THE EXCITED STATE IN CHEMICAL PHYSICS

PART 2

Edited by J. Wm. McGOWAN

Department of Physics and the Centre for Interdisciplinary Studies in Chemical Physics
The University of Ontario
London, Ontario, Canada

Volume XLV

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INTRODUCTION

This volume of the Advances in Chemical Physics is the second to be devoted entirely to studies of the excited states of molecules. Since the publication of the first volume, there has been continued expansion of the subject. The contributions in this volume, which cover a variety of topics, supplement the earlier articles and report the results and interpretations based upon later technology. Just as for the earlier volume it is hoped that this and succeeding volumes will supplement the rather broadly scattered literature and provide an introduction both for the interested student and the working scientist.

S. RICE

PREFACE

Following the direction established by its predecessor, this second volume of *The Excited State in Chemical Physics* further summarizes theoretical and experimental information available from a variety of sources. It deals with the production of excited atoms, ions, and molecules; the elastic and inelastic scattering of these species; and the production of excited products following collision.

In the five years since the first volume was published, there has been increased interest in the chemistry within gas lasers and the chemistry induced by laser radiation, the kinetics and photochemistry within fusion and industrial plasmas, as well as in the normal and perturbed lower and upper atmosphere. And, since the Three Mile Island accident there has been renewed interest in radiation damage to living and nonliving things. This state of affairs has not only precipitated a variety of spectroscopic studies, but has also brought more attention to the nonspectroscopic aspects of excited state production and the interaction of excited species. The latter topic was stressed in the earlier volume and the emphasis is retained here.

Each chapter was prepared by one or more authorities in excited state chemistry and physics, who summarize much of the latest work and new technology and review research in their areas of expertise. The choice of material and approach is as timeless as it is timely, since the experimental and theoretical techniques reviewed can be applied much more broadly than just within the immediate context.

The combination of theory with experiments dealing mainly with the excited state makes this volume invaluable for the research student as well as for the seasoned scientist, especially in such areas as laser development and laser chemistry, the chemical physics and kinetics of the atmosphere, studies of flames, and related topics.

This project has continued to receive the support of many groups and has been completed largely because of the assistance granted by the Office of Standard Reference Data, National Bureau of Standards. To this office and to many others we owe much.

As editor of this volume I must express my most sincere appreciation to those who have worked hard on the various chapters, who have reviewed the material with me, and who have been patient as this volume has slowly come together.

J. William McGowan

London, Ontario
February 1981

CONTENTS

CHAPTER ONE

CONTINUUM OPTICAL OSCILLATOR-STRENGTH MEASUREMENTS BY ELECTRON SPECTROSCOPY IN THE GAS PHASE

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Contents

I. INTRODUCTION

A. Oscillator Strengths and Electron Spectroscopy

The absolute intensity of dipole-allowed transitions is conveniently expressed in terms of $f(0)$, the optical (dipole) oscillator strength. The quantity $f(0)$ is simply related to the absorption coefficient and also to the cross section for absorption or emission of radiation (see Section II). The concept of oscillator strength developed from the classical picture of the atom in which the electrons were envisaged to be in free oscillation at given frequencies about an equilibrium position with respect to the massive nucleus. The oscillator strength $f(0)$ was defined as the number of electrons in free oscillation at a given frequency and was thus considered to be related to the intensity of absorption at a given frequency. The total oscillator strength was thus equal to the total number of electrons in the atom. Subsequently, the quantum theory of atomic structure emerged, giving a description of the atom involving both bound (discrete) and continuum (ionized) states. A very large number of transitions can occur between these states—far in excess of the number of atomic electrons. Nevertheless, the historical oscillator strength terminology has been retained in assigning an absolute scale for the probability of transition between two energy states. Thus for all possible processes n, the total sum of oscillator strengths is such that $\Sigma_n f_n(0)$ equals the total number of electrons in the atom. The sum is over all discrete and continuum states and is discussed further in Section II.

Optical oscillator strengths have traditionally been measured by optical absorption and lifetime methods.[1] Such measurements have of necessity been restricted to those regions of the electromagnetic spectrum where suitable exciting photon sources are available. Consequently, relatively few measurements have been made in the vacuum ultraviolet (UV) and soft-X-ray regions since sufficiently intense tunable (continuum) light sources have not generally been available, at least above 20 eV. It is now apparent that electron storage rings will, in principle, supply sufficiently intense continuum radiation to allow a wide range of such measurements to be made. However, even with the increasing availability of synchrotron radiation to date, such information is scarce and many experiments, particularly those involving photoionization phenomena, are extremely difficult to carry out. Quantitative spectroscopy at ultraviolet UV and X-ray energies is of fundamental chemical interest since it involves many of the higher electronic states of valence electrons and all inner-shell excitations as well as all ionization processes. This type of quantitative information is necessary for a more complete understanding of processes such as those that occur in radiation-induced decomposition, aeronomy, high-temperature chemistry, and discharge phenomena. Furthermore, such experimental data are urgently needed for the formulation and evaluation of quantum-mechanical procedures.

In the last decade electron spectroscopy in its various forms has been proven a valuable spectroscopic tool for determining the bound and ionized energy levels of atoms and molecules. The principal achievements of photoelectron, electron impact, and Auger and Penning ionization electron spectroscopy are given in a number of recent publications.[2] Of these methods, gas-phase photoelectron spectroscopy (PES) has provided by far the largest amount of data. However, the attention of photoelectron spectoscopists has been primarily focused on the energies of the ejected electron, and little quantitative work on absolute intensities has been reported, in part because of the paucity of calibrated tunable light sources in the far UV, as discussed earlier. Another problem has been that, for ease of construction, most PES spectrometers have been designed to sample ejected electron spectra at 90° to the photon beam. The intensity is thus modulated by the variation of the (usually unknown) asymmetry parameter, β, for each state, with energy. Although this effect can be avoided by sampling at the so-called magic angle[3] (54.7° for unpolarized radiation), few spectrometers have been constructed in this configuration. However, the most serious problem in PES is that little attempt has been made to correct for the electron-transmission efficiency of the analyzer. As discussed in Section IV, such corrections may be very significant, even over a few electron volts, but it has been only recently that such corrections have been considered. The few quantitative PES experiments that have been reported are discussed in Section V.

By contrast, a growing number of quantitative fast-electron-impact experiments have been used in recent years as an alternative method of obtaining optical oscillator strengths. One of the major aims of this chapter is to draw attention to these methods, to review their principal achievements and potentialities, and, where possible, to make comparisons with directly determined optical data. Using the Born approximation, Bethe[4] laid the theoretical groundwork in 1930, showing that a quantitative relationship exists between photon absorption and the scattering of fast charged particles (see Section II). More recently, these ideas have been discussed in depth by Inokuti[5] and Kim.[6] The early work of Franck and Hertz[7] had shown in many ways the qualitative similarity between electron impact and photon absorption. For example, the processes of excitation, ionization, and dissociation could all be induced by electron bombardment of molecules. The first quantitative evidence demonstrating this relationship came from the total cross-section measurements by Miller and Platzmann.[8] However, it was the pioneering differential electron-scattering studies by Lassettre and his co-workers 9-11 that gave the main impetus leading to the development of modern quantitative electron-impact spectroscopy. Lassettre and his group at the Mellon Institute have subsequently made the dominant contribution to the measurement of optical oscillator strengths for discrete transitions by electron-energy-loss spectroscopy. This work has involved the extrapolation of generalized oscillator strengths to zero momentum transfer to obtain the optical oscillator strength (see Section II).

More recently these ideas have been extended very effectively by van der Wiel and his co-workers, 12-17 giving rise to the development of a variety of "photon-simulation" experiments using high-energy, small-angle electron scattering. These studies are significant in that the chosen experimental conditions approach the optical limit (see Section II) sufficiently closely so that dipole oscillator strengths are measured directly. These experiments have provided the major portion of the continuum oscillator strength data that are available in the literature to date. Much of this work is discussed in Sections IV and V.

B. Energy Transfer In Electron and Photon Experiments

The ability of fast electrons to excite dipole-allowed (optical) transitions can be qualitatively understood in terms of what has been called "pseudophotons" or the "virtual photonfield." Figure 1 illustrates the principal effects occurring when a fast electron interacts with a target molecule via a distant collision (large impact parameter and thus small scattering angle). As the electron passes by, the target experiences a sharply pulsed electric field of which the perpendicular component is significant. Ideally, in the limit the E field will approach a δ function that, if Fourier transformed into the frequency domain, would afford the perfect spectroscopic "light" source consisting of a continuum composed of all frequencies at equal intensities. In practice, the pulse will have a narrow but finite width, and there will be a falloff in intensity of "pseudophotons" at high frequencies. (It should be stressed that this method does not simulate photons; rather, under the appropriate conditions, the electron-impact differential cross section is related to the optical cross section by kinematic factors alone.[5,14]) Nevertheless, a sufficiently wide spectral range can readily be achieved in the laboratory, and the effective high-energy transfer limit in electron-scattering experiments is usually determined by other factors (see Section II).

For a molecule AB, we may compare the processes of photoabsorption and electron-impact excitation as follows:

$$h\nu(E) + \mathrm{AB} \rightarrow \mathrm{AB}^* \qquad \textit{Photoabsorption} \qquad (\mathrm{I.1})$$

$$e(E_0) + \mathrm{AB} \rightarrow \mathrm{AB}^* + e(E_0 - E) \qquad \textit{Electron-impact excitation} \qquad (\mathrm{I.2})$$

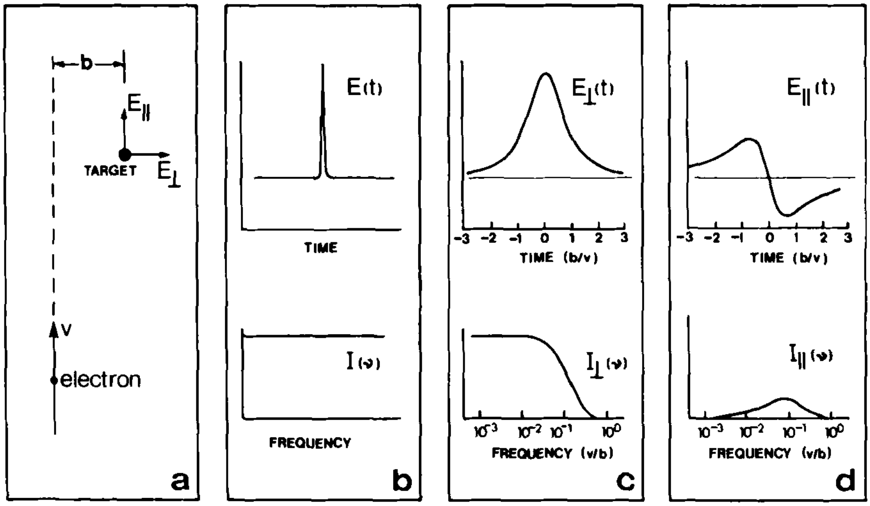

Figure 1. Electric field, $E(t)$, and corresponding frequency spectrum, $I(\nu)$, associated with distant collision of fast electron and molecular target: (*a*) collision parameters—v, electron velocity and b, impact parameters; (*b*) idealized case for very fast electron; (*c*, *d*) realistic picture.

where E is the energy of quantum state AB* and E_0 is the impact energy of the electron. From these expressions it is apparent that the resonant photon energy E in photoabsorption is analogous to the energy loss of the incident electron when scattered by the target in the electron-impact process. In other words, we may "equate" the photon energy with energy loss.

It should be noted that the electron-impact process is nonresonant; the important consequences of this are discussed in the text that follows. In effect, a fast electron (E_0) offers the target a "white-light" continuum of "pseudophotons" that are absorbed with a frequency-dependent probability that can be quantitatively related to the optical oscillator strength via the Bethe–Born relation (see Section II). The *net* result is that under the appropriate experimental conditions we may perform *quantitative* measurements equivalent to photoabsorption and so on using techniques of fast-electron-impact and electron-energy-loss spectroscopy (see Section III). As discussed earlier,[14] it is of particular advantage to exploit this relationship in the UV and soft-X-ray regions of the spectrum where continuum light-source availability is very restricted, with the exception of synchrotron radiation. However, the latter source is only available at a few locations and is of enormous expense. Even where synchrotron radiation is available, use of the photons is still subject to the well-known difficulties of optical spectroscopy at short wavelengths,[14] which include low reflectivity, order overlapping, and efficient monochromation. Dispersion of synchrotron radiation leads to changes in polarization and also modifications of photon flux that necessitate calibration of the effective photon intensity for ionization oscillator-strength measurements.[18] It has been pointed out by Inokuti[5] that use of electron impact instead of photons can have some additional advantage because of the nonresonant nature of electron-impact excitation. This property eliminates line-saturation effects that occur when the natural line width is narrower than the experimental photon bandwidth.

Since ionization is only a special case of excitation it is also possible to simulate the photoionization process using fast electrons. We may compare the processes

$$hr(E) + \mathrm{AB} \rightarrow [\mathrm{AB}^+ + \mathrm{e_{ej}}] \qquad \text{Photoionization} \tag{I.3}$$

$$e(E_0) + \mathrm{AB} \rightarrow [\mathrm{AB}^+ + \mathrm{e_{ej}}] + \mathrm{e_{sc}}(E_0 - E) \qquad \text{Electron-Impact ionization} \tag{I.4}$$

where $\mathrm{e_{ej}}$ is the electron ejected from AB on ionization and $\mathrm{e_{sc}}$ is the fast-scattered electron.

It is apparent that in both cases energy E is deposited in $[\mathrm{AB}^+ + \mathrm{e_{ej}}]$ and that, as in the case of excitation, the photon energy is analogous to the electron energy loss. However, since there are now two electrons sharing the excess energy in electron-impact ionization, it is necessary to use time correlation (coincidence techniques) for the simulation of photoionization

Table I.
Photon-Simulation Experiments[a]

PHOTON EXPERIMENT	ELECTRON-IMPACT EQUIVALENT	TYPICAL REFERENCES
Photoabsorption	Electron-energy-loss spectroscopy	25
Photoionization mass spectrometry (fragmentation)	Electron–ion coincidence (e–ion)	149,166
Total photoionization	Electron energy loss—total ejected electron, coincidence (e, 2e)	24
Photoelectron spectroscopy	Electron energy loss—selected ejected electron, coincidence (e, 2e)	23,194
Photofluorescence (of ionic states)	Electron-energy-loss—electron–ion–photon (triple) coincidence	191

[a]Various aspects of the instrumentation and techniques used in these experiments as well as conventional PES are discussed in Section IV.

experiments. The possible photoexcitation and ionization experiments that have been simulated are summarized in Table I.

C. Scope of This Review

This article is essentially restricted to a consideration of the measurement of optical oscillator strengths by methods employing various forms of electron spectroscopy. Targets are restricted to atoms and molecules in the gas phase, and only absolute or relative *quantitative* measurements are generally included (i.e., only those experiments in which electron transmission and ion kinetic energy are accounted for, at least on a relative basis). Generalized oscillator strengths are discussed only insofar as they relate to the derivation of optical oscillator strengths. Detailed accounts of generalized oscillator strength measurements can be found in the work of Lassettre et al.[9–11] and Bonham and Fink,[19] who have studied various aspects of the Bethe surface. Oscillator-strength measurements for discrete transitions using electron-impact spectroscopy have been the subject of two recent detailed reviews by Lassettre.[10,11] Some notable studies have also been made by Geiger.[20] Therefore, this chapter emphasizes optical oscillator-strength measurements for continuum processes involving energy transfers in excess of $\sim$10 eV. Attention is focused on: (1) photoabsorption $f(0)$ measurements by electron-impact spectroscopy, (2) partial ionization (electronic state) $f(0)$ measurements using photoelectron spectroscopy and electron–electron coincidence, (3) total ionization $f(0)$ measurements using total (e,2e) and (e–ion) coincidence with mass analysis, and (4) partial ionization (fragmentation) $f(0)$ measurements using (e–ion) coincidence with mass analysis.

Attention is given to results for the noble gases (including multiple ionization processes) as well as energy transfer and fragmentation in diatomic and small polyatomic molecules. In Section II the theoretical background of the methods is discussed and a sufficient framework developed to enable the laboratory worker to design experiments as well as to understand and interpret the data. The current status of oscillator-strength calculations is discussed in Section III. Section IV discusses some aspects of the experimental methods used in oscillator-strength measurements by electron spectroscopy. Finally, a discussion is given in Section V illustrating some of the more significant oscillator-strength measurements that have been made to date using electron-spectroscopic techniques. No attempt has been made to give tables of oscillator-strength data in this review. In many cases this most useful form of data is available in the original published articles. We would like to take this opportunity to exhort authors of forthcoming publications to provide such tables of data in addition to diagrams since this greatly facilitates the use and comparison of oscillator strengths.

II. THEORETICAL BACKGROUND

A. Introduction

In optical experiments the absorption of radiation is governed by the Beer–Lambert law. If $I_0(E)$ is the measured intensity of a beam of electromagnetic radiation of energy E and $I(E)$ that following absorption by a gas of thickness L containing n molecules per unit volume, then:[21]

$$I(E)=I_0(E)\exp[-\sigma_t(E)nL] \tag{II.1}$$

where $\sigma_t(E)$ is the optical cross section for absorption that has units of area.

An analogous expression holds for electron scattering, except that in such an experiment we usually desire to measure that proportion of the incident beam (of impact energy E_0) that has lost energy E. In general, the intensity of such an inelastically scattered beam will depend on the polar angles θ_s, ϕ_s (with respect to the main beam) at which it is measured. If the incident electron beam has an intensity I_0, the inelastically scattered beam will have an intensity

$$I_{sc}(\theta_s,\phi_s,E,E_0)=\int_{\Delta\Omega_d} I_0 nL\frac{d^2\sigma_{el}}{d\Omega}(\theta_s,\Phi_s,E,E_0)\,d\Omega \tag{II.2}$$

where $\Delta\Omega_d$ is the solid angle subtended by the detector at the scattering region and σ_{el} is the electron-impact cross section. Both expressions (II.1) and (II.2) are idealized in that corrections are usually needed in practice for pressure-dependent effects. These corrections are especially significant in optical work in the near UV since $\sigma_t \ll \sigma_{el}$.

The cross section σ is a fundamental property of the molecule and as such is related to the molecular wave functions for the two states between which a transition is induced. Hence it is desirable to separate the contributions to σ that arise from purely kinematic quantities such as the impact energy of the electron beam from those that depend solely on the properties of the molecule. To this end, a dimensionless quantity, the oscillator strength, is introduced in optical absorption spectroscopy, defined by the relation[22]

$$f_{0m}(0)=2E\sum_{\alpha} A_\beta\left|\hat{\mathbf{e}}\cdot\left\langle\psi_{m\alpha}\left|\sum_{i=1}^{N}\mathbf{r}_i\right|\Psi_{0\beta}\right\rangle\right|^2 \tag{II.3}$$

in which $\Sigma_\alpha A_\beta$ denotes a summation over the degenerate excited states $\psi_{m\alpha}$ and an average over the degenerate initial states $\Psi_{0\beta}$, $\hat{\mathbf{e}}$ is a unit vector in the direction of the electric field, and the equation is written, for convenience, in atomic units. The summation within the bracket is over the N electrons in the molecule.

An analogous quantity, the generalized oscillator strength, is found to be useful in electron-scattering theory. It is a function of the momentum $\mathbf{K}$ transferred from the incident electron to the molecule and has the form[5]

$$f_{0m}(\mathbf{K})=\frac{2E}{|\mathbf{K}|^2}\cdot\sum_{\alpha}A_\beta\left|\left\langle\Psi_{m\alpha}\middle|\sum_{i=1}^{N}e^{i\mathbf{K}\cdot\mathbf{r}_i}\middle|\Psi_{0\beta}\right\rangle\right|^2 \qquad \text{(II.4)}$$

The cross sections $\sigma_t(E)$ and $\sigma_{el}(\theta_s,\phi_s,E,E_0)$ are related[5,21] to those two oscillator strengths through the equations

$$\sigma_t(E)=\frac{\pi}{c^2}\cdot f(0) \qquad \text{(II.5)}$$

and

$$\sigma_{el}(\theta_s,\phi_s,E,E_0)=\frac{2}{E}\cdot\left|\frac{\mathbf{k}_f}{\mathbf{k}_i}\right|\cdot\frac{|f(\mathbf{K})|}{|\mathbf{K}|^2} \qquad \text{(II.6)}$$

where $\mathbf{k}_i$ and $\mathbf{k}_f$ are the incident and scattered electron momenta, respectively. It is clear from equation (II.4) that

$$\underset{|\mathbf{K}|\to 0}{Lt}\, f_{0m}(\mathbf{K})=2E\sum_{\alpha}A_\beta\left|\hat{\mathbf{K}}\cdot\left\langle\Psi_{m\alpha}\middle|\sum_{i=1}^{N}\mathbf{r}_i\middle|\Psi_{0\beta}\right\rangle\right|^2 \qquad \text{(II.7)}$$

where $\hat{\mathbf{K}}$ is unit vector in the direction $\mathbf{K}$. Comparison of equations (II.7) and (II.3) shows that they are numerically identical, and thus in low-momentum-transfer scattering experiments we may replace the unit electric vector by the unit vector $\mathbf{K}$. It is this close analogy between electron scattering and optical absorption spectra that we wish to exploit in the simulation experiments (see Table I).

If the energy transfer E is sufficiently large, ionization occurs and the oscillator strength and cross section become continuous functions of E. To preserve the simplicity of equations (II.1) and (II.2), relationships (II.5) and (II.6) must be modified such that[5,21]

$$\sigma_t(E)=\frac{\pi}{c^2}\cdot\frac{df(0)}{dE} \qquad \text{(II.8)}$$

$$\sigma(\theta_s,\phi_s,E,E_0)=\frac{2}{E}\cdot\left|\frac{\mathbf{k}_f}{\mathbf{k}_i}\right|\cdot\frac{1}{|\mathbf{K}|^2}\cdot\frac{df(\mathbf{K})}{dE} \qquad \text{(II.9)}$$

Although the oscillator strengths are dimensionless, their derivatives with respect to E are not, and units become a significant problem in continuum absorption. In cgs (electrostatic) units, equation (II.8) reads[21]

$$\frac{df(0)}{dE} = \frac{mc}{e^2\pi h}\sigma_t(E) \tag{II.10}$$

where $\sigma_t(E)$ is expressed in square centimeters and E in ergs. More normally, E is expressed as a frequency $\bar{\nu}$ in wave numbers, when we have

$$\frac{df(0)}{d\bar{\nu}} = \frac{mc^2}{e^2\pi}\sigma_t(\bar{\nu}) \tag{II.11}$$

The cross section $\sigma_t(E)$ may also be expressed in units of megabarns (1 Mbarn $= 10^{-18}$ cm^2). Under these circumstances, inverting (II.10) we have

$$\sigma(\text{Mbarns}) = 1.76\times 10^{-10}\frac{df}{dE(\text{ergs})} \tag{II.12}$$

If E is expressed in electron volts (eV), we find

$$\sigma(\text{Mbarns}) = 109.75\frac{df}{dE(\text{eV})} \tag{II.13}$$

It should be noted that these expressions hold only for excitation to the continuum and that comparison of electron scattering and optical absorption for discrete transitions is only possible if the resolution of both types of experiment is known.

The problem with equations (II.8) and (II.9) is that the definitions of the two cross sections appear to change abruptly with passage through the ionization threshold. A full discussion of this has been given by Fano and Cooper,[29] and it suffices here to point out that we may define differential cross sections

$$\frac{d\sigma_t(E)}{dE} = \frac{\pi}{c^2}\frac{df(0)}{dE} \tag{II.14}$$

$$\frac{d\sigma_{\text{el}}(\theta_s,\phi_s,E,E_0)}{dE} = \frac{2}{E}\cdot\left|\frac{\mathbf{k}_f}{\mathbf{k}_i}\right|\frac{1}{|\mathbf{K}|^2}\cdot\frac{df(\mathbf{K})}{dE} \tag{II.15}$$

The cross section defined in (II.15) is related to the observed intensity of the scattered beam by the expression

$$\int_{E}^{E+\Delta E} \frac{dI_{sc}(\theta_s, \phi_s, E, E_0)dE}{dE} = \int_{E}^{E+\Delta E} \int_{\Delta\Omega d} I_0 nL \frac{d^3\sigma_{el}}{dE\,d\Omega}(\theta_s, \phi_s, E, E_0)\,dE\,d\Omega \tag{II.16}$$

A similar expression may be written for optical absorption when the exponent in (II.1) is sufficiently small. Substituting equation (II.15) in (II.16), we may obtain the generalized oscillator strength over some region ΔE by simple integration.

B. Molecular Processes

The energy transferred by the photon or electron to the molecule may be lost by the latter in a number of different ways. If this energy is lower than the ionization threshold, the usual pathways are (1) reradiation or (2) dissociation into neutral fragments or charged fragments (from ion-pair processes); in other words:

$$\begin{array}{l} A-B \xrightarrow{E} (AB)^* \overset{h\nu}{\rightsquigarrow} AB \\ \qquad\qquad\;\; \llcorner\!\!\longrightarrow A' + B', A^+ + B^-, A^- + B^+, \cdots \end{array}$$

If A' or B' are not in their ground state, further fragmentation or radiation may occur. Radiation from AB^* may not give the ground state, and further fluorescence may take place. In the target region energy may also be lost by collision with other molecules or with the walls of the target chamber.

If the energy is higher than the ionization threshold, the preceding processes may still occur, but we also have the possibility of two types of ionization process:

$$\begin{array}{lll} & \overset{E}{\longrightarrow} AB^+ + e_{ej} & \text{Molecular ionization} \\ AB & & \\ & \searrow A^+ + B + e_{ej} & \text{Dissociative ionization} \end{array}$$

In energy transfers above the ionization threshold, it is usual for several different ionization processes to occur with probabilities depending on E. The measured optical oscillator strength for absorption is thus a sum corresponding to a variety of different processes. Denoting this total optical oscillator (ionization potential): strength by $df(0)/dE$, we have, for

$E > IP$

$$\frac{df(0)}{dE} = \sum_i \frac{df^i(0)}{dE} + \sum_n \frac{df^n(0)}{dE} \tag{II.17}$$

where we have partitioned the oscillator strength into two sets of processes, those involving ionization (i) and those involving neutral processes (n). The ionization efficiency η is then given by

$$\eta = \left(\sum_i \frac{df^i(0)}{dE} \right) \left(\frac{df(0)}{dE} \right)^{-1} \tag{II.18}$$

The individual partial oscillator strengths $df^i(0)/dE$ for each ionization process are individual functions of E. It is usual to define the branching ratio b_i as

$$b_i = \left[df^i(0)/dE \right] \left[\sum_i df^i(0)/dE \right]^{-1} \quad \text{and} \quad \sum b_i = 1 \tag{II.19}$$

Characterization of the neutral processes is far more difficult, and little information is available at present. However, studies on some simple molecules (see Section V) have indicated that the ionization efficiency approaches unity quite rapidly as the energy loss increases above threshold, suggesting that, except where transitions to Rydberg states just below a new ionization threshold are significant, the dominant mode of energy loss in the far UV is by ionization often accompanied by molecular fragmentation.

C. Born Approximation

Consider a beam of electrons incident along the $+z$ direction. The wave function is of the form $\exp(i|\mathbf{k}_i|z)$, and the current is given by[26]

$$\mathbf{j}_i(\mathbf{r}) = Re\left(\psi^* \frac{\nabla}{i} \psi \right) = |\mathbf{k}_i| \hat{\mathbf{z}} \tag{II.20}$$

where $\hat{z}$ is a unit vector in the $+z$ direction. This corresponds to a current of one electron per second with momentum $\mathbf{k}_i$. If the electron is scattered inelastically, the outgoing wave function will be a spherical wave, emanating from the scattering center. Such a wave function may be represented by a function that behaves asymptotically at large values of r as

$$\psi_f = \frac{\exp(i\mathbf{k}_f\mathbf{r})}{\mathbf{r}} \cdot f(\theta, \phi) \tag{II.21}$$

where $f(\theta,\phi)$ is some angular function. The scattered current may be calculated using equation (II.20) and is

$$\mathbf{j}_{sc}(r)dA = |\mathbf{k}_f|\hat{\mathbf{r}}\left|\frac{f(\theta,\phi)}{r^2}\right|^2 dA \tag{II.22}$$

where dA is the area of the detector.

The cross section $\sigma_{el}(\theta,\phi,E,E_0)$ is measured using the detectors, and since we expect it to be proportional to both the solid angle subtended by the detector and to the incident current, we have

$$\mathbf{j}_{sc}(\mathbf{r})dA = \mathbf{j}_i(\mathbf{r})\sigma_{el}(\theta,\phi,E,E_0)\cdot\frac{dA}{r^2} \tag{II.23}$$

where $\sigma_{el}(\theta,\phi,E,E_0)$ is introduced as a proportionality constant. We have, comparing (II.22) and (II.23) and using (II.20),

$$\sigma_{el}(\theta,\phi,E,E_0) = \frac{|\mathbf{k}_f|}{|\mathbf{k}_i|}|f(\theta,\phi)|^2 \tag{II.24}$$

Thus to calculate the cross section, we need only calculate the asymptotic part of the scattered electron wave function. This is straightforward, at least for first-order perturbation theory. Provided that the time scale during which the perturbation of the molecule by the impact electron occurs is small compared to the time scale for electronic motion, we find[26]

$$f(\theta,\phi) = \frac{-1}{2\pi}\int \exp(i\mathbf{K}\cdot\mathbf{r})\langle\Psi_m|V|\Psi_0\rangle d\mathbf{r} \tag{II.25}$$

where the perturbing potential V is given by

$$V = \frac{-\Sigma_{p=1}^{M} Z_p}{|\mathbf{r}-\mathbf{R}_p|} + \Sigma_{i=1}^{N}\left(\frac{1}{(\mathbf{r}-\mathbf{r}_i)}\right) \tag{II.26}$$

in atomic units, $\mathbf{R}_p$ are the nuclear coordinates, and $\mathbf{r}_i$ are those of the electrons.

In addition to the assumptions underlying the use of first-order perturbation theory, a number of other assumptions underlie equation (II.25).

1. In effect, the equation has been derived under the assumption of infinite nuclear mass. This is accurate enough for electron scattering, but for proton and atom scattering a coordinate transformation is needed, the details of which are given in Mott and Massey.[26]

2. All relativistic effects have been ignored. Corrections for impact energies of less than 10 keV are very small, but above this level a careful distinction must be drawn between the velocity and energy of the electron. Corrections to first order have been given by Inokuti.[5]
3. All exchange effects have been neglected. For fast incident electrons inducing discrete transitions, this is a very accurate assumption, but if ionization occurs, and especially if the energies of the two outgoing electrons are comparable, such effects are likely to be of great importance. For the most part we are concerned here with ionization to energy levels only a few tens of volts into the continuum using electron energies of very high incidence and, under these circumstances, the effects of exchange are practically negligible.[26-28]

To derive an expression for the oscillator strength, we must consider equation (II.25) more closely. Assuming that the electronic part of the wavefunctions Ψ_m and Ψ_0 are orthogonal, integration over the nuclear attraction part of V(II.26) will vanish. The electron-repulsion part may be simplified by interchanging the order of integration in (II.25) and considering first the integration over $\mathbf{r}$. We find

$$\sum_i \int \exp(\mathrm{i}\mathbf{K}\cdot\mathbf{r}) \int\cdots\int \Psi_m^*\left(\frac{1}{|\mathbf{r}-\mathbf{r}_i|}\right)\Psi_0 d\mathbf{r}_1\cdots d\mathbf{R}_M d\mathbf{r}$$
$$= \sum_i \int\cdots\int \Psi_m^*\left(\int \frac{\exp(\mathrm{i}\mathbf{K}\cdot\mathbf{r})}{|r-r_i|}\,d\mathbf{r}\right)\Psi_0 d\mathbf{r}_1\cdots d\mathbf{R}_M d\mathbf{r} \quad \text{(II.27)}$$

The integral in brackets is well known to have the value $(4\pi/|\mathbf{K}|^2)\exp(i\mathbf{K}\cdot r_i)$, so[26]

$$f(\theta,\phi) = (-2/|\mathbf{K}|^2)\sum_i \langle\Psi_m|\exp(i\mathbf{K}\cdot r_i)|\Psi_0\rangle \quad \text{(II.28)}$$

Recalling the definition of the generalized oscillator strength (II.4) and using equation (II.24), we find

$$\sigma_{\mathrm{el}}(\theta,\phi,E,E_0) = \frac{2}{E}\cdot\frac{|\mathbf{k}_f|}{|\mathbf{k}_i|}\cdot\frac{1}{|\mathbf{K}|^2}\cdot f_{0m}(\mathbf{K}) \quad \text{(II.29)}$$

provided we sum and average equation (II.28) in the usual way.

The generalized oscillator strength defined by (II.4) has a number of important properties that have been listed by Inokuti.[5] Of great importance practically are the sum rules

$$S(\mu,K) = \left(\sum_m + \int_m\right) E_m^{\mu} f_{0m}(K) \quad \text{(II.30)}$$

where $S(\mu, K)$ is convergent for $-1 \leqslant \mu \leqslant +2$ and E_m is the energy loss associated with the transition $0 \rightarrow m$. For our purpose the most significant is

$$S(0,K) = \left(\sum_m + \int_m \right) f_{0m}(K) = N \tag{II.31}$$

where N is the total number of electrons in the molecular system. This is an analogue of the well-known optical sum rule

$$S(0,0) = \left(\sum_m + \int_m \right) f_{0m}(0) = N \tag{II.32}$$

Its importance lies in the fact that it may be used, at least for simple molecules, to place the measured photoabsorption spectrum on an absolute scale. However, great care should be exercised in the use of (II.31) and (II.32) since the summation includes transitions from valence orbitals to inner orbitals already occupied. Such transitions cannot be seen, of course, and thus calibration of subshell photoabsorption spectra by this method will give results that are only approximate.[123]

Clearly, if $|\mathbf{K}|$ is small, the exponential term in (II.4) may be expanded and we obtain a series of the form[9,30]

$$f_{0m}(\mathbf{K}) = 2E\left[\varepsilon_1^2 + \left(\varepsilon_2^2 - 2\varepsilon_1\varepsilon_3\right)|\mathbf{K}|^2 + \left(\varepsilon_3^2 - 2\varepsilon_{24} + 2\varepsilon_{15}\right)|\mathbf{K}|^4 + \cdots + \right] \tag{II.33}$$

$$= f_{0m}(0) + |\mathbf{K}|^2 f_{0m}^{(1)}(0) + |\mathbf{K}|^4 f_{0m}^{(2)}(0) + \cdots + \tag{II.34}$$

where

$$\varepsilon_n = \frac{1}{n!} \sum_i \langle \Psi_m | (\hat{\mathbf{K}} \cdot \mathbf{r}_i)^n | \Psi_0 \rangle$$

and the unit vector $\hat{\mathbf{K}}$ is defined as previously. Two things are important here. The first is that, as foreshadowed earlier, the limiting value of $f_{0m}(\mathbf{K})$ as $\mathbf{K} \rightarrow 0$ is indeed the optical value. The second is that, as a consequence of sum rules (II.31) and (II.32), we have, at once

$$\left(\int_m + \sum_m \right) f_{0m}^{(1)}(0) = 0 \tag{II.35}$$

The sum rule has been checked by Backx et al., who found, in addition that $K^2 \cdot f_{0m}^{(1)}(0)$ was much smaller than $f_{0m}(0)$ for the molecules studied.[31]

D. Derivation of $f(0)$ from Electron-Impact Measurements

The quantity **K**, the momentum transferred to the molecule, is, from the preceding paragraphs, a fundamental quantity in the theory of electron scattering. It may be obtained from purely kinematic considerations. Consider Fig. 2*a* (i.e., Fig. 1*a* of Hamnett et al.[23]). If $\mathbf{k}_i$ and $\mathbf{k}_f$ are the initial and scattered momenta of the incident electron, we have, from conservation of momentum,

$$\mathbf{K} = \mathbf{k}_i - \mathbf{k}_f \tag{II.36}$$

$$|\mathbf{K}|^2 = |\mathbf{k}_i|^2 + |\mathbf{k}_f|^2 - 2|\mathbf{k}_i||\mathbf{k}_f| \cos\theta \tag{II.37}$$

where θ is the angle shown. Further, conservation of energy tells us that

$$|\mathbf{k}_i|^2 - |\mathbf{k}_f|^2 = 2E \tag{II.38}$$

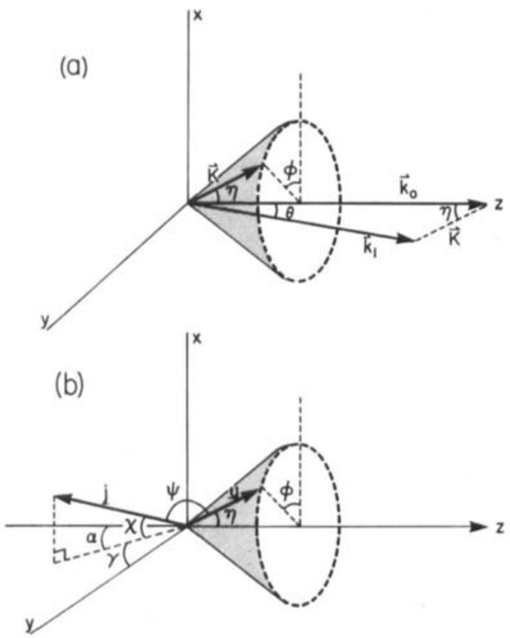

Figure 2. (*a*) Illustration of forward scattering geometry: $\mathbf{k}_0$ is momentum of the electrons in main beam defining z axis; $\mathbf{k}_1$ is momentum of forward scattered electron, with polar angles $\theta, \phi + \pi$; **K** is momentum transfer vector with polar angles η, ϕ; (*b*) geometry of ejected electrons, collected in narrow slit along z axis. Corresponding acceptance angles are χ and $\gamma (\chi \ll \gamma)$; j and u are unit vectors in directions of ejected electron and momentum transfer **K**, respectively.

where E is the energy loss. If E_0 is the incident energy

$$|\mathbf{k}_i|^2 = 2E_0$$

$$|\mathbf{K}|^2 = 2E_0 + (2E_0 - 2E) - 2\sqrt{2E_0}\cdot\sqrt{2E_0 - 2E}\cdot\cos\theta \qquad \text{(II.40)}$$

Since E, E_0, and θ are experimentally measurable, $\mathbf{K}$ may be obtained.

Now, if we desire to make $|\mathbf{K}|^2$ as small as possible, we desire E to be very small compared to E_0 and θ also to be very small. Under these circumstances, (II.40) may be written to second order in θ and the dimensionless parameter $x = (E/2E_0)$

$$|\mathbf{K}|^2 = 2E_0(x^2 + \theta^2) \qquad \text{(II.41)}$$

If $|\mathbf{K}|$ is so small that we may replace $f_{0m}(\mathbf{K})$ by $f_{0m}(0)$ as in equation (II.34), the cross section σ may be written from (II.29) as

$$\frac{d^2\sigma_{\text{el}}}{d\Omega_{\text{sc}}}(\theta, \phi, E, E_0) = \frac{2}{E}\cdot\left|\frac{\mathbf{k}_f}{\mathbf{k}_i}\right|\cdot\frac{1}{2E_0(x^2+\theta^2)} f_{0m}(0) \qquad \text{(II.42)}$$

Integrating over ϕ is straightforward, and we find

$$\frac{d\sigma_{\text{el}}}{d\theta} = \frac{4\pi}{E}\left|\frac{\mathbf{k}_f}{\mathbf{k}_i}\right|\cdot\frac{\sin\theta}{2E_0(x^2+\theta^2)}\cdot f_{0m}(0) \qquad \text{(II.43)}$$

If the half angle of acceptance of our detector is θ_0 and we are concerned with θ_0 very small, that is, with forward scattering, integration with respect to θ may be carried out analytically. We find[23]

$$\sigma_{\text{el}}(E, E_0) = \left[\frac{2\pi}{EE_0}\cdot\left|\frac{\mathbf{k}_f}{\mathbf{k}_i}\right|\log_e\left(\frac{x^2+\theta_0^2}{x^2}\right)^{1/2}\right] f_{0m}(0) \qquad \text{(II.44)}$$

Thus the forward scattered cross section may be seen as a product of the oscillator strength and a purely kinematic factor. Thus from a knowledge of the inelastic scattering cross section σ in the forward direction, we may, provided $\theta_0 \ll 1$ and $x \ll 1$, obtain *optical* oscillator strengths. Comparing (II.44) and (II.5), the cross section σ_{el} can be seen to be much greater than the optical cross section σ_t for small values of E, but that σ_{el} falls away much more rapidly than does σ_t with increasing values of E. This may be brought out clearly by considering the behavior of (II.44) if θ_0 is very small with respect to x. We then have

$$\sigma_{el}(E,E_0) \sim \frac{\pi}{E_0 E} \cdot \left|\frac{\mathbf{k}_f}{\mathbf{k}_i}\right| \cdot \frac{\theta_0^2}{x^2} \cdot f_{0m}(0) = \frac{4\pi E_0 |\mathbf{k}_f| \theta_0^2}{|\mathbf{k}_i|} \cdot \frac{f_{0m}(0)}{E^3} \qquad \text{(II.45)}$$

and comparison with (I.5) shows that $(\sigma_{el}/\sigma_t) \sim (1/E^3)$. If $\theta_0 \approx x$, the decrease in σ_{el} with increasing E is less dramatic. In practice, x and θ_0 may easily be made sufficiently small for equation (II.44) to constitute a very good approximation. Impact energies of a few kiloelectron volts upward have been routinely used, and θ_0 values of less than 10^{-2} radians are sufficient for equation (II.44) to be valid for up to ~100-eV energy loss.[13,14] First-order corrections to (II.44) using equation (II.34) have been derived experimentally by Backx et al.[31] and found to be insignificant for the gases studied (H_2, He, and CH_4). The oscillator strengths derived may be normalized using the sum rule of equation (II.32) or by comparison with absolute optical data at a single point.

In situations where the impact energy has been insufficiently high to allow the use of equation (II.44), equation (II.29) must be used. The generalized oscillator strength $f(\mathbf{K})$ may then be obtained as a function of $\mathbf{K}$. Clearly, a sensitive test of the Born approximation will be the fact that $f(\mathbf{K})$ must be independent of the incident energy E_0. Lassettre and Skerbele[10] have recently reviewed work in this field and have shown that, although this independence holds at quite low impact energies for many transitions in the discrete part of the absorption spectrum, it is by no means universally true. It is clear, however, that we may invert equation (II.29) and use it as phenomenological definition of the generalized oscillator strength

$$f_{0m}(\mathbf{K}) = \left|\frac{\mathbf{k}_i}{\mathbf{k}_f}\right| \cdot \frac{|\mathbf{K}|^2 E}{2} \cdot \sigma_{el}(\theta,\phi,E,E_0) \qquad \text{(II.46)}$$

Lassettre et al.[33] were able to show that even if the Born approximation does not hold, we still find

$$\underset{|\mathbf{K}|\to 0}{Lt}\, f_{0m}(\mathbf{K}) = f_{0m}(0) \qquad \text{(II.47)}$$

Unfortunately, in practice the lowest value of $|\mathbf{K}|$ that may be conveniently measured at impact energies less than 500 eV is still too large for the limit described by (II.47) to be obtained accurately. However, the approach has been proven sufficiently useful for a number of absolute measurements to be made, and comparison with optical data has been very fruitful.[10]

E. Continuum Effects and (e,2e) Coincidence Experiments

The equations used to define $f_{0m}(0)$ involve averaging over all initial degenerate states of the molecule and summing over all final states as in (II.4). If the energy loss is sufficiently large that ionization occurs (and assuming $\eta = 1$), the effect of summing over all final states is, in effect, to sum over all possible angles of ejection of the ionized electron.[5] Clearly, however, the very act of measuring the intensity of the ejected electrons at a given angle selects out of all possible directions of ejection certain specific ones. Thus the preceding formulas must be modified if we wish to account for the results of photoelectron or dipole-electron coincidence experiments in which the intensities of forward scattered and ejected electrons are measured simultaneously. We need, in fact, an expression for the oscillator strength differential in the polar angle of ejection.

The kinematics of the situation for the case of "optical limit" type (e,2e) experiments are illustrated in Fig. 2*b* (Fig. 1*b* of Hamnett et al.[23]), which shows the direction of the ejected electron **j** as a function of the two polar angles χ and γ. The angle between **j** and the vector **K** is denoted by ψ. Provided the forward scattering kinematics are such that $|\mathbf{K}|$ is small and we may approximate $f(\mathbf{K})$ by $f_{0m}(0)$, then,* as is well known, regardless of the detailed form of the continuum wave function, provided that Ψ_m is orthogonal to Ψ_0[3,35]

$$\frac{d^3f^i(0)}{dE\,d\Omega_j} = \frac{1}{4\pi}\frac{df^i(0)}{dE}\left(1 + \frac{\beta_i}{2}(3\cos\psi - 1)\right) \tag{II.48}$$

Where β_i is the usual asymmetry parameter and is a function, in general, of E. An analogous expression holds in PES except that ψ is then the angle between the direction of ejection and the electric vector of the incident radiation.

For the (e,2e) experiment we may, by analogy with equation (II.29), define a cross section

$$\frac{d^5\sigma_{\mathrm{el}}}{dE\,d\Omega_s\,d\Omega_j} = \frac{2}{4\pi E}\cdot\left|\frac{\mathbf{k}_f}{\mathbf{k}_i}\right|\cdot\frac{1}{|\mathbf{K}|^2}\left(1 + \frac{\beta_i}{2}(3\cos^2\psi - 1)\frac{df^i(0)}{dE}\right) \tag{II.49}$$

This fivefold differential cross section† thus measures the probability of

*For clarity of notation in discussion, we now denote the differential oscillator strength $df_{0m}(0)/dE$ for the ionization process $(0\to m)$ by $df^i(0)/dE$ as given in 2.18). The notation of the type $df_{0m}(0)$ is used in Sections II.C and II.D since this is more commonly employed in scattering theory.

†The term σ_{el} is a function of $E, E_0, \theta_s, \phi_s, \chi$ and γ, but the variables have been omitted for simplicity.

simultaneously detecting an electron scattered into the direction $\theta, \phi(\theta \ll 1)$ and an electron ejected in the direction (χ, γ) at a given E, E_0. Integration of (II.49) over the acceptance angles for the forward and ejected electron detectors leads to a rather complicated expression for the resultant coincidence intensity, which is usually written as[23]

$$I_{\text{coinc}}(\alpha, E, i) \sim [1 + C_\alpha(E)\beta_i] \frac{df^i(0)}{dE} \tag{II.50}$$

where $C_\alpha(E)$ is a purely kinematic function defined elsewhere,[23] and $df^i(0)/dE$ is the oscillator strength for that ionization process defined by the energy of the ejected electron. The function $C_\alpha(E)$ has the interesting property that for angle α (defined in Fig. 2*b*) equal to 54.7°

$$C_\alpha(E) = 0 \tag{II.51}$$

to first order. Thus[23]

$$I_{\text{coinc}}(54.7°, E, i) \sim \frac{df^i(0)}{dE} \tag{II.52}$$

and for a given energy loss, we may measure the coincidence intensity for all ionization processes i and derive the branching ratios b_i defined in equation (II.19). Knowledge of the total oscillator strength also enables calculation of the ionization efficiency defined by (II.18). It can then be seen that the coincidence technique provides a flexible alternative to photoelectron spectroscopy in that it is experimentally far easier to vary the energy loss E than the incident photon frequency at a known (relative) ionizing flux.

III. CALCULATION OF OSCILLATOR STRENGTHS

We recall that the definition of the generalized oscillator strength may be written [see (II.4)]

$$f_{0m}(\mathbf{K}) = \frac{2E}{|\mathbf{K}|^2} \cdot \sum_\alpha A_\beta \left| \left\langle \Psi_{m\alpha} \left| \sum_{i=1}^{N} \exp(i\mathbf{K}\cdot\mathbf{r}_i) \right| \Psi_{0\beta} \right\rangle \right|^2$$

We have used the Born–Oppenheimer approximation to factor $\Psi_{0\beta}, \Psi_{m\alpha}$ into electronic and nuclear parts and have further assumed that the former are orthogonal to enable us to reduce V. Both wave functions may be approximated by products of electronic, nuclear rotation and vibrational wave functions. The last of these may be factored out at once, and integration over the $3N-6$ normal coordinates will lead to the usual Franck–Condon factors. Rotation is more difficult. If, as is usual, the rotational states are not resolved, summing and averaging over the rotational wave functions is, at normal temperatures, equivalent to the situation where molecules would be classically rotating. Thus we must consider all possible orientations of $\mathbf{r}_i$ with respect to $\mathbf{K}$, which is equivalent to considering $\mathbf{K}$ to have all possible orientations with respect to the molecule. The effect of this has been discussed by a large number of authors, and the resultant equations are well known in the literature.[3, 35–37]

These expressions may be considerably simplified if we assume that Ψ_0 and Ψ_m may be expanded as antisymmetrized products of spin orbitals. Making the further assumption that no relaxation occurs, that is, that Ψ_m and Ψ_0 may be described by the *same set* of spin orbitals, we have

$$\left\langle \Psi_{m\alpha} \left| \sum_{i=1}^{N} \exp(i\mathbf{K}\cdot\mathbf{r}_i) \right| \psi_{0\beta} \right\rangle = \int \phi_{m\alpha}(\mathbf{r})\left[\exp(i\mathbf{K}\cdot\mathbf{r})\right]\phi_{0\beta}\, d\mathbf{r} \qquad \text{(III.1)}$$

corresponding to a transition from an orbital $\phi_{0\beta}$ occupied in the ground state to $\phi_{m\alpha}$, which is unoccupied in the ground state. This is usually termed the *single-electron approximation* and has been extensively used as a first-order theory.[36–38] The optical analogue is obtained by allowing $|\mathbf{K}|\to 0$, and clearly

$$f_{0m}(0) = 2E \sum_{\alpha} A_\beta |\hat{\mathbf{K}}\cdot\langle\phi_{m\alpha}|\mathbf{r}|\phi_{0\beta}\rangle|^2 \qquad \text{(III.2)}$$

For continuum transitions an analogous expression must be used. In both discrete and continuum transitions several problems may arise:

1. The excited state is, in general, an open-shell system, and $\phi_{m\alpha}$ must be coupled correctly to the remaining orbitals. This coupling is straightforward for transition to non-Rydberg-like orbitals, but for highly excited Rydberg levels coupling the angular momentum correctly is a source of some difficulties, as Veldre et al. have pointed out.[39] In the case of ionization, especially from open-shell ground states, additional selection rules, based on fractional parentage coefficients, must be included. These have been discussed recently by Cox et al.[40]
2. A fundamental requirement of the derivation of (III.1) and (III.2) is that $\phi_{m\alpha}$ must be orthogonal to $\phi_{0\beta}$. If they are not initially orthogonal, they must be Schmidt orthogonalized in the normal way. However, such orthoganalization may lead to serious errors even in simple systems, as Bell and Kingston found for the helium $1^1S\to 3^1S$ transition.[41]

3. The most serious problem in continuum transitions is the form of the radial part of $\phi_{m\alpha}$. An immense amount of work has been reported on possible forms for $\phi_{m\alpha}$, and the conclusion seems to be that for ionized electrons with kinetic energies above a few hundred electron volts, approximating $\phi_{m\alpha}$ by a plane wave $\exp(i\mathbf{k}_{ej}\cdot\mathbf{r})$ is fairly satisfactory numerically. Unfortunately, the use of simple plane waves is attended by a fundamental disadvantage, namely that the angular dependence of the photoelectron signal is predicted to be of the form[42]

$$I \sim I_0 \cos^2\psi \tag{III.3}$$

which comparison with (II.48) shows to be generally incorrect (i.e., except where β is always equal to 2). It has been pointed out that this defect may be remedied by orthogonalizing the plane wave to the orbitals as discussed in paragraph 2 of this list.[36] Unfortunately, there are no measurements of β at sufficiently high energies for this procedure to be checked experimentally. It is clear from the preceding discussion that the normal plane-wave method will not, in general, yield good results near the ionization threshold. Two avenues of improvement have been suggested within the single-particle approximation framework.
   a. For diatomic molecules exact one-electron functions are available for H_2^+ in ellipsoidal coordinates. These are used as the basis for a much more accurate calculation of the continuum wave function. This approach has been used by Tuckwell for N_2 and O_2 [43] and by Itikawa for H_2.[44] Similar calculations for H_2 have also been reported by Shaw and Berry.[45] Very recently Hirota[46] has succeeded in extending these methods to CO and has reported distorted Coulomb wave calculations that are in encouragingly good agreement with experiment.[18,171,172] These calculations are limited to the energy region below 20 eV.
   b. Single-center expansion methods have been explored by Burke and co-workers.[47-50] The molecular wave function is expanded about the center of mass of the molecule, and the problem is treated as a pseudoatomic one. Although the scattering equations are substantially simplified by this approach, the computation becomes formidable for more complex molecules.

A related but somewhat different approach has been suggested by the recently introduced MS–Xα method. Calculation of the continuum functions within this method is relatively straightforward,[51,52] and the method has been applied to the K-shell X-ray absorption spectrum[53] of N_2 and very recently to photoionization of N_2 and CO near threshold.[54] This last calculation is very encouraging in that close agreement at an absolute level with many of the features seen in the photoelectron spectra at different incident photon energies may be obtained.

It has become clear from recent theoretical work that many of the effects seen in the variation of oscillator strength with energy loss cannot be explained within the single-particle model. All the inert gases show complicated resonances extending over many electron volts, which result from correlation effects involving the remaining "passive" electrons. A major theoretical advance was the development and use of the random-phase approximation with exchange (RPAE) or time-dependent Hartree–Fock perturbation theory by Amusia and Cherepkov.[55] Within this theory we must return to equation (II.4) and include all electrons in the calculation. Very impressive agreement has been obtained by the Russian group,[55] not only for optical oscillator strengths, but also for generalized oscillator strengths for the inert gases. Recently this method has been extended[56, 57] to open-shell atoms and calculations on the photoionization cross section of chlorine have also appeared.[58] Unfortunately, extension to molecules has not yet proved possible. Related to these methods are those of Kelly and co-workers, who have calculated cross sections for a number of atoms and, using a one-center expansion technique, for CH.[59, 60] However, the computational complexities of this Hartree–Fock perturbation method seems to preclude their general application to molecules at the moment.

Although several computational advances have been made in recent years, it appears that in the foreseeable future, calculations of the oscillator strengths for molecules will remain firmly grounded within the one-electron framework. The very encouraging success of Davenport's calculations[54] on N_2 and CO using the MS–Xα technique may signpost the best route until the computational problems of extending the RPAE method to molecules have been overcome. It should also be noted that the recent moment-theory calculations of oscillator strengths for photoabsorption and partial photoionization reported by Langhoff, McCoy, and co-workers hold great promises in that the results are significantly more accurate than the MS–Xα calculations.[53,54] Impressive results have been obtained for valence shells of N_2[216] and CO[217] and also for the K-shell of N_2.[218]

IV. EXPERIMENTAL CONSIDERATIONS

A. Electron Analyzers and Transmission Efficiency

Many detailed descriptions of devices and techniques used in electron spectroscopy are to be found in the literature. Accordingly, in this section we give only a general discussion highlighting items of special concern in making quantitative measurements. Scattered or ejected electrons may be energy analyzed by means of electric and/or magnetic fields. The properties and performance of many commonly used types of electron analyzer are to be found elsewhere.[61] For quantitative electron spectroscopy, electrostatic selectors are generally preferred over magnetic analyzers because of the problems of fringing fields. Fringe magnetic fields can interfere with the performance of associated electron-optical elements. The most generally useful types of electrostatic analyzer are the 180° hemispherical,[62] the 127° cylindrical,[63] and the cylindrical mirror analyzer.[64] However, Wien filters (crossed electric and magnetic fields) have also been used effectively for quantitative work at low resolution by Van der Wiel.[65] Very high resolution (0.004 eV) has also been achieved by Geiger[20] using a Wien filter and higher (10 to 50 keV) impact energies.

Operation of electron analyzers at high resolving power necessitates considerable attenuation (to less than a few milligauss) of the earth's magnetic field together with any other AC or DC (alternating or direct current) magnetic fields that may be present. This may be achieved with Helmholtz coils and/or mumetal shielding (mumetal must be hydrogen annealed after all fabrication procedures have been completed). Careful attention must also be given to minimizing AC pickup by the spectrometer and its associated electronic controls. In particular, pickup must be suppressed by eliminating ground loops and using coaxial and triaxial shielding where necessary as well as the employment of suitable filtering. To reduce ripple, care must be taken to ensure that all floated power supplies have a low impedance path to ground.

For quantitative analysis of ejected and scattered electrons, it is usually necessary that the resulting spectra be corrected for the transmission efficiency of electrons, which will often vary significantly with energy. This "chromatic aberration" is the result of the electron optical lens effects (change of focal length) that occur whenever electrons are accelerated or retarded into an analyzer operating with a constant pass energy. These effects can be considerable, as is shown in Fig. 3, which shows the transmission curve obtained[66] for a 127° analyzer with a simple double-aperture retarding system. The transmission factor varies by at least an order of magnitude over a few volts. It should be noted that the exact form of the curve will depend not only on the particular geometry, but also on the pass energy of the electron spectrometer.

Although transmission effects can be accounted for more readily by scanning the analyzer electric field while allowing the electrons to enter on a field free path, this mode of operation is not usually convenient since it results in a changing energy resolution ($\Delta E/E$ is constant rather than ΔE) over the spectrum. An alternative procedure to minimize differences in

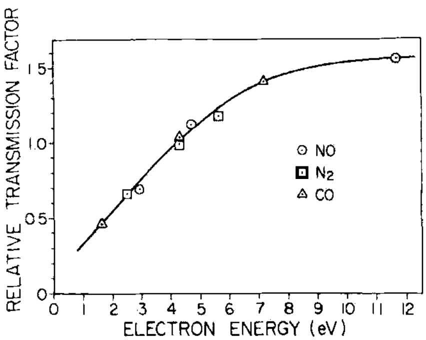

Figure 3. Relative transmission correction factor for an electron spectrometer.[66]

transmission is to construct the spectrometer inputs and/or outputs with multielement (zoom) electron lenses. An excellent compilation of design data for a wide variety of electron optical lenses suitable for electron spectrometers is to be found in a recent book by Harting and Read.[67] Other useful lens designs have been given by Heddle.[68] Detailed and useful treatments of electron-spectrometer design have been given by Lassettre[10], Kuyatt and Simpson,[69] Read et al.[70], and Noller et al.[71]

In the case of high-resolution electron-impact spectroscopy (i.e., if the exciting bandwidth <0.4 eV) it is necessary to monochromate the incident electron beam. A schematic representation of the typical requirements for a high-resolution electron-impact energy-loss spectrometer is shown in Fig. 4. Electrons from either an indirectly heated oxide cathode or a directly heated filament are produced in the gun with a Maxwell–Boltzmann distribution of energies, with a full width at half maximum (FWHM) of 0.4–1.0 eV depending on the cathode material, temperature, and gun design. For spectroscopy in which only modest resolution is needed, the incident unmonochromated beam may be used directly in the collision chamber. However, if information is required for more closely spaced electronic or vibrational states, an energy analyzer is needed to function as a monochromator to select a suitably narrow slice from the distribution. The electron beam is then accelerated to a final energy E_0 at the collision region, where it is scattered by a high-density gas target produced either by a jet or by using a "gas-tight" collision chamber. The latter has generally been found superior for quantitative work since a more homogeneous gas density is obtained. A rotatable "gas-tight" collision chamber allowing wide angular variation has been described by Tam and Brion.[72] Electrons inelastically scattered or ejected in the collision region are sampled by an energy analyzer. The scattered (ejected) electrons are accelerated (or retarded) to the appropriate constant pass energy of the analyzer by the application of a voltage [which effectively compensates the energy loss (E)