REVIEW ARTICLE

PCCP
www.rsc.org/pccp

Odyssey and oddity: Photo- and collision processes you would not expect†

R. Stephen Berry

Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois, USA

Received 25th August 2004, Accepted 25th November 2004
First published as an Advance Article on the web 7th December 2004

A long-standing investigation of one intriguing collision process, Penning detachment, involved a series of theoretical studies and then experiments intended to exhibit the phenomenon. After some exploratory studies, the experiments, to our surprise, produced clear, unambiguous results that were due to an altogether different process. Identifying and pursuing that process required further theory as well as more experiments. The outcome, reviewed here, has been (a) predicted cross sections for Penning detachment of electrons from negative atomic and cluster ions; (b) predictions of cross sections for resonant two-photon and above-threshold three-photon ionization, (c) measurements of cross sections for superelastic collisions of slow electrons with excited atoms, and, still in progress, (d) theoretical values for cross sections of such superelastic collisions. The experimental method offers a new way to carry out studies of collisions of slow electrons with very high energy resolution.

Introduction

Among atomic collision processes, one of the best and longest known and most studied is Penning ionization, ionization produced when an excited species collides with a neutral whose ionization potential is less than the excitation energy of the energy donor. A classic example is ionization of argon atoms when they collide with metastable helium atoms in their lowest triplet state: $He^*(2\ ^3S) + Ar \rightarrow He(1\ ^1S) + Ar^+ + e^-$. This is one member of a rich, well-studied class of processes including autoionization, associative ionization and its reverse, dissociative recombination. In striking contrast, the corresponding process involving an excited species colliding with a negative ion to produce two neutrals and a free electron, symbolically $A^* + B^- \rightarrow A + B + e^-$, has almost not been studied at all. By analogy with Penning ionization, we call the latter process 'Penning detachment'. This article is a recounting of the efforts of our group to study this process, and of the surprising directions in which those efforts have led us.

One aspect of Penning detachment that makes it intriguing is the striking difference between the cross sections one might expect it to show, in contrast to those of Penning ionization. The latter involves the collision of two neutrals, with only van der Waals attractions to bring the colliding species together. The former, in contrast, involves the attraction of an ion and an electronically excited and hence very polarizable neutral, so one might expect much larger cross sections for Penning detachment than for Penning ionization. If Penning detachment does have large cross sections, then one might expect it to be important in converting anions to neutrals in electric discharges and plasmas. We ourselves found it a natural explanation for the fate of negative ions in vapors of partially-dissociated alkali halides, particularly behind shock waves in gases containing these salt vapors. Consequently we were led to conduct theoretical studies, first to make rough estimates and then to compute more accurate values for the cross sections of the process. There was a long period between those first estimates in 1971 and the 'serious' calculations in 1997, in which there were no experiments that investigated the process. Hence we began an effort at that time to observe Penning detachment and measure cross sections for this phenomenon. The course of events was not at all what we had anticipated. The first unequivocal experiments that showed low-energy electrons with what seemed to be the expected energies turned out to involve a process or processes that could not be Penning detachment at all, because the 'verification' experiments that were supposed to show that we were observing collisions of anions with excited atoms in fact showed that negative ions were not involved at all with the production of free electrons. In this discussion, we review the theoretical studies of Penning detachment and the implications of those calculations for our expectations, and then the elucidation of the processes that we were actually observing, and the opportunities that these results suggest.

The outcome, as discussed below, is that the studies became studies of photoprocesses of magnesium atoms, specifically of two processes: superelastic scattering (SES) of low-energy electrons produced by resonant two-photon ionization that collide with other excited Mg atoms, and above-threshold ionization (ATI), a three-photon, single-atom process. The former dominates but the latter is also observable, particularly with two-color excitation. Both one-color and two-color experiments were carried out. Using one laser beam of the resonant frequency to excite Mg ($2\ ^1P$) and another with variable frequency to ionize made it possible to scan the low-energy continuum, *e.g.* for resonances.

Penning detachment: theoretical studies

There had been virtually no notice of Penning detachment as a theoretical subject when we carried out our first rough analysis. One brief experimental paper[1] in 1969 had reported the products of collisions of O^- and O_2^- with electronically excited O_2, in the context of ion-molecule reactions in the atmosphere. Then, in 1971, Benjamin Blaney and I[2] used a semiclassical, adiabatic approach with no regard for the effect of the attractive potential on the collision trajectories, to estimate the cross sections for this process, and for the competing photon emission, for a variety of excited atomic energy donors colliding

† Presented at the Third International Meeting on Photodynamics, Havana, Cuba, February 16–20, 2004.

DOI: 10.1039/b413092h

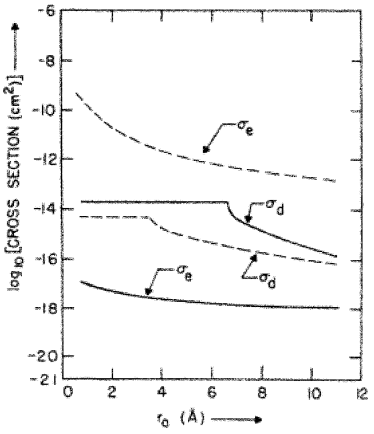

Fig. 1 Estimated cross sections, σ_d and σ_e, for Penning detachment and photon emission, respectively, for $Ca^* + H^-$ (solid curves) and for $H^* + H^-$ (dashed curves), as functions of r_0, the maximum impact parameter for which the collision is considered to produce a significant probability of reaction. This was a very simplified model, much refined in later calculations.

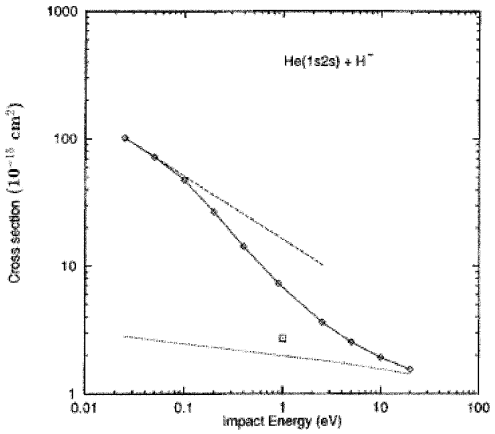

Fig. 2 Penning detachment cross sections for $H^- + He(1s2s\ ^1S)$ from the calculations of Martín *et al.*[3] The continuous curve with diamonds is based on the fullest calculations of this reference; the dashed curve that does not drop off so rapidly at higher energies; the low dotted line gives the results of Blaney and Berry.[2]

with a variety of atomic negative ions. Fig. 1 shows some typical cross sections that show how Penning detachment dominates, except in the one special case included in the figure, of $H^* + H^-$, for which photoemission has the larger cross section. Cross sections computed from those early estimates ranged from 2.7×10^{-15} cm^2 for $He^*(2\ ^1S) + H^-$, to 1.9×10^{-14} cm^2 for $Ca^*(3\ ^1D) + H^-$ and 2.0×10^{-14} cm^2 for $Ca^*(3\ ^1D) + C^-$.

Sixteen years later, a much more thorough theoretical study yielded even larger cross sections, first for collisions of H^- with $He^*(1s2s\ ^1S)$ and with Li* in several excited states[3] and then of H^- with Li* and Ca* also in several excited states.[4] These calculations treated the nuclear motions classically and the electronic interactions, quantum-mechanically, with Gaussian bases and discretized continuum states. Cross sections were evaluated with both accurate classical trajectories and trajectories based simply on the Langevin ion-neutral potential of the form $-\alpha/2R^4$ (with R the internuclear distance) were examined, and these were compared with the cross sections of the earlier calculations that used only straight-line trajectories. The collision energies spanned the range from 25 meV to 20 eV, a range one might find in discharges and in hot gases dissociated and ionized as, for example, behind shock waves. Results of the first of these studies, in Figs. 2 and 3, show how large these cross sections can be, especially at very low collision energies. The cross sections can exceed 10^{-13} cm^2, truly astonishing when one is used to values more like those for elastic scattering or Penning ionization.

Most of the cross sections increase as the collision energy drops, but there are exceptions. The Penning detachment channel for $H^- + Li^*(3d)$ closes, as a result of a barrier in the interaction potential, below an energy just above 0.1 eV, which reveals itself by the dramatic fall-off in this cross section at low energies.

One further study completed this series of investigations. That was the evaluation of cross sections for Penning detachment from negative alkali clusters Na_7^- and Na_{19}^- by collision with $Na^*(3s3s\ ^1P)$.[5] The cross sections for detachment from clusters were very much the same magnitude, with about the same kind of energy dependence as was found for detachment from atomic anions. The general implication, not at all surprising, is that the interactions in Penning detachment have such long ranges that the geometric size of the systems plays little role in determining the probability of the detachment reaction. It is quite possible that this result is a consequence of the negative charge being distributed throughout the entire cluster, fairly homogeneously. Were the target of similar size but composed of an insulating material with a local site at which the negative charge resides, then the cross section might well be smaller, due to a traditional steric effect. The donor would have to collide with the anion in the vicinity of the localized charge. This is a speculation, and could be investigated experimentally and theoretically.

The cross sections, all well in the range 10^{-15} cm^2 to 10^{-13} cm^2, gave a strong indication that it would be straightforward to observe Penning detachment experimentally, and to measure those cross sections with considerable precision. It turned out that there were some considerable surprises.

Experimental venture and unexpected results

Our experimental program was directed toward simple collisions of atomic anions in a beam with excited atoms in an effusing vapor, hence a single-beam process. The detached electrons entered a magnetic bottle spectrometer that collected them and fed them to a detector that would recognize their arrival time and of course the number of electrons coming in each time window.[6] The systems we explored were a variety anions of electronegative atoms and optically-excited alkaline earth atoms. The excited Mg atoms were produced by radiation at 285.2 nm, resonant with the 3s → 3p excitation of Mg. The radiation was produced by a Nd:YAG laser, doubled in frequency by a KDP crystal, so, even with optical density filters, the radiation was rather intense.

The initial results were encouraging but not clear or conclusive, as we searched for a favorable combination of negative

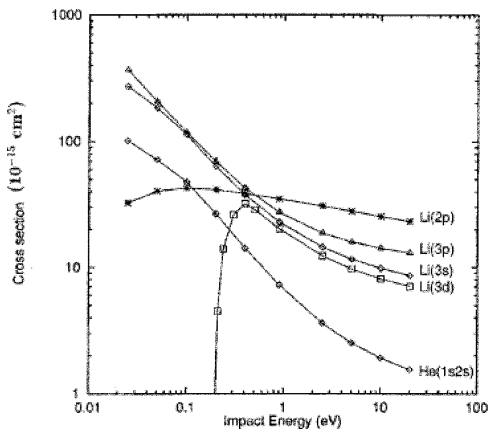

Fig. 3 Comparison of the Penning detachment cross sections for $H^- + He^*(1s2s\ ^1S)$ with those for $H^- + Li^*(1s^2, 3s, 3p, 3d)$.

ion and neutral energy donor. Signals were weak, and noise levels were high. However, when we used O^- and Mg*(3s3p ^{1}P), we immediately obtained clear signals, peaks in the electron intensities at unambiguous and expected times. One peak, at the longest time, was a clear consequence of the high intensity of the exciting laser; it was due to electrons with approximately 1.21 eV of energy, produced by resonant two-photon ionization of Mg atoms. At least one peak corresponded, within plausible uncertainty, to the energy expected of an electron released from O^- by absorption of a photon from an excited Mg atom.

Naturally, we carried out the appropriate experiments to attempt to verify that we were indeed seeing Penning detachment. We carried out collisions with no optical excitation, and got no signal. We carried out experiments with optical excitation but with no Mg, and we again got no strong signal. (There were presumably some electrons set free by photodetachment from the O^-, but the light beam was focused to be slightly away from the beam of negative ions.) Then we carried out experiments with Mg atoms and optical excitation, but with no O^-, and, to our great surprise, we obtained the same signal we had attributed to Penning detachment of O^-. We were clearly observing a process or processes associated with Mg and its optical excitation; the oxygen had nothing to do with what we saw.

What were we observing? There were two possible processes: resonant, multiphoton above-threshold ionization (resonant ATI), and superelastic scattering of the photoelectrons produced by resonant, two-photon absorption. One peak at 5.50 eV, due to the fastest electrons, corresponded to the energy of three of the 285 nm photons, and could be produced by either three-photon absorption in an ATI process, or by superelastic scattering of electrons by Mg(^{1}P) that fall to the ground state as they give their energy to the electrons. There was also one other peak at an energy of 2.70 eV, between that of those high-energy electrons and the 1 eV of the electrons from resonant, two-photon ionization. Their energy corresponded to that of electrons superelastically scattered by Mg(^{1}P) that are de-excited only to Mg(^{3}P), rather than to the ground state. The occurrence of that peak at 2.70 eV is very strongly suggestive that superelastic scattering is at least one of the processes we were observing. Fig. 4 shows our first preliminary report of these observations.[7] At that time, we were not yet able to carry out the crucial experimental tests, specifically the dependence on not only light intensity (which we could to then) but, more important, the dependence on the concentration of Mg atoms in the effusive stream. Hence we could not yet say definitively how much of the signal came from ATI and how much came from superelastic scattering. Meanwhile, we had started a new set of theoretical calculations that would tell us the cross sections for the resonant two-photon and resonant three-photon ATI processes. This work is discussed below.

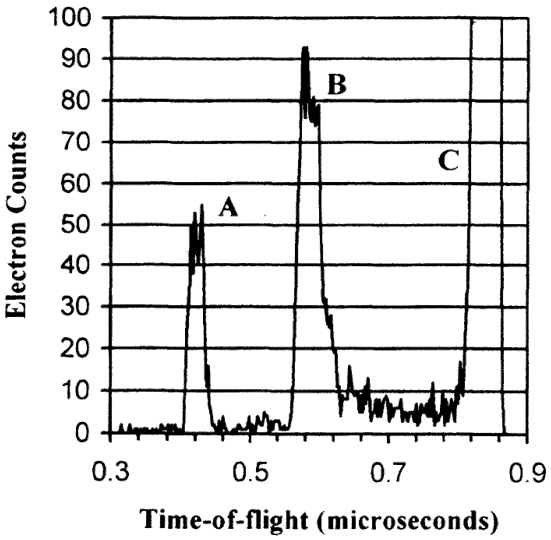

Fig. 4 Time-of-flight spectrum of electrons from photoexcitation of Mg(^{1}S) with resonant light at 285.2 nm. The electron energies correspond to: peak A, 5.50 eV; peak B, 2.70 eV, and the very intense peak C, to 1.21 eV.

Definitive experiments

Refining the apparatus and adjusting the conditions of the experiments enabled us to carry out measurements that established that the processes we were observing (apart from resonant, two-photon ionization) were both superelastic scattering and ATI. We were able to measure cross sections for these processes over a range of low collision energies. This work is described in a fuller treatment, but is summarized here.[8] The emphasis of the effort was primarily on the superelastic scattering. These experiments are very much in the tradition of a number of earlier studies of superelastic electron scattering by atoms.[9,10]

The experiments have utilized both one-color and two-color excitation/ionization, always with a first step at the resonant frequency for Mg. When only one color was used, the source was a Continuum Nd:YAG laser, frequency-doubled. The second color was generated by a Lumonix excimer and a tunable dye laser. The energy range of the photoelectrons that were subsequently scattered ran from essentially 0 to 270 meV. The magnetic bottle spectrometer collected over 95% of the electrons. Incidentally, the line shapes of the electrons' time-of-flight peaks were due primarily to the variation in path lengths, not to the energy distributions of the electrons, so that it will be possible to use these line shapes to study the angular distribution of electrons produced in photoprocesses. This will, of course, require using light with variable direction of polarization.

The definitive characteristics of ATI and superelastic scattering in these experiments are their dependence on the density of the Mg atoms. ATI must be linear, and superelastic scattering, quadratic, unless the density of Mg is so high that the medium becomes optically dense. Fig. 5 shows a typical one-color photoelectron time-of-flight spectrum, and Table 1 shows the dependence of the intensities of the three peaks, A, B and C, on the density of Mg atoms. The result is unambiguous; peaks A and B involve two, not one, magnesium atoms, one to be the source of electrons and the other, to be in the ^{1}P excited state and scatter the electron superelastically. Peak A corresponds to de-excitation of Mg*(^{1}P) to the ground ^{1}S state, and peak B, to de-excitation to the metastable ^{3}P state. Further evidence is the dependence of these peaks on the intensity of the radiation, as

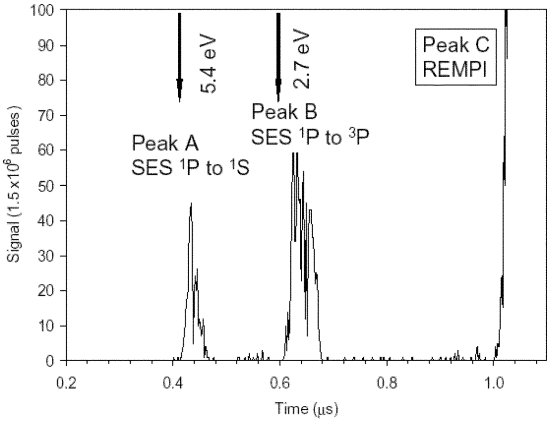

Fig. 5 Time-of-flight spectrum as in Fig. 4, with the later, refined apparatus.[8] 'REMPI' here refers to the resonant, two-photon ionization of Mg through its first ^{1}P state.

Table 1 Magnesium density dependence of the electron time-of-flight peaks in Fig. 5. The evidence is clear that because peak C defines linear dependence on the Mg density, peaks A and B depend essentially quadratically on that density. The densities are relative, and simply show that while peak C varies linearly, peaks A and B increase faster, consistent with quadratic dependence, on density

	ρ_1	ρ_2	ρ_3
Peak C, resonant two-photon ionization	1.0	2.3 ± 0.2	8.0 ± 0.8
Peak A	1.0	8.5 ± 0.8	50 ± 5
Peak B	1.0	6.1 ± 0.6	48 ± 5

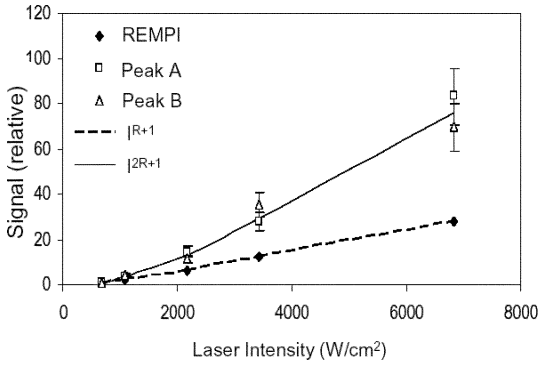

Fig. 6 Dependence of the intensities of peaks A, B and C of Fig. 5 on the intensity of the radiation in the one-color experiments.[8]

shown in Fig. 6. Peaks A and B require three photons, while peak C is only quadratic in the light intensity. This last evidence would not be sufficient, however, to distinguish superelastic scattering from ATI, in the absence of the information on the dependence of the intensities on the Mg density.

With two frequencies of radiation, one can see both superelastic scattering and ATI. Fig. 7 is an example of a time-of-flight spectrum done with two colors.

The two-color experiments made it possible to determine absolute cross sections for superelastic scattering of electrons with very low energies and with very narrow distributions of energy. The degrees of indeterminacy in the energy distributions were determined primarily by the bandwidth of the radiation and somewhat by the angular distributions of the emitted electrons; the sources produced pulses of approxi-

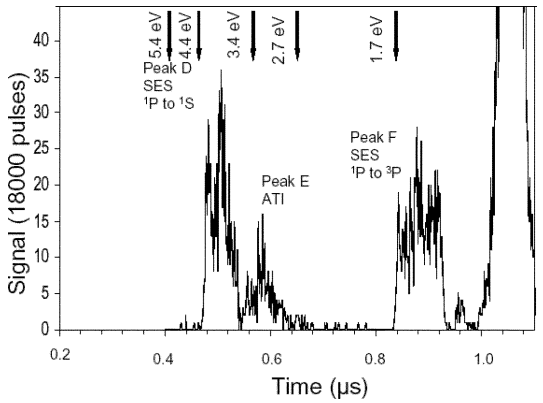

Fig. 7 Typical two-color time-of-flight spectrum. The nonresonant frequency is 370.45 nm. The very small peaks at 5.4 and 2.7 eV are due to one-color superelastic scattering, as in Fig. 5. The very large, unlabeled peak at the long-time end of the scale is peak C, the resonant two-photon peak. The peaks at 4.4, 3.4 and 1.7 eV arise from two-color processes. Their dependence on density of Mg shows that peaks D and F are due to superelastically scattered electrons, and that peak E requires only one Mg and is therefore due to above-threshold ionization.[8]

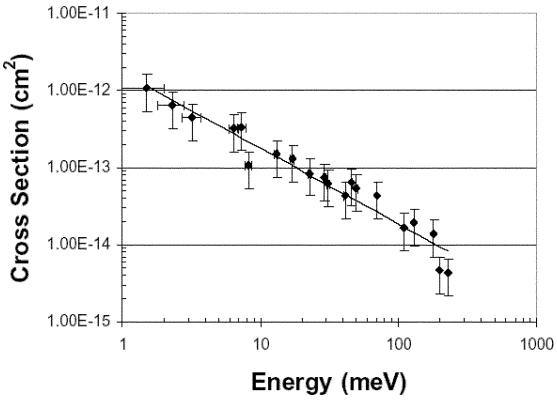

Fig. 8 Cross sections for superelastic scattering of low-energy electrons from Mg*(^{1}P) to produce Mg(^{1}S).[7]

mately 7 ns duration; consequently the absolute uncertainty of the photoelectron energies was 0.5 meV due to the dispersion in the arrival time of the electrons at the detector. The angular distributions determined the range of path lengths traveled by the electrons, and hence the spread of arrival times even for electrons of precisely the same energy. Fig. 8 shows the cross section for superelastic scattering to the ground state of Mg as a function of energy from approximately 0.5 meV to almost 220 meV. More details of the cross section measurements and the behavior of the cross sections for very low-energy electrons are given in the fuller discussion.[8]

The most general inference we can draw from this experimental effort is the recognition that one can now study processes involving very slow electrons with very high energy resolution, by producing the electrons *via* photoionization or photodetachment. Total cross sections of processes such as superelastic scattering become accessible and can be made quite accurate. As these experiments were done, the greatest source of uncertainty was the density of the Mg atoms. Presumably this factor is amenable to considerable refinement. Whether it will be possible to extract angular dependences of the secondary scattering processes by somehow deconvoluting line shapes remains an open question.

Further theoretical studies

Theoretical work on these processes is still going on, especially for superelastic scattering. However, there are definitive results now for the two-photon and three-photon, one-color ionization of Mg.[11,12] These results were produced in a collaboration with the Madrid group of F. Martín and co-workers. The principal interests for the two-photon case are probably the total cross sections, the angular distributions and especially the resonant peaks that appear in the energy dependence of the cross section. One important conclusion from the

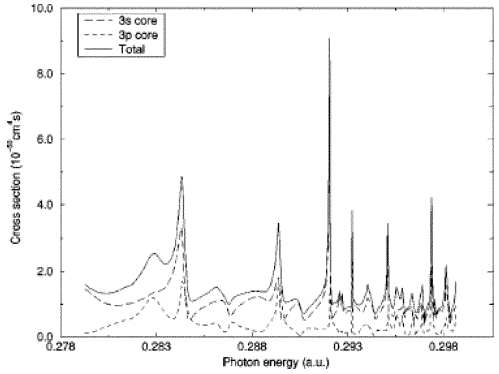

Fig. 9 Cross sections for two-photon above-threshold-ionization (ATI) for Mg. Partial cross sections for Mg^+ to be left in the 3s (long dashes) or 3p (short dashes) state and the total (solid curve).[11]

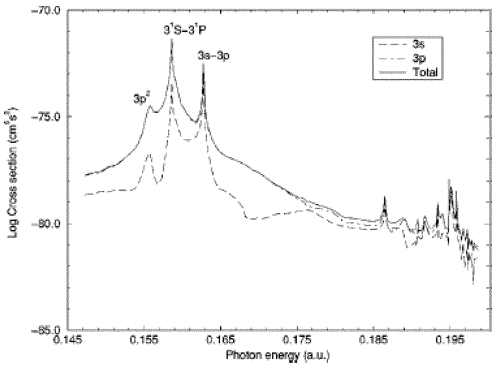

Fig. 10 Cross sections for the three-photon, one-color, above-threshold-ionization of Mg. The ordinate is a logarithmic scale. The dashed curve corresponds to the channel in which the Mg^+ is left in its 3s state; the dash–dot curve, to the final 3p state. The solid curve gives the total cross section. The highest peak corresponds to resonant excitation of the Mg from its ground state to its first excited ^1P state.[12]

two-photon study was the importance of electron correlation in the intermediate state of the process.

In the three-photon studies, we also included a treatment of two-photon ATI with the first excited ^1P state of Mg as the initial state. The comparison of this process with the full three-photon process enables us to identify the effects of coherence of the first, resonant step with later steps. The energy range of the photons in this work was from approximately 3.9 to 6 eV. There are many resonances due to quasi-bound, autoionizing states of doubly-excited magnesium (Fig. 9). Perhaps the most interesting is the excited state in which both valence electrons leave the 3s level. An example of the results from this study is given in Fig. 10. As with the two-photon process, resonances clearly enhance the cross sections for specific channels and thereby, for the total process.

Conclusion

This review of our odyssey into a surprising course of research illustrates how science can function. We may well have a clear view of what we are trying to find and study, even with strong grounds for our expectations. Nevertheless, we are always obliged to carry out even what may seem to be the most obtuse, obvious tests of the validity of how we interpret what we see. Those attempted validations, especially when they *do not* support our expectations, can open altogether new doors and directions for our understanding or for our ways to study natural phenomena. In the story presented here, we set out to observe a process we had every expectation of observing, and instead, found ourselves studying two altogether different processes and introducing a new method to carry out high-resolution studies of collision processes of slow electrons. It has been a lesson in the importance of keeping one's mind open, of being skeptical about one's own work, and especially about being flexible enough to change direction when the evidence tells us we should.

Acknowledgements

The author wishes to acknowledge the absolutely central contributions of his collaborators H. Bachau, Tahllee Baynard, Benjamin Blaney, Scott Darveau, Fernando Martín, Richard Niedziela, Brad Prutzman and Arthur Reber, who made this work happen. The work was supported in part by the National Science Foundation.

References

1 F. C. Fehsenfeld, D. Albritton, J. A. Burt and H. I. Schiff, *Can. J. Chem.*, 1969, **47**, 1793–1795.
2 B. Blaney and R. S. Berry, *Phys. Rev. A*, 1971, **3**(4), 1349–1355.
3 F. Martín and R. S. Berry, *Phys. Rev. A*, 1997, **55**(2), 1099–1107.
4 F. Martín and R. S. Berry, *Phys. Rev. A*, 1997, **55**(6), 4209–4212.
5 F. Martín, M. E. Madjet, P. A. Hervieux, J. Hanssen, M. F. Politis and R. S. Berry, *J. Chem. Phys.*, 1999, **111**(19), 8934–8938.
6 P. Kruit and F. H. Read, *J. Phys. E*, 1983, **16**, 313–324.
7 S. A. Darveau and R. S. Berry, in *Resonance Ionization Spectroscopy '98*, ed. J. C. Vickerman, I. Lyon, N. P. Lockyer and J. L. Parks, American Institute of Physics, College Park, MD, 1998, pp. 253–256.
8 T. Baynard, A. Reber, R. Niedziela, S. Darveau, B. Prutzman and R. S. Berry, Threshold Behavior of Electron-Atom Superelastic Scattering in Magnesium, , 2004, submitted.
9 I. V. Hertel and W. Stoll, *J. Phys. B*, 1974, **7**(5), 583–592.
10 J. J. McClelland, M. H. Kelley and R. J. Celotta, *Phys. Rev. A*, 1989, **40**(5), 2321–2329.
11 A. Reber, F. Martín, H. Bachau and R. S. Berry, *Phys. Rev. A*, 2002, **65**, 63413.
12 A. Reber, F. Martín, H. Bachau and R. S. Berry, *Phys. Rev. A*, 2003, **68**, 63401.

