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Current state of the theory of Penning ionization is reviewed, in terms of the problems currently under consideration, the physical concepts underlying various recent theories, and some of the approaches that appear tractable or desirable for work in the near future.

The Penning ionization process, in which a metastable atom or molecule A^* collides with another atom or molecule B, to leave A unexcited and B^+ as an ion,

$$A^* + B \rightarrow A + B^+ + e \tag{1}$$

is one member of a class of irreversible energy conversion processes in which irreversibility is due to the loss of an electron into its continuum. Others include associative ionization, in which the final state of $(A + B^+)$ is a bound vibrational state rather than a free state of relative translational motion, thus,

$$A^* + B \rightarrow AB^+ + e; \tag{2}$$

chemi-ionization, often used to label the entire set of processes but probably more usefully restricted to processes in which A and B are in states only thermally populated at ordinary temperatures, e.g., ground states:

$$A + B \rightarrow AB^+ + e; \tag{3}$$

associative detachment, the analogue of (2) or (3) with negative ions B^- instead of neutral B's:

$$A^* + B^- \quad \text{or} \quad A + B^- \rightarrow AB + e, \tag{4}$$

and other less common processes such as electron detachment from negative ions in collisions with metastables:

$$A^* + B^- \rightarrow A + B + e. \tag{5}$$

(This last process has been predicted but has not yet been observed (1).) All these can be put under the general heading of Auger ionization process: ionization occurs

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as the result of a loss of energy by some other internal part of the atomic-molecular system.

Three groups of questions arise for the theoretical analyses of Penning and related ionization processes:

(1) How does energy flow to the electron, to enable it to escape? What degree of freedom supplies this energy? From where does the electron leave? What causes the electronic motion to couple with the supplying mode? What selection rules govern this coupling?

(2) How rapidly does the ionization occur? What are the key factors controlling the rate or probability of ionization? What aspects of the phenomenon must be determined accurately in order to understand the phenomenon quantitatively, the potential surfaces, the trajectories, the coupling matrix elements, the wave functions?

(3) How does each model relate to observables? What cross sections, partial, total or differential, can be predicted and measured? (There are at least ten). How is Penning ionization related to other ionization processes?

I make two criticisms of the present state of affairs in this field. First, I charge that the calculation of total ionization cross sections is not an adequate test for any model in this field, at least at the present time. Because the process is an allowed decay, all models give total cross sections falling in the range of about 10–50 Å². Theorists must be willing to calculate other, more constraining properties, such as relative cross sections for various possible final channels, or differential cross sections, or Penning electron energy distributions.

Second, there has been something of a mismatch between the choices of examples for theoretical and experimental investigations of this problem. It would be helpful if a few systems could be selected for study from both approaches. For one, we would like to propose the system He* + Li; there are clearly others comparably attractive. The criteria are clear: the systems must be simple enough to be tractable for theorists, yet accessible enough under laboratory conditions that experimentalists can make meaningful measurements of partial and differential cross sections, not only total ionization cross sections.

No full-blown quantum mechanical theory of Penning ionization has actually been applied nor is it likely that such a theory is required. We seem to be getting a steadily-improving picture, quantitative as well as qualitative, of the Penning process from semi-classical and even highly simplified models. (The only apparent exceptions might be cases in which one particle is a hydrogen atom, such as He* + H. There are predicted quantum phenomena in certain channels of the associative ionization of H* + H, which might be lost in a semiclassical calculation, but it remains to be seen whether these will be observable.) The simplest picture of the Penning process has the colliding particles moving along a classical trajectory determined by the initial relative velocity v and impact parameter b; the probability of ionization, $P(R)$, is a function only of the interparticle distance

R. The ionization cross section $\sigma(v)$ is then

$$\sigma = 2\pi \int_0^\infty b\,db \int_{-\infty}^\infty P(R)\,f(R,\,b,\,v)dR, \tag{1}$$

where $f(R,\,b,\,v)$ is the trajectory term, the probability, per unit length, that a particle trajectory with initial velocity v and impact parameter b will be found within dR of R.

The assumption that $P(R)$ depends only on R contains two other assumptions. Both are probably valid for Penning ionization because the outgoing electron leaves fast relative to times required for significant nuclear motion. One is the adiabatic assumption, that the electrons equilibrate continuously during the collision. The other is the assumption that events along different parts of the trajectory do not generate interference effects.

Another assumption introduced by Cermak and Herman (2) and now made in almost all treatments of Penning ionization is the validity of the Franck–Condon approximation, that the internuclear position *and momentum* of the colliding pair do not change significantly during the ionization event. (One treatment that seems to disregard this approximation is that of Micha, Tang and Muschlitz (3, for experimental data also see 4). Setser and his collaborators have described some Penning processes as violating the Franck–Condon picture, but their usage of this term is slightly different from the one we have just described, and deserves some mention (5, 6). We have described Franck–Condon behavior with respect to the coordinates and momentum of relative motion of the colliding pair. Richardson, Setser, Albritton and Schmeltekopf, for example, in studying collisions of $\mathrm{He}(2^3S)$ and O_2, have compared the vibrational distribution in the product $O_2(A^2\Pi)$ ions with Franck–Condon distribution for the process $O_2(^3\Sigma) + h\nu \rightarrow O_2^+(^2\Pi) + e$. They find that the vibrational and rotational distribution of $O_2^+(A^2\Pi)$ from the Penning process has far more species in excited states than does the Franck–Condon distribution from photoionization. Hence this process does not satisfy the Franck–Condon approximation *with respect to an internal coordinate* of the target. Thus it is important to keep in mind which coordinate one means, when discussing persistence of nuclear position and momentum. We can begin to interpret the non-Franck–Condon behavior in the internal coordinate,[3] but such large deviations might be difficult to explain if they were to be detected for the collision coordinate.

Theories of Penning ionization range from the extremely phenomenological approach of Bell, Dalgarno and Kingston (7) through a variety of microscopic theories based on several formalisms, including the dipole–dipole model (8–12), a critical radius model (13), the optical model (14–16) the semiclassical model

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[3] When $\mathrm{He}(2^3S)$ collides with O_2 to form $O_2^+(A^2\Pi)$, a π-electron is removed from the O_2 and, as the text describes, is probably transferred to the 1s orbital of He. The most probable geometry for this process is $\mathrm{He}\cdots O$, not $\mathrm{He}\cdots O\text{–}O$, because of the spatial distribution of the π-electrons.

$$\begin{array}{c} | \\ O \end{array}$$

Hence it is not surprising that the O_2 molecule receives a torque in this process and leaves with rotational excitation.

(17–20), a trajectory model with a Beutler–Fano resonance (21), and a semi-empirical combination of phenomenology and trajectory calculations (22). Bell's calculation (23) is probably the closest to a full quantum-mechanical treatment, in this case for He(2^3P) + H.

The most phenomenological approach begins with the assumption that Penning ionization cross sections σ_P are proportional to some other cross section. Bell, Dalgarno and Kingston pointed out that if σ_P were proportional to the momentum transfer cross section, σ_P would be independent of temperature T, but if σ_P were proportional to the gas-kinetic cross section, σ_P would vary as $T^{-\frac{1}{3}}$. The difficulty with this approach is that it is not easy to pick out weak temperature dependences from experimental data, and the proportionality factor must be inferred from some other source, such as a microscopic model. Again, this approach has not been used to infer partial or differential cross sections. Olson's phenomenological treatment, based on arbitrary adjustments of the He*–Ar interaction potential, gives a good representation of much of the data on this system, including an apparent inflection or maximum in σ_P as a function of collision energy E, but the results obtained by Howard, Riola, Rundel and Stebbings (24) are apparently not in accord with the model potential.

Microscopic theories can be related back to the classical model in which the probability of ionization $P(R)$ is a function of the interparticle distance R, the relative velocity v, and a lifetime $\Gamma(R)$ equal to $2\pi|V(R)|^2$, where $V(R)$ is the coupling matrix element connecting initial bound and final ionized states:

$$P(R) = 1 - \exp\left[-2\int dR\,\Gamma(R)\hbar^{-1}v(R)^{-1}\right] \qquad (2)$$

Various approximate treatments of $\Gamma(R)$ have included these:

$$\Gamma(R) = Ae^{-aR};$$
$$\Gamma(R) = |f(R)|^2\cos(\phi_i - \phi_f),$$

where ϕ_i and ϕ_f are the semiclassical phases of the initial and final wave functions at R. Such an expression can be put into Eq. (2) and used with the method of stationary phases, or integrated along the trajectory. The dipole–dipole model, applicable when the excited projectile A* can radiate to transform itself into the ground state species, A, when B becomes B$^+$, can be written with $V(R)$ as $\mu_A\mu_B R^{-3}$, where μ_A and μ_B are transition dipole matrix elements that are usually assumed independent of R. This is quite analogous to Förster's model for energy transfer.

More elaborate quantum mechanical models, such as those of Miller et al. (17–19) are based on antisymmetrized wave functions and allow for both direct ionization and "exchange" ionization as indicated by Fig. 1. If the general coupling $V(R)$ indicated by (– – –) is replaced by dipole radiation, in the direct mechanism, one obtains the Förster type of mechanism. The difficulty with the dipole–dipole model is well-known: in Penning ionization, processes involving He(2^3S) have cross sections only slightly smaller than those involving He(2^1S); a dipole–dipole model (which allows some admixture of P states during collision) would make the latter orders of magnitude larger than the former.
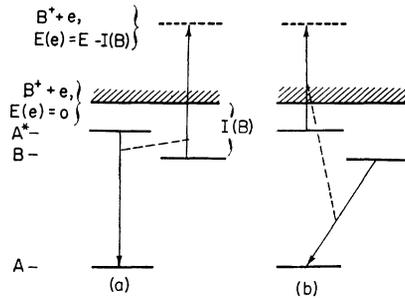
FIG. 1. Schematic representation of Penning ionization mechanisms for A* + B → A + B+ + e. (a) Direct; (b) exchange.

The direct mechanism was the basis of the treatments of Katsuura, Watanabe and Matsuzawa (9–11), Sheldon (12) and of Smirnov and Firsov (8). Hotop and Niehaus pointed out the need for the exchange mechanism (25). The processes $He(2^1S) + H$ and $He(2^3S) + H$ illustrate the difference: in the former case, both the direct and exchange mechanisms are allowed in a compound-state picture in which spin is conserved. In the case of triplet helium, only the exchange mechanism is possible but the direct mechanism is not. We might make a very tentative inference that the difference between the two cross sections, $30.3 \pm 15\% \times 10^{-16}$ cm^2 for $He(2^1S) + H$ and $20.5 \pm 15\%$ for $He(2^3S) + H$ (26) is due to the direct contribution; this would be quite reasonable if the potential curves for both cases were similar up to the region of R in which ionization occurs.

The present state of the theoretical description of Penning ionization is fairly encouraging. The semiclassical trajectory model of Miller (17–19) and the theory developed by Fujii, Nakamura and Mori (16) (but there is an error in the potential for He singlets on H in this work (14–15)) seem capable of giving good total, partial and differential cross sections, provided the input data—the potential surfaces and the coupling matrix element—are accurate. At the present time, it seems that the limitations on the accuracy of the theoretical calculations of the various Penning cross sections are in the accuracy of these quantities. Even where there might be questions about the limitations of the way calculations have been done, as in the case of the stationary phase approximation used by Miller, Slocomb and Schaefer (19), it is quite clear how to go beyond these particular approximations to improve the trajectory calculations, provided that one's surfaces are accurate enough to give reliable trajectories and phases.

The present weakness in the form of unreliable coupling elements is clear in the comparison of the forms of V_{12} found by Bell (23) and by Miller, Slocomb and Schaefer (19) for $He(2^3S) + H(1^2S)$. In both cases, the coupling elements oscillate considerably over the interaction range, but their forms are so different that, if one didn't already know, it might be difficult to recognize that they are supposed to represent the same function!

One question that theorists have worried about relates to the shape of the coupling element. This is the question of the range of R over which transitions are likely to occur. In the case of associative ionization of $H + H^*$, some transitions occur over a broad range of R, and others are confined to very narrow shells (27).

If Penning ionization were to occur in a narrow range, as the Landau–Zener–Stueckelberg model would have it, then the theory could be done more simply than if a broad range of R were involved. When one looks at the form of the coupling matrix elements of Bell or of Miller, Slocomb and Schaefer, one would think that the broad range description would be necessary. However the situation is not really as bleak as that.

From the calculations of Miller, Slocomb and Schaefer, it appears that the lifetime for autoionization of the compound system $|\text{He}(2^3S) + \text{H}(1^2S)|$ is a very sharply increasing function of R. The lifetime is 3×10^{-13} sec when $R = 6$ a.u., and 1.6×10^{-14} sec when $R = 4$ a.u. "Collision times" for this system are typically 10^{-13} sec. Hence any collision with a distance of closest approach less than 4 a.u. will almost certainly lead to Penning ionization, and any collision with a closest approach greater than 5 a.u. is unlikely to produce ionization. Here we are apparently justified in making approximate calculations with a "critical radius" model. MacGregor and I generalized this to a "critical crease" model in treating the process $\text{CH} + \text{O} \rightarrow \text{HCO}^+ + e$ (26).

The coupling operator $V(R)$ is usually assumed to be electron–electron interaction. Strictly, this usually implies that the zero-order states that define the channels are diabatic approximate states, not adiabatic approximate states, in the transition region, in the sense that the full adiabatic, electronic Hamiltonian for fixed R is nondiagonal for such basis functions (29). The channel-defining functions are usually taken to correspond to an intuitively appealing physical situation that we would like to think is nearly capable of persisting through the transition region. Typically, a single electronic configuration may define each channel, for purposes of a computation. If one works with a representation fully diagonal in the adiabatic Hamiltonian at all R, the coupling to the electronic continuum via electron–electron interaction is automatically included in a single channel.

One can conjecture that as A* and B approach, the highest occupied orbital of A* might approach the ionization limit of the compound (AB)* system and pass adiabatically into the continuum. Mulliken has pointed out (30) that some excited state orbitals of simple diatomics, such as BH, are valence-like for large internuclear distances and Rydberg-like for smaller R, and that the binding energies of these so-called "semi-Rydberg" orbitals grow smaller as R decreases. Whether any such orbitals can approach the continuum is not known. One could imagine such "adiabatic shedding" to be observable as a form of associative or Penning ionization in which an inner electron goes from B to A via a continuously changing molecular orbital.

Mary Baldacchino-Dolan[4] has examined the system He* + Li for possible adiabatic shedding. Although the $2s$ orbital of He becomes Rydberg-like at small R, it remains a bound molecular Rydberg orbital even at fairly small R (1.5 bohr).

The kinetic energy distribution of Penning electrons has been used by Hotop and Niehaus to infer shapes of potential curves (31). This analysis has its origins

[4] M. Baldacchino-Dolan, private communication. (Preliminary results were presented by this writer at the Symposium.)

in the application of the Franck–Condon approximation. As it has been used, one can either infer the probability $P(R)$ if the upper and lower potential curves are known, or, if one assumes a form for $P(R)$, one can infer the shape of an unknown upper state potential. We can make reasonable assumptions about the form of the electronic coupling between states, but we should recognize that the equivalent of a density-of-states factor also appears, which takes the form of a denominator factor $|d[V_{\text{final}}(R) - V_{\text{initial}}(R)]/dR|$ in the Landau–Zener model. This density of states *may* not play an important role in determining $P(R)$, but we must be aware of its existence.

An area that is beginning to challenge theorists now is the determination of the angular distribution of Penning electrons, stimulated by the measurements of Hotop and Niehaus (32). The results for $He(2^1S)$ and $He(2^3S)$ on H_2 indicate "backward" peaking of the Penning electrons—the electrons go in the direction of the He source, more so in the case of triplet He* than with singlet He*. A simple shadow model with a critical radius R_0 (see appendix) gives an angular distribution qualitatively consistent with this picture: $d\sigma_P/d\theta = (\frac{1}{2})\pi R_0^2 (1 - \cos \theta)$. That the differential cross section for $He(2^1S)$ is flatter than that for $He(2^3S)$ might be taken to suggest that the exchange process follows a shadow model, being rather short-range, and that the direct process might give a more nearly isotropic distribution of Penning electrons, as a result of its longer interaction range. One might be cautious about the use of a shadow model because of the diffraction of the outgoing electron by the two scattering heavy particles. Indeed, if one looked only at the calculations of Bell and of Fujii, Nakamura and Mori, in which only the first two partial waves, $l = 0$ and $l = 1$, were included, one would discard the shadow model entirely. However, the calculations of Miller, Slocomb and Schaefer show that partial waves up through $l = 6$ contribute to the outgoing wave for $He(2^3S) + H$, which is certainly enough to explain why a shadow model works reasonably well for this problem.

In conclusion, let me summarize and reiterate a plea. The adiabatic semiclassical theory of Penning ionization is apparently going to be reasonably good for quantitative results, provided we obtain good potentials and coupling functions. Cruder models based on sharp cutoffs and critical radii give reasonably good estimates for cross sections because transition probabilities for ionization are sharply decreasing functions of internuclear distances. When we come to polyatomic systems, we shall have to worry much more about finding the fraction of trajectories that reach reactive parts of the potential surfaces than about the exact form of the coupling functions. It is especially important now for experimentalists and theorists to concentrate on determining many partial and differential cross sections of a few, well-selected systems, if we are to be able to evaluate our apparent understanding of the Penning ionization process.

APPENDIX: A SHADOW MODEL

We suppose the incoming metastable particle is a point traveling in the z direction, with respect to which θ is measured. When the metastable reaches a distance R_0 from the center of the target, an outgoing wave leaves from the point of con-

tact. This wave is assumed, in this model, to be hemispherical, going outward from the tangent plane at the point of contact. No diffraction effects are included at all. Each unit of solid angle receives its intensity from a portion of the sphere whose projected area is the difference between a semicircle of area $\pi R_0^2/2$, and a semi-ellipse of area $(\pi R_0^2 \cos \theta)/2$, so that the point at $\theta = \pi$ receives intensity from the full back hemisphere of the target. Each scattering point on the target contributes $(2\pi)^{-1}$ of its flux to each unit solid angle it "sees"; this factor just cancels the 2π from integration over ϕ, so that $d\sigma_P/d\theta = \frac{1}{2}\pi R_0^2(1 - \cos \theta)$.

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