Electron Scattering Spectroscopy

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1 Introduction

In electron scattering spectroscopy, transitions between molecular energy states are induced by bombardment of the target species with free electrons. This kind of spectroscopy has several advantages over conventional spectroscopy. It is relatively easily applied to transitions in the vacuum ultraviolet region of the spectrum, an experimentally difficult region, optically; it picks up optically forbidden transitions; it can detect weak transitions underlying strong absorption bands; and it allows measurement of electron affinities of excited-state as well as ground-state species. It does, of course, have disadvantages which account for the fact that such an apparently versatile tool has not been more widely applied in chemistry. Experimental techniques, especially for handling electrons of low energy (the most chemically interesting region) are difficult—each electron spectroscopist would appear to have his own recipe for success. Added to this, it is essentially a low-resolution method; while the practical limit to resolution may be $\sim$ 1 meV, 'working' resolutions are still at best *ca.* 30—50 meV (250—400 cm^{-1}). However, these limitations are being overcome and the volume of published work in electron spectroscopy is increasing rapidly. Indicative of its growing importance is the recent appearance of several excellent review articles written by leading workers in the field. Lassettre[1] has described inelastic scattering of electrons by atmospheric gases with emphasis on the relation to optical excitation processes. Berry[2] and Brion[3] give comprehensive literature surveys, between them covering the literature up to about 1971. Trajmar *et al.*[4] detail some of their own experiments. Dillon's article[5] includes useful theoretical relationships and experimental detail.

This present Review is directed specifically at chemists, its purpose being to identify, for the non-specialist, the unique features of the method. Its applications to systems of chemical interest are illustrated through two particular processes, namely the excitation of forbidden electronic transitions and the formation of short-lived negative ions.

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[1] E. N. Lassettre, *Canad. J. Chem.*, 1969, **47**, 1733.
[2] R. S. Berry, *Ann. Rev. Phys. Chem.*, 1969, **20**, 357.
[3] C. E. Brion, in 'Mass Spectrometry', ed. A. Maccoll (MTP International Review of Science), Physical Chemistry, Series 1, Vol. 5, Butterworths, London, 1972, p. 55.
[4] S. Trajmar, J. K. Rice, and A. Kuppermann, *Adv. Chem. Phys.*, 1970, **18**, 15.
[5] M. A. Dillon, 'Creation and Detection of the Excited State', ed. A. A. Lamola, Marcel Dekker, New York, 1971, Vol. 1, Part B, p. 357.

2 Basic Concepts

In a typical electron scattering experiment (Figure) a molecular beam is crossed by a beam of monoenergetic electrons. Scattered electrons are collected and their intensity is measured as a function of incident electron energy E_i, final energy E_f, and scattering angle θ. Electrons which are scattered inelastically must have excited internal energy states of the molecule and so, for these, $\Delta E = E_i - E_f$ can be equated with a molecular transition energy.

The intensity of a transition, say to the nth energy level, is measured as a cross-section Q_n, the electron analogue of extinction coefficient. Q_n is the probability that an electron will excite that particular transition in travelling unit distance through the gas at unit number density. The total collision cross-section Q, the probability of any transition occurring under these conditions, is

$$Q = \Sigma Q_n + Q_{el} \tag{1}$$

where Q_{el} is the elastic scattering cross-section. Scattering need not be isotropic, so θ is an important experimental parameter and a differential cross-section σ_n must be defined. This gives the probability that an electron will be scattered into the solid angle $d\Omega = \sin\theta d\theta d\phi$, where ϕ is the azimuthal scattering angle. It follows that

$$Q_n = \int_0^{2\pi}\int_0^{\pi} \sigma_n \sin\theta d\theta d\phi \tag{2}$$

Also, by analogy with the Beer Law, transmitted electron current I_t and incident current I_0 are related by

$$I_t = I_0 \exp(-nQl) \tag{3}$$

where n is the molecule number density and l the path length.

3 Theoretical Considerations

A. General.—In the quantum theory of scattering, the incident electron beam is described as a plane wave, wavelength $\lambda = 2\pi/k$, where k is the wavenumber. The angular momentum, J, of any wave about the scatterer is quantized and given by

$$J = \hbar[l(l + 1)]^{\frac{1}{2}} \tag{4}$$

where $l = 0, 1, \ldots$. Following spectroscopic notation, a wave for which $l = 0$ is an s-wave, one for which $l = 1$ is a p-wave, and so on. In quantum theory, the effect of a scatterer on the electron is to introduce a phase shift η_l into each wave-train. Cross-sections are expressed in terms of these phase shifts. At low electron energies,

$$\sigma = \frac{1}{4k^2}\left|\Sigma(2l + 1)\{\exp(2i\,\eta_l) - 1\}\, P_l(\cos\theta)\right|^2 \tag{5}$$

$$Q = \frac{1}{k^2}\,\Sigma \sin^2 \eta_l \qquad (6)$$

The summations are over all the partial waves that 'see' the molecule. $P_l(\cos\theta)$ is the Legendre polynomial; this term describes the angular distribution of scattered electrons.

B. The Born Approximation.—The theoretical problem is the calculation of phase shifts in real situations. This has been sorted out satisfactorily only for electrons of high energy. For these, perturbation theory which assumes that the phase shifts are small is applicable. Briefly, in this, the Born approximation, the electron–molecule interaction is taken as the Coulomb interaction between incident and bound electrons. Cross-sections are then expressed in terms of a transition matrix, ϵ:

$$\epsilon = \langle \psi_0 | \Sigma \exp(\mathrm{i}\boldsymbol{K}_n \cdot \boldsymbol{r}_s) | \psi_n \rangle \qquad (7)$$

The differential cross-section for excitation to the nth excited state is, in atomic units

$$\sigma_n = \frac{4k_f \epsilon\epsilon^*}{k_i K_n^4} \qquad (8)$$

$\hbar k_f$ and $\hbar k_i$ are the momenta of scattered and incident electrons respectively; $\mathbf{K}_n = \mathbf{k}_i - \mathbf{k}_f$, *i.e.* $K_n^2 = k_i^2 + k_f^2 - 2k_i k_f \cos\theta$; $\boldsymbol{r}_s$ is the co-ordinate of the sth bound electron. The matrix element has been related to optical properties through expansion of ϵ in powers of K_n:

$$\epsilon = \sum \frac{K_n^l (\mathrm{i})^l}{l!}\,\epsilon_l \qquad (9)$$

Truncating the expansion after the first few terms,

$$\epsilon\epsilon^* = K_n^2 \epsilon_1^2 + K_n^4[\tfrac{1}{4}\epsilon_2^2 - \tfrac{1}{3}\epsilon_1\epsilon_3] \qquad (10)$$

In fact, ϵ_1 is the matrix element of the electric dipole moment and ϵ_2 has been equated with the electric quadrupole moment matrix element.[1,5] That is, for electric dipole-allowed transitions, $\epsilon_1 \neq 0$, while for electric quadrupole-allowed transitions $\epsilon_1 = 0$ and $\epsilon_2 \neq 0$. Expressions for excitation of dipole-allowed (σ_d) and quadrupole-allowed (σ_q) transitions are obtained by making the appropriate substitutions in equation (8). Thus, for a transition in which the electron energy loss is W and where $\bar{E}$ is the median energy, $\bar{E} = (E_i + E_f)/2$, in forward scattering,

$$\sigma_d = \frac{8k_f \bar{E}}{k_i W^2}\,\epsilon_1^2 \qquad (11)$$

$$\sigma_q = \frac{k_f}{k_i}\,\epsilon_2^2 \qquad (12)$$

Further, in the Born approximation, the differential cross-section for triplet excitation through electron exchange is given by σ_{T},

$$\sigma_{\mathrm{T}} = \frac{4C^2k_f}{k_i^5}\,\epsilon\epsilon^* \tag{13}$$

where C is a constant.

Equations (8), (11), (12), and (13) show that (i) as the incident electron energy is reduced, the intensity of a quadrupole-allowed transition increases relative to that of a dipole-allowed transition and (ii) for spin-forbidden transitions, the scattered electron intensity increases with decreasing electron energy and increasing scattering angle. One other important result follows in the Born approximation: for any transition, the relative differential cross-sections for excitation of different vibrational levels do not vary with incident electron energy or scattering angle.

C. Generalized Oscillator Strength.—The interpretation of an electron energy-loss spectrum in relation to the above theoretical expressions is facilitated by use of the generalized oscillator strength, f_n. For a transition of energy loss W, this is defined as[1,5]

$$f_n = 2W\epsilon\epsilon^*/K_n^2 \tag{14}$$

or

$$f_n = (W/2)\,(k_i/k_f)K_n^2\sigma_n \tag{15}$$

Ideally, all parameters on the right-hand side of equation (15) are measurable, so for a transition f_n may be obtained as a function of K_n^2 and this used to give information on its transition matrix. Lassettre[1] has described how f_n measurements lead to assignments for forbidden transitions in molecules.

The generalized oscillator strength has a property which may be valuable for the testing of molecular wavefunctions. For Rydberg excited states, a plot of f_n against K_n^2 shows a minimum; this minimum is associated with a node in the orbitals of the electron which is excited and so is not apparent in valence-shell transitions. This characteristic Rydberg minimum seems to be present in the so-called V state of ethylene,[6] although this particular state does not show other properties associated with Rydberg states, *e.g.* it does not change in shape and position when the molecule is put into the condensed phase.[7] These somewhat contradictory observations support the theoretical conclusions that the V state is not, as is usually written, $\pi\pi^*$, but includes contributions from other configurations. The pure $\pi\pi^*$ state is Rydberg-like and lies significantly above 7.6 eV, where the V state is.[7]

One more interesting aspect of the generalized oscillator strength may be mentioned. The following relationship for singlet–triplet energy differences has been derived:[8]

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[6] K. J. Miller, S. R. Mielczarek, and M. Krauss, *J. Chem. Phys.*, 1969, **51**, 26.

[7] R. S. Mulliken, *Chem. Phys. Letters*, 1974, **25**, 305.

[8] E. N. Lassettre and M. A. Dillon, *J. Chem. Phys.*, 1973, **59**, 4778.

$$E_S - E_T = (\pi g W)^{-1} \int_0^\infty K_n^2 f_n \mathrm{d}K \qquad (16)$$

W is the excitation energy to the singlet excited state, g is its degeneracy, and f_n its generalized oscillator strength. This equation, applicable where the Born approximation is valid, has been tested for several states in helium and carbon monoxide for which both ($E_S - E_T$) and f_n are known. It offers the intriguing prospect of positioning a triplet state from experimental measurements on the corresponding singlet at high electron energies.

D. Scattering of Low-energy Electrons.—As the energy of the incident electron is reduced, so it has time to associate more intimately with the molecule and the interaction is no longer a small perturbation; the Born approximation does not apply. In fact, no single theory is available for low-energy electron scattering and our understanding of the collision processes comes mainly from experiments. However, these have demonstrated that the conclusions of the Born approximation may be extrapolated to low energies where the theory is no longer valid and, in general, (i) high-energy electrons are scattered predominantly in the forward direction with excitation of optically allowed transitions, (ii) symmetry-forbidden transitions are best sought at intermediate electron energies (30—100 eV) and large scattering angles to avoid swamping by allowed transitions, (iii) for spin-forbidden transitions, cross-sections maximize within a few eV of threshold and large-angle scattering is apparent, and (iv) the ratios of the differential cross-sections for members of a single progression are roughly constant with θ and E_i and equal the ratios of the Franck–Condon factors. This last point is an important one which has no parallel in photon absorption. If, in an allowed transition, relative peak intensities change from the Franck–Condon factors as E_i or θ is varied, then one must suspect contributions from an underlying transition.

4 Experimental

A. Energy-loss Spectrometers.—A successful electron scattering spectrometer must incorporate a high-resolution monochromator and electron energy analyser (Figure). These normally involve passage of the electrons through electrostatic and/or magnetic fields, tuned to transmit only electrons of a narrow energy range.[4,5] The most popular instruments are the 180° concentric-sphere deflector and the 127° coaxial-cylinder deflector, both electrostatic devices. A useful spectrometer employs one of these as monochromator with an identical post-collision analyser. These must be used in conjunction with electron lenses which (i) ensure that the energy-selected incident beam is parallel over a wide range of energies and (ii) focus scattered electrons into the analyser. The publication of calculated parameters for suitable lenses has made easier the design of spectrometers of predetermined properties. In the spectrometer, the electron beam may be crossed with a molecular beam and the analyser tuned to scan ΔE. The resulting energy-loss spectrum of scattered intensity against energy loss for fixed E_i is analogous to a Raman spectrum. Alternatively, the analyser is set to a fixed ΔE and scattered intensity recorded as a function of incident energy. This traces the excitation function of a single transition. Other operational modes are possible.

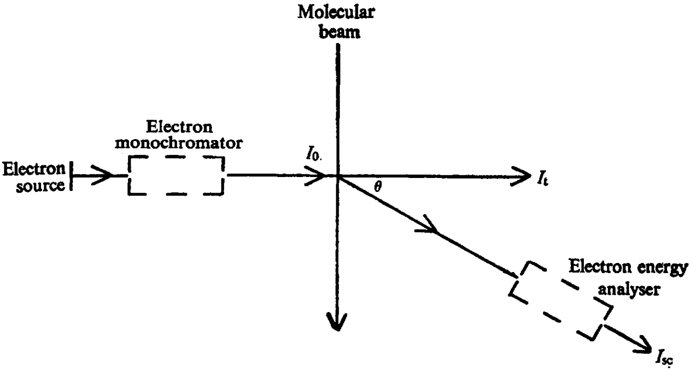

Figure *Schematic diagram of a typical electron energy-loss spectrometer. The incident electron beam is energy-selected in a suitable monochromator. The monochromatic beam, energy* E_i, *crosses a molecular beam.* I_0 *is the intensity of the incident beam,* I_t *is the intensity of the transmitted (unscattered) electron beam, and* I_{sc} *the intensity of electrons scattered through angle* θ. *The energy of the scattered electrons is* E_f *and this is determined in the energy analyser*

B. Threshold Energy-loss Spectrometer.—In a threshold energy-loss spectrum only scattered electrons with near-zero energy are collected. Then, scattered current against E_i gives a spectrum comparable to a conventional optical spectrum in that energy loss equals incident energy. Its value in chemistry lies in the fact that spin-forbidden transitions are frequently strongly excited at threshold energies (Section 3D). The experiment may be performed by adding to the target gas a small amount of a scavenger molecule which attaches zero-energy electrons. SF_6 is a suitable scavenger; with it, a spectrum is obtained by collection of SF_6^- as a function of E_i. An alternative and more widely used technique employs the so-called electron trap. In this, the collision region incorporates a shallow potential well, such that electrons whose energy is less than the well-depth are retained in the well and eventually migrate to the scattered-electron collector. The trapping procedure requires a strong magnetic field in the direction of the incident beam so that, as happens in the electron-scavenger experiment, all angular discrimination is lost. However, the trap does have advantages over the scavenger experiment in that it can identify transitions excited *via* transient negative-ion intermediates (see Section 6) and a modification to the simple trap has been described which allows measurement of excitation functions to a few eV above threshold without loss of resolution.[9] The trap must

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[9] F. W. E. Knoop, H. H. Brongersma, and A. J. H. Boerboom, *Chem. Phys. Letters*, 1970, **5**, 450.

be used with a monochromator which functions in the presence of the axial magnetic field, and retarding potential difference techniques have been most frequently used for energy selection. Recently, a trap has been employed together with a trochoidal electron monochromator, a device which selects energy through the combined action of crossed electric and magnetic fields. In this combination, the magnetic field 'contains' the very low-energy electrons so it can be operated from zero-incident energy upwards.[10]

5 Applications—Excitation of Forbidden Transitions

Ethylene is a prototype for larger unsaturated molecules, so its low-lying electronic states are important both experimentally and theoretically. U.v. spectra and excited states of ethylene and its alkyl derivatives have been treated in a review.[11] The lowest excited state of the mono-olefins, the *T* state ($\pi \rightarrow \pi^*$) is strongly excited in electron impact at near-threshold energies, and this affords a relatively simple means of positioning it. The Table gives some results taken from threshold energy-loss spectra.[12] Triplets other than the *T* state have not yet been unambiguously located. The first Rydberg state of ethylene, the *R* state ($\pi \rightarrow 3s$) lies at 7.28 eV onset energy. Two groups of workers find that, in electron impact, the relative intensities of the vibrational progression of this state depart from that seen optically, suggesting an underlying forbidden transition at *ca.* 7.5 eV.[4,13]

Table. *Position of the T state and the ground-state resonance in some olefins. The energy, in* eV, *refers to the position of maximum intensity*

Molecule	*T State* *Electron impact*[12]	*u.v.*[11]	*Shape resonance*
$CH_2{=}CH_2$	4.2	4.6	1.87
$MeCH{=}CH_2$	4.35	4.2	2.2
$EtCH{=}CH_2$	4.25		2.0
cis-MeCH=CHMe	4.3		2.3
trans-MeCH=CHMe	4.4	4.1	2.4
$Me_2C{=}CHMe$	4.2	3.7	2.3
$Me_2C{=}CMe_2$	4.1	3.65	2.0

The only direct experimental information on the triplet manifold of acetylene comes from electron scattering experiments. Transitions at 5.2 and 6.1 eV have differential cross-sections characteristic of spin-forbidden transitions and so have been assigned to triplet levels.[4] These transitions are also seen in threshold excitation spectra which further reveal, at 8.0 eV, a state which is absent from the u.v. spectrum.[14] This has been assigned as a third triplet, probably that

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[10] A. Stamatovic and G. J. Schulz, *Rev. Sci. Instr.*, 1970, **41**, 423.

[11] A. J. Merer and R. S. Mulliken, *Chem. Rev.*, 1969, **69**, 639.

[12] D. F. Dance and I. C. Walker, *Proc. Roy. Soc.*, 1973, **A334**, 259.

[13] E. N. Lassettre, A. Skerbele, M. A. Dillon, and K. J. Ross, *J. Chem. Phys.*, 1968, **48**, 5066.

[14] D. F. Dance and I. C. Walker, *J.C.S. Faraday II*, 1974, **70**, 1426.

corresponding to the $\tilde{C}(^1\Pi)$ state, the first Rydberg excited state. Calculations support this assignment.[15] A discrepancy in the relative intensities of the vibrational progression of this $\tilde{C}$ state indicates an underlying spin-forbidden transition at 8.37 eV.[4] The energy-loss spectrum for 40 eV electrons shows structure between 6.35 and 7.25 eV which has been ascribed to two hitherto unknown states, the one at 6.35—6.79 eV being linear and weakly allowed and the other at 6.70—7.25 eV being bent.[13] In no alkyl-substituted acetylene is a triplet below *ca.* 5 eV apparent.[14]

Electron impact has helped to establish that the two lowest triplets of butadiene lie at 3.2 and 4.9 eV respectively.[16] Calculated positions agree with these and confirm the interpretation of these as pure valence excited states.[17] In 1,3,5-*trans*-hexatriene the triplets appear at 2.6 and 4.2 eV.[18]

Excitation of a π electron in benzene to the lowest π^* orbital gives states of symmetry B_{2u}, B_{1u}, and E_{1u}. The spin-allowed transitions to $\tilde{A}\,^1B_{2u}(S_1)$, $\tilde{B}\,^1B_{1u}(S_2)$, and $\tilde{C}\,^1E_{1u}(S_3)$ are at 5.0, 6.1, and 7.0 eV respectively. For 50 eV electrons, the relative intensities of the $\tilde{B}\,^1B_{1u}$ progression change with angle, suggesting an underlying transition. It was originally suggested that this might be a valence transition to the $^1E_{2g}$ state (S_4), but this is not in accord with calculations which invariably place S_4 at a higher energy than S_3.[19] Electron scattering locates the lowest triplets, $\tilde{a}\,^3B_{1u}$ and $\tilde{b}\,^3E_{1u}$, at 3.9 and 4.7 eV respectively. The third triplet, $\tilde{c}\,^3B_{2u}$, is probably at 5.6 eV.[20,21]

The interpretation of the u.v. spectra of carbonyl compounds is complicated by the overlap of Rydberg with valence excited states. Electron scattering work can extract Rydberg series and this should help in calculations on excited states.[22] The forbidden $n \rightarrow \pi^*$ triplets are excited at threshold.[23] Work on the 'parent' molecule CO_2 has unravelled an energy-loss spectrum to find transitions consistent with excitation of $^3\Sigma_u^+$, $^{1,3}\Pi^-$, $^{1,3}\Sigma_u^-$, and $^{1,3}\Delta_u$ states between 7 and 10 eV.[24] All these are absent from the u.v. spectrum.

Some interesting problems have arisen as a result of electron scattering studies on water. In water, the $OH(^2\Pi) + H(^2S)$ dissociation limit lies at 5.11 eV relative to the ground state while the $O(^3P) + H_2(^1\Sigma_g^+)$ limit is at 5.03 eV. Singlet states excited in the u.v., starting with the $\tilde{A}$ state (onset 6.66 eV, vertical transition energy 7.5 eV), are Rydberg-like. A dipole-forbidden, quadrupole-allowed transition to the $^1A_2$ state is expected between the $\tilde{A}$ and $\tilde{B}$ states but has not yet been observed. The optical spectrum is reproduced in electron

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[15] D. Demoulin and M. Jungen, *Theor. Chim. Acta*, 1974, **34**, 1.

[16] O. A. Mosher, W. M. Flicker, and A. Kuppermann, *J. Chem. Phys.*, 1973, **59**, 6502.

[17] T. H. Dunning, R. P. Hostenny, and I. Shavitt, *J. Amer. Chem. Soc.*, 1973, **95**, 5067.

[18] F. W. E. Knoop and L. J. Oosterhoff, *Chem. Phys. Letters*, 1973, **22**, 247.

[19] P. J. Hay and I. Shavitt, *Chem. Phys. Letters*, 1973, **22**, 33.

[20] F. W. E. Knoop, 'Excited States of Atoms and Molecules', Ph.D. Thesis, Leiden, 1972.

[21] J. P. Doering, *J. Chem. Phys.*, 1969, **51**, 2866.

[22] R. H. Huebner, R. J. Celotta, S. R. Mielczarek, and C. E. Kuyatt, *J. Chem. Phys.*, 1973, **59**, 5434.

[23] W. T. Naff, R. N. Compton, and C. D. Cooper, *J. Chem. Phys.*, 1972, **57**, 1303.

[24] R. I. Hall, A. Chutjian, and S. Trajmar, *J. Phys.* (*B.*), 1973, **6**, L264.

impact at high incident energies. At lower energies, additional features emerge. A very weak energy loss, at 4.5 eV, has been reported by several independent groups of workers.[25] Experimentalists like to assign it $\tilde{a}^3B_1$. This implies a bound triplet state. However, no calculation has produced an appropriate attractive potential for the $^3B_1$ state and the consensus of opinion among theoreticians is that the lowest triplet state of water is dissociative.[26] A transition at 7.2 eV, detected in a threshold excitation experiment, is nearer to the predicted $^3B_1$ position.[27] An additional weak transition at *ca.* 9.2 eV, seen in an electron trap, may be another triplet or the quadrupole-allowed $^1A_2$ state.[27] The differential cross-section of a transition at 9.81 eV suggests a spin-forbidden transition and it has been assigned to the triplet corresponding to the $\tilde{D}$ state at 10.17 eV.[25,26] Clearly, more work is called for to identify the 4.5 eV energy-loss process, should it prove real, and to locate the $^1A_2$ state and low-lying triplets.

Very weak features resembling the 4.5 eV feature in water have been reported for methanol[27] (4.4 eV), dimethyl ether[20] (4.5 eV), and ammonia[28] (4.4 eV). All these were seen in threshold excitation spectra and interpreted as triplets.

Results have been reported for a number of other chemically interesting species. The threshold excitation spectrum of azulene is dominated by a structured peak at 2.44 eV.[29] Several triplet states are calculated to lie in this region. Low-lying triplets have been assigned in a number of nitrogen-containing ring compounds.[30]

Energy-loss processes experienced by slow electrons transmitted through or reflected from thin molecular films at low temperatures have been interpreted in terms of electronic excitation, including excitation of forbidden transitions.[31] However, it has been pointed out that the analysis of the experimental measurements in these studies is not straightforward and correlation of an apparent energy-loss peak with a transition in the sample molecule may be erroneous[32].

6 Electron–Molecule Resonances (Temporary Negative Ions)

A negative ion in the gas phase, if it is to be detected, must survive for some microseconds. Such an ion is formed by attachment of an electron to a molecule which has a positive electron affinity, normally in its ground electronic state. The existence of more ephemeral negative ions, lifetimes 10^{-12}—10^{-15} s, has been demonstrated in electron scattering experiments. These negative ions, more commonly called electron–molecule resonances, are formed when the incident electron finds itself with just the right energy to be accommodated temporarily in an orbital of the target molecule. The molecule can be in its ground or an excited state. The resonance may lie above or below the parent electronic state.

[25] S. Trajmar, W. Williams, and A. Kuppermann, *J. Chem. Phys.*, 1973, **58**, 2521.
[26] W. A. Goddard and W. J. Hunt, *Chem. Phys. Letters*, 1974, **24**, 464.
[27] F. W. E. Knoop, H. H. Brongersma, and L. J. Oosterhoff, *Chem. Phys. Letters*, 1972, **13**, 20.
[28] R. N. Compton, J. A. Stockdale, and P. W. Reinhardt, *Phys. Rev.*, 1969, **180**, 111.
[29] R. H. Huebner, W. F. Frey, and R. N. Compton, *Chem. Phys. Letters*, 1973, **23**, 587.
[30] M. N. Pisanias, L. G. Christophorou, J. G. Carter, and D. L. McCorkle, *J. Chem. Phys.*, 1973, **58**, 2110.
[31] K. Hiraoka and W. H. Hamill, *J. Chem. Phys.*, 1973, **59**, 5749.
[32] M. E. Harrigan and H. T. Lee, *J. Chem. Phys.*, 1974, **60**, 4909.

In the former case it is classified a shape resonance—so called because the shape of the 'effective' molecular potential is responsible for trapping the electron; in the latter case it is a Feshbach resonance. (The nomenclature is taken from nuclear physics.) A species whose ground state has a negative electron affinity may possess excited states with positive electron affinities. Rydberg excited states frequently support bound resonances. These bound (Feshbach) resonances have lifetimes of 10^{-12}—10^{-13} s and so have time to vibrate. Shape resonances tend to have shorter lifetimes and while some survive sufficiently long to have well-defined vibrational structure, others are broad (width $\Gamma = \hbar/\tau$, where τ is lifetime) and structureless.

The identification and positioning of resonances is clearly of intrinsic interest. In addition, resonances provide important routes for the excitation of molecules by electrons, for a resonance may decay to a lower-lying molecular state and a free electron:

$$M + e_1 \rightarrow M^- \rightarrow M^* + e_2 \qquad (17)$$

Shape resonances prefer to decay to the parent molecular state. The enhancement of the inelastic cross-section for this state, at the resonance energy, may provide the only means of detecting a short-lived resonance. For long-lived resonances, the existence of a resonance phase shift η_{lr} in an electron wave [equations (5) and (6)] leads to rapid variations in the total collision cross-section at the resonance energy. So, such a resonance is detectable in the total collision cross-section through fine structure whose spacing equals the vibrational spacing of the negative ion. For a short-lived resonance, the corresponding structure is broad and not distinguishable from that due to simple potential scattering.

If scattering is predominately *via* a single resonance state, only one phase shift η_{lr} contributes to the cross-section at the resonance energy. Its l value may sometimes be deduced from measurement of the angular distribution of the scattered electrons, through the $P_l(\cos\theta)$ term of equation (5). This facilitates identification of the electron configuration of the resonance.[33]

A resonant intermediate may also decay with dissociative attachment into a neutral species and a conventional negative ion:

$$AB^- \rightarrow A + B^- \qquad (18)$$

Most electron-impact dissociative processes may be understood completely in terms of the resonance intermediate model.

The importance of resonances in electron–molecule collision interactions was first recognized by Schulz and the best work in molecular resonance spectroscopy has emanated from his laboratory.[34] A recent comprehensive review details results for several diatomic molecules.[35]

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[33] F. H. Read, *J. Phys.* (*B.*), 1968, **2**, 893.

[34] L. Sanche and G. J. Schulz, *J. Chem. Phys.*, 1973, **58**, 479.

[35] G. J. Schulz, *Rev. Mod. Phys.*, 1973, **45**, 423.

7 Resonances in Polyatomic Molecules

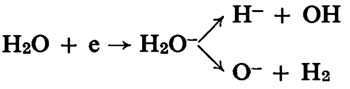
Shape resonances associated with the ground electronic state are widespread in molecules. The Table (p. 473) lists the positions of such shape resonances in some mono-olefins.[12] These arise from accommodation of the extra electron in the π^* molecular orbital. Ethylene itself also shows a bound resonance. Its parent is the first Rydberg excited state, the *R* state, which has a positive electron affinity of *ca.* 0.5 eV. This resonance comprises two electrons in the $3s\ a_{1g}$ Rydberg orbital, bound by the field of the ground-state positive ion, $C_2H_4^+$. Its average vibrational spacing is 165 ± 5 meV, probably associated with C–C symmetric stretching vibrations of the negative ion.[34] It has been observed that many Rydberg states derived from $3s$ orbitals in atoms and diatomic molecules have an electron affinity of *ca.* 0.5 eV.[34] Bound resonances have not been detected in any alkyl-substituted ethylenes.[12]

Acetylene has a shape resonance at ~ 1.7 eV formed by trapping of an electron in the π^* orbital of the ground-state molecule. This resonance shifts to higher energies on substitution of the acetylenic hydrogen by alkyl groups. In propyne it is at 3.0 eV, in but-1-yne at 2.8 eV, and in but-2-yne at 3.6 eV. The lowest Rydberg state of acetylene supports a bound negative ion.[14]

The benzene shape resonance, benzene plus a π^* electron, is at 1.1 eV; its vibrational spacing is *ca.* 127 meV. Some broad structure in the total collision cross-section of benzene at 4—6 eV has been interpreted in terms of a second ground-state shape resonance where the electron occupies the highest unfilled π^* orbital.[34] The degeneracy of the two lowest π^* orbitals of benzene is removed on replacement of CH by N, so that pyridine has two closely spaced low-lying resonances at 0.8 and 1.3 eV, arising from trapping of the electron in each of these two orbitals.[36] Similar double resonances are apparent in other N-heterocyclic molecules.[30] This kind of experimental information should help in calculations on the effect of N-incorporation into aromatic rings.

Carbonyl compounds have shape resonances close to the ground-state shape resonance of carbon monoxide at 1.7 eV; these are: acetone (1.6 eV), acetaldehyde (1.2 eV), acetophenone (0.95 eV), benzophenone (0.75 eV), and benzaldehyde (0.72 eV).[23]

Water displays a number of resonances.[34] Two negative ions between 9 and 12 eV survive sufficiently long to have vibrational structure. They are Feshbach resonances, perhaps belonging to the $\tilde{D}$ and $\tilde{F}$ excited states. Dissociation leading to $H^- + OH$ and $O^- + H_2$ is caused by electrons of *ca.* 6.5 and 8.8 eV energy.



$$H_2O + e \rightarrow H_2O^- \begin{cases} \nearrow H^- + OH \\ \searrow O^- + H_2 \end{cases} \tag{19}$$

The negative ion intermediates are repulsive and have not been positively identified. A ground-state shape resonance has not been explicitly observed in water, probably because it is too short-lived. Calculations indicate that the

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[36] R. H. Huebner, R. N. Compton, and H. C, Schweingler, *Chem. Phys. Letters*, 1968, **2**, 407.

lowest H_2O^- state ($^2A_1$) is attractive in the Franck–Condon region along both the H–OH and O–H_2 dissociative co-ordinates, in which case it can decay only to the ground-state molecule plus a free electron.[37]

In the work of Hamill *et al.* on electron energy losses in thin solid films, it appears that, in several systems, distinct energy losses occur in the energy region of known resonances.[31] These observations cannot be simply interpreted in terms of single-molecule resonances; the interpretation of the experimental data requires more sophisticated analysis than has yet been applied.[32] In the condensed phase, temporary capture of an electron by a single molecule should not be important; rather resonances are expected to be associated with trapping of the electron by molecular aggregates. The processes by which electrons lose energy to liquids and solids has important implications in radiation chemistry and it would seem appropriate further to explore relations between resonance spectroscopy in gaseous and condensed phases.

8 Conclusions

In this Review an attempt has been made to acquaint chemists with aspects of electron scattering spectroscopy which are particularly relevant to chemistry. A wide range of molecules await exploration in electron scattering using what are becoming fairly routine experimental techniques. Of course, as spectrometers of improved resolution become available, the range and detail of the information on molecular energy states which will become accessible will increase enormously. Recently, for example, photoionization of a metastable barium beam inside the cavity of a He–Cd laser has produced an electron beam with less than 1 meV energy spread.[38] Also, a new technique has been developed for obtaining threshold excitation spectra with a resolution of about 12 meV.[39]

Perhaps, in time, electron scattering spectroscopy will become as familiar to chemists as photoelectron spectroscopy now is.

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[37] C. R. Claydon, G. A. Segal, and H. S. Taylor, *J. Chem. Phys.*, 1971, **54**, 3799.
[38] A. C. Gallagher and G. York, *Rev. Sci. Instr.*, 1974, **45**, 662.
[39] S. Cvejanovic and F. H. Read, *J. Phys. (B.)*, 1974, **7**, 1180.