{N+1}\chi_{N+1,1}\rangle$$

as well as a contribution from the non-adiabatic coupling (arising from the principal value integral shown above).

The non-adiabatic coupling integral involves a sum over all of the displacements (labelled j) of the M nuclei (each with mass m_j) in the molecule

$$H_{\text{non-adiabatic}} = \sum_{j=1}^{3M} \frac{-1}{2m_j}\left\langle \Psi_{N+1}\chi_{N+1,1}\middle|\nabla_j{}^2\middle|\Psi_{N,\text{KE}}\chi_{N,0}\right\rangle$$

and can be rewritten in an approximate form (because terms involving second derivatives of the electronic or vibration/rotation functions are ignored as is usually justified) that makes its physical meaning easier to explain:

$$H_{\text{non-adiabatic}} = \sum_{j=1}^{3M} \frac{-1}{m_j}\langle \Psi_{N+1}|\nabla_j|\Psi_{N,\text{KE}}\rangle\langle \chi_{N+1,1}|\nabla_j|\chi_{N,0}\rangle$$

.

These matrix elements will be significant, and the resulting vibration/rotation-to-electronic energy flow will be facile, if (i) there is a geometrical distortion of the molecule (*i.e.*, a coordinate corresponding to the gradient ∇_j) along which the orbital occupied by the excess electron in Ψ_{N+1} (*i.e.*, the anion HOMO) is strongly modulated (so $|\nabla_j \Psi_{N+1}|$ is large), (ii) the anion and neutral vibrational functions have large $\langle \chi_{N+1,1} | \nabla_j | \chi_{N,0} \rangle$ matrix elements (*e.g.*, differ by one quantum number in the most basic harmonic approximation, and notice this is not the conventional Franck–Condon integral), and (iii) the de Broglie wavelength of the ejected electron $\lambda = \frac{h}{\sqrt{2m_e \mathrm{KE}}}$ is similar in magnitude to the size of the anion's HOMO (otherwise $|\langle \Psi_{N+1} | \nabla_j | \Psi_{N,\mathrm{KE}} \rangle|$ will be small). Several years ago, I derived equations[24] governing such vibration-to-electronic energy transfer processes, and we later applied this theory[25] to interpret some data from Carl Lineberger on NH^-. It is such non-adiabatic couplings that give rise to the ability of the anion to not only eject an electron *via* a direct electric dipole processes but to also "shake off" an electron using vibration-to-electronic energy flow, which is what the non-adiabatic terms describe.

As was the case for including non-adiabatic coupling matrix elements within widely used software packages, the same is true when it comes to including such effects on spectral line shapes. The vibration/rotation components $\langle \chi_{N+1,1} | \nabla_j | \chi_{N,0} \rangle$ might be rather straightforward to include, but the electronic integrals $|\langle \Psi_{N+1} | \nabla_j | \Psi_{N,\mathrm{KE}} \rangle|$ are more complicated and have not (yet) been made routinely available. I expect it will be several years before these contributions to line shapes and cross-sections will become accessible to the broad community of experimental and theoretical scientists studying ion spectroscopy.

In summary, the pressing issues for the theory community to address and for the experimentalists to keep track of include:

1. Ongoing improvements to functionals used in DFT and TDDFT – overcoming dispersion and long-range error issues;
2. Ongoing efforts to bring linear-scaling (*i.e.*, computational costs scaling linearly with system size) to CC theory as well as to other commonly used correlated methods;
3. Improved computational efficiency in Monte Carlo and explicitly correlated methods and incorporation of the ability to evaluate derivatives of the energy (*e.g.*, for energy gradients and electric polarizabilities);
4. Ongoing improvements in the ease of implementation of stabilization and CAP methods (most likely within EOM-CC) to more easily identify stationary points that produce energies and widths of metastable states; extension of the theory to allow oscillator strengths between bound and metastable states to be treated;
5. Inclusion of non-adiabatic coupling matrix elements within software modules that locate conical intersections and carry out surface hopping/switching dynamics simulations on these surfaces;
6. Inclusion of non-adiabatic bound-to-continuum matrix elements within spectral line shape calculations to permit vibration/rotation-to-electronic energy flow to be studied and Fano line shapes to be simulated.
7. Because many of the spectroscopic methods that have been developed are of the "action type" (*e.g.*, loss of ions of mass $(\mathrm{H_2O})_n\mathrm{He}^-$ when a He atom is ejected by absorption of an IR photon exciting an O–H stretch), the theoretical

description of the line shape (*i.e.*, action yield as a function of photon energy) is complicated. Reaching that milestone will require very close collaboration between experimental and theoretical groups because the theoretical scientist has to be convinced to include (i) simulation of the primary IR photon absorption event, (ii) the energy flow from the nascent O–H vibration to the He atom (at present, we usually assume this energy flow is fast and does not depend on which vibrational mode is excited), and (iii) the rate of He-atom ejection (which depends on the density of translational states of the He atom). Clearly, this will require a theory person who can handle electronic structure and molecular dynamics aspects of the problem.

8. In addition to advances within the areas of *ab initio* electronic structure theory and molecular dynamics highlighted above, I think it is essential for theoreticians to also continue to develop physically motivated model theories as illustrated by Ken Jordan in his FD manuscript (DOI: 10.1039/c8fd00199e). By creating a model Hamiltonian that focuses on one electron while realistically treating that electron's interactions with the remaining molecular structure, those workers are able to expand studies to much larger systems including clusters of C_{60} molecules. Of course, the invention of such models requires the theoretician to be fully aware of the most important interactions and phenomena to include. For this reason, it is crucial for the theoretician to be in close contact with experimental researchers for whom the products of such studies can be of much value.

9. Although many electronic structure methods do reasonably well in evaluating harmonic vibrational frequencies, one sometimes needs a description of the system's vibrations and rotations beyond the harmonic level. For "floppy" molecules/ions and fluxional molecules/ions and for characterizing the Born–Oppenheimer energy surface far from local minima, this is especially important. My colleague, Ryan Steele, and others are trying to advance this area by focusing on using a local-mode picture that also shows promise for reducing the scaling of the computational cost with system size.

4. Conclusions

I hope I have made it clear that I think the balance of methods development and applications to real-world (or reductively approximated) chemical problems is being wisely handled by today's ion spectroscopy community as reflected in this FD. I think it should be clear to the participants of this FD that the theory community is developing new tools just like the experimental community is doing, and that it is wise for the two communities to stay in close communication. I also hope I have made clear my concerns about how we need to be cautious about choosing model systems and about how we treat solvation/environment effects; both issues are important if we want gas-phase spectroscopic studies to be of help in understanding molecules as they usually occur in nature and in our bodies. Finally, I hope I have illustrated that theory needs to continue to improve the computational efficiency of its tools and to develop and implement (in widely available software packages) the techniques I have enumerated here if our (theory's) impact on the spectroscopy of gaseous ions is to be optimized.

Conflicts of interest

There are no conflicts to declare.

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