Maxima and minima in the angular dependence of the $[np)(n+1)s]$ transition in the rare gases observed by high-energy electron impact spectroscopy*

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A minimum and a maximum in the generalized oscillator strength are observed as a function of momentum transfer for the $[np)(n+1)s]$ transition in Ne, Ar, Kr, and Xe using 25-keV incident electrons. The results indicate that the occurrence of these extrema is due to zeros in the first Born scattering amplitude, and the positions of the extrema are found to be in excellent agreement with available Hartree-Fock calculations.

The existence of minima and maxima in the generalized oscillator strength[1] $f(K, E_n)$ for dipole-allowed bound-state transitions in atoms as a function of momentum transfer K has been predicted for a number of cases.[2-4] It was shown that the positions of these extrema as a function of momentum transfer relate to the nodal properties of the radial parts of the atomic orbital wave functions of the initial and final states. Subsequent theoretical studies have proposed similar behavior in other atoms,[5] in molecules such as H_2O,[6] and C_2H_4,[7] and in transitions from the excited states of He.[8] Experimental observations of structure thought to be due to this mechanism have been reported in Xe (minimum and maximum), Kr (minimum),[3] Hg,[9] C_2H_4,[10] and H_2O.[11] However, all of the previous experimental studies were conducted with incident electron energies below 600 eV.

Recently, Hanne and Kessler, in a detailed study of the angular dependence of the excitation of the $6\,^1P_1$ state of atomic Hg,[12] using incident electron energies between 60 and 600 eV, showed that the position of the minimum depended on the incident energy in addition to the expected first Born dependence on the momentum transfer. The results of Hanne and Kessler were later confirmed when Skerbele and Lassettre,[13] remeasured these transitions in mercury using 300 – 500 eV incident electrons. The results of these studies raised the question as to whether the proposed first Born mechanism was in fact the correct one. The first Born interpretation of these results was also called into question by the theoretical investigations of Geltman and Hidalgo,[14] and Huo.[15] These authors concluded that the first Born approximation *is not obeyed at large scattering angles* even in the high incident energy limit. However, in the same limit for a *fixed value of momentum transfer, the first Born limit is approached.* Therefore, experimental measurement of these extrema in the generalized oscillator strengths using high incident electron energy, where no significant deviation from the first Born approximation is expected at the momentum transfer values in question, should be of considerable interest. This article reports the measurement of the minimum and maximum positions of the $[np)(n+1)s]$ transitions in Ne, Ar, Kr, and Xe, using 25-keV incident electrons. The present experiment gives a valuable check on the previous measurement for Xe and Kr by Kim *et al.*,[3] with 400-eV incident electrons, and reports for the first time the K values for the extrema in Ne and Ar, and the maximum position in Kr which have been predicted to exist by theoretical calculations.[2,5]

The high-energy electron spectrometer used in this work which employs a Möllenstedt energy analyzer,[16] has been described elsewhere.[17] The resolution was set to be slightly better than 1 eV. This enables resolution of the dipole allowed $[np)(n+1)s]$ transition from the quadrupole allowed $[np)(n+1)p]$ transitions in Ne, Ar, and Kr, but not in Xe. Different J levels will not be resolved; however, we expect contributions from excitations to triplet states to be small for Ne and Ar but not for Kr and Xe because of spin orbit mixing.[18] The electron gun was biased with respect to the analyzer such that only the electrons with energy loss corresponding to a narrow range surrounding a particular transition were recorded by the detector. The scattered cross section as a function of momentum transfer was measured in an angular scanning mode, in which the electron gun was rotated at a constant angular velocity of 0.03°/sec, while the scattered electron intensity was recorded with the aid of a multichannel scaler. A complete angular scan, with 256 data points, spanning a momentum-transfer range of $K \sim 0$ to $K \simeq 5.5$ a.u., took about 4 min. The transitions studied here are those to the $2p)3s$ state in Ne ($E_n = 16.7$ eV), to the $3p)4s$ state in Ar ($E_n = 11.7$ eV), to the $4p)5s$ state in Kr ($E_n = 10.3$ eV) and to the $5p)6s$ state in Xe ($E_n = 8.6$ eV). The measurement was repeated at least four times for each transition. Agreement

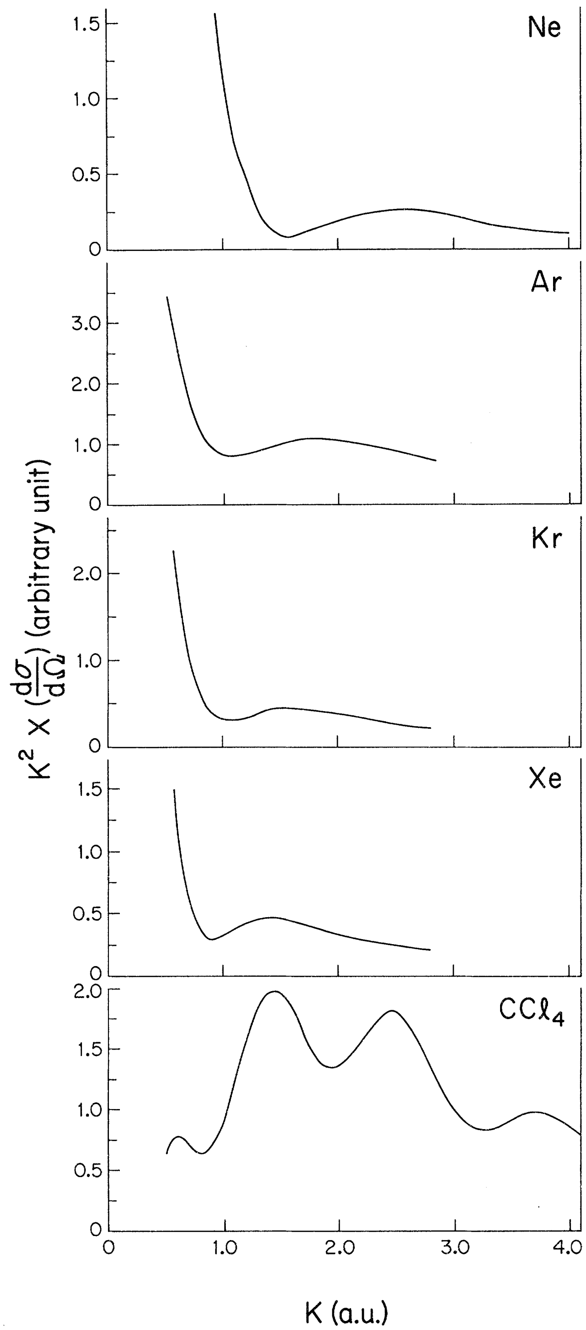

FIG. 1. The relative generalized oscillator strength (proportional to $K^2 d^2\sigma_n/d\Omega dE_n$) of the rare-gas $[np)(n+1)s]$ transition as a function of momentum transfer. The statistical uncertainty in the total number of electrons detected at $K \sim 2$ was 15%, 3%, 6%, and 5% for Ne, Ar, Kr, and Xe, respectively. The last figure shows the dependence of the cross section for elastic scattering from CCl_4 on the momentum transfer, which is used here for calibration of the momentum-transfer scale. The CCl_4 data has an average statistical uncertainty of 0.1%.

between different measurements was excellent. The measured cross section was then converted to a relative generalized oscillator strength in the standard way utilizing corrections for relativistic[1] and exchange effects.[19] A minimum followed by a maximum in the generalized oscillator strength $f(K, E_n)$ was observed in each case as shown in Fig. 1. Positions of the minima and maxima followed the expected trend of occurring at smaller momentum transfer as the atomic number increases. Averaged values for the positions of the minimum and maximum were obtained for each case and are given in Table I where they are compared with available experimental and theoretical results.

The momentum-transfer scale was further calibrated by scanning, under identical conditions, the elastic-scattering cross section of carbon tetrachloride, the angular dependence of which is well documented in the literature.[20] This calibration, shown at the bottom of Fig. 1, showed that the rotation rate of the electron gun was in-

TABLE I. Experimental values of the momentum transfer K (a.u.) for minima and maxima in $f(K, E_n)$ in the rare-gas $[np)(n+1)s]$ transitions, and comparison with other experimental and theoretical results.

	Minimum		Maximum	
Atom	Expt.	Theory	Expt.	Theory
Ne	1.63 ± 0.05	1.7 [b]	2.72 ± 0.10	2.6 [b]
$[2p)3s]$		2.04 [c]		3.39 [c]
Ar	1.12 ± 0.05	1.2 [b]	1.72 ± 0.10	1.8 [b]
$[3p)4s]$		2.7 [c]		3.01 [c]
		1.20 [d]		1.69 [d]
Kr	1.02 ± 0.05	1.1 [b]	1.58 ± 0.10	1.6 [b]
$[4p)5s]$	0.95 [a]	0.83 [c]		1.16 [c]
		1.10 [e]		
Xe				
$[5p)6s]$				
$^1P_1$		0.97 [b]		1.4 [b]
		0.99 [c]		1.16 [c]
	0.94 ± 0.05	0.93 [e]	1.38 ± 0.10	1.4 [e]
	0.84 [a]		1.20 [a]	
$^3P_1$		0.98 [b]		1.4 [b]

[a] Reference 3.

[b] Y.-K. Kim (private communication). Calculated from relativistic Hartree-Fock wave functions.

[c] Reference 5. Theoretical calculations using hydrogenic wave-functions.

[d] Values obtained from Fig. 3 of Ref. 2 where momentum transfer K was given in units of Å^{-1}. These values are based on calculations made with numerical Hartree-Fock wave functions and were misquoted in Table III of Ref. 5 as being in a.u..

[e] Theoretical values quoted in Ref. 3 based on calculations made with Hartree-Fock wave functions.

deed constant and the momentum-transfer scale was correct to within the stated experimental error.

An additional calibration of our method was carried out by making an angular scan of the relative generalized oscillator strength of the combined He $1s)2p$ and $1s)2s$ transitions, which can be compared with very reliable theoretical calculation.[21] In this case the quadrupole allowed $1s)2s$ transition ($\Delta E = 20.61$ eV) was not resolved from the $1s)2p$ transition ($E_n = 21.21$ eV). The measured cross section is, therefore, the sum of the cross sections of the two transitions. The relative cross section, after being converted to a relative generalized oscillator strength curve was scaled to Kim and Inokuti's theoretical calculations[21] at $K^2 = 0.3$ a.u., as shown in Fig. 2. The agreement between the experimental and theoretical results is excellent except for $K^2 > 5$ a.u., where the background (which will be discussed later) contributes significantly to the apparent cross section. As was predicted by the theory, no extrema were found. The good agreement confirms that this angular scanning technique is suitable for studying the angular dependence of inelastic scattering cross sections.

The positions of the minima for Kr and Xe, and the maximum for Xe are slightly higher than the experimental result of Kim *et al.*,[3] and are in even better agreement with their calculations using Hartree-Fock wave functions. From the experimental results[9,12,13] and the theoretical calculations of Madison and Shelton[22] it is known that as the incident electron energy increases the values of K for the positions of the minima and maxima both appear to approach the first Born limiting values from below. The close agreement with the experimental results quoted in Ref. 3 argues that our results acquired at over a 60-fold increase in incident electron energy have reached the first Born limit. The agreement in the case of Xe also suggests that possible shifts in the extrema from our failure to resolve the quadrupole transition cannot be serious. The results obtained here are in exceedingly good agreement with the unpublished relativistic Hartree-Fock values of Kim.[23] The result for Ar is also in excellent agreement with the calculation of Bonham.[2] However, the calculation of Miller,[5] using hydrogenic wave functions with effective nuclear charges, gave much higher K values for Ne and Ar, indicating that the choice of orbital exponents in these cases was not the optimum one.

According to the first Born approximation, the observed minima should correspond to true zeros in the scattering amplitude. The intensity value at the minima observed in this study is not zero. There are several causes for not observing zero intensity minima[1]:

(i) The present resolution does not allow the separation of different J levels in an electronic state. In this experiment the angular scan was repeated with small changes of the average energy loss measured by the spectrometer in the vicinity of the transition peak energy loss. This corresponds to different weighted averaging of the two J-level contributions to the cross section. No apparent changes in the positions of the minima

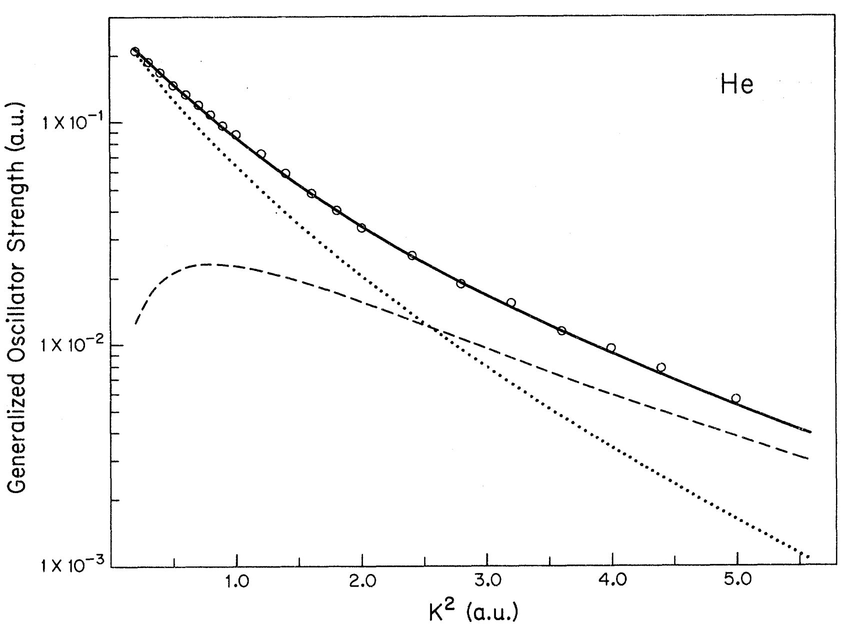

FIG. 2. Generalized oscillator strengths of the $[1s)2p]$ and $[1s)2s]$ transitions in helium as a function of momentum transfer. Dashed line, $[1s)2s]$ transition as calculated in Ref. 15; dotted line, $[1s)2p]$ transition as calculated in Ref. 15; solid line, sum of $[1s)2s]$ and $[1s)2p]$ calculated transitions; triangles, experimental values which have been scaled to the theoretical values at $K^2 = 0.3$ a.u. The experimental uncertainties are about 0.7% at $K^2 = 0.5$ a.u., and about 10% at $K^2 = 5$ a.u.

and maxima were observed. On the other hand, when an appreciable part of the adjacent energy-loss peak at higher energy loss is sampled, the maxima and minima were appreciably diminished in intensity. Since features in the GOS for different J values can be expected to occur at quite different K values, these observations mean that the features of the $J=0$, 2 components are thoroughly mixed with the $J=1$ component at our energy resolution.

(ii) Small non-first-Born contributions may exist in the measured cross section, even at such high-incident energy, as indicated in the detailed discussions given elsewhere.[14,15,24]

(iii) A monotonic decreasing background exists in the recorded signal. Under the present experimental procedure, it is not possible to determine the background contribution exactly and hence to subtract it from the signal. The background is known to be monotonic and structureless, and hence will not seriously affect the determination of the position of the extrema. It does, however, make normalization of the experimental cross section to an absolute scale uncertain, hence no attempt has been made to determine the absolute scale. The advantages of a continuous angle scan over a series of separate measurements at selected angles, which can be more readily normalized to an absolute scale, are that fluctuations in experimental conditions, which may cause spurious extrema, are minimized and significantly less data collection time is required.

(iv) Although care was taken to reduce multiple scattering, small contributions from this source, especially at the largest angles, cannot be ruled out. The source of this correction comes from the same electron being scattered by two different atoms, one elastically at or near the scattering angle under consideration and the other inelastically at or near zero angle. Since the elastic intensity is monotonically decreasing, the multiple scattering will not introduce maxima or minima in the angular dependence but may produce a slight shift in the positions of the first-Born maxima and minima. This possibility has been considered in the assignment of the uncertainties.

(v) It is also conceivable that improved wave functions will result in the prediction of non-zero minima. However, studies using limited configuration interaction on Mg, Ca, Sr and Ba[25] indicate that the minima are still true zeros, although their location as a function of K may be changed.

Although multiple extrema are found to occur in theoretical calculations,[4,26,5] only one minimum and one maximum have been observed in either this study or in any of the previous experiments. Due to the rapid decrease of the intensity in successive maxima predicted by theory, the detection of even the second maximum will be either impossible or highly uncertain with the present experimental technique. Furthermore, even at our high-incident energies, higher-order Born corrections can be expected to be more important at the large K values at which such features are predicted to exist.

The agreement between this study and that reported in Ref. 3 and the unpublished theoretical results of Kim, would seem to verify the proposed first-Born mechanism[2,3] for the occurrence of maxima and minima in the generalized oscillator strength for dipole allowed transitions in the rare gases as a function of momentum transfer. Note that theoretical studies already exist which suggest that further improvements in the theory will lead to changes in the present theoretical predictions of the order of 0.1 a.u. in K.[25,27] This means that the use of observed maxima and minima as a tool for assigning Rydberg transitions in molecular spectra[6,7,10,11] can be carried out with renewed confidence. In addition accurate absolute measurements of the generalized oscillator strength at a minimum position as a function of the incident-electron energy could yield valuable information on the failure of the Born approximation in those cases where sophisticated wave functions indicate a true zero within the first-Born theory. Future work in this laboratory will be directed toward developing techniques for carrying out multiple-angle scans to obtain signal averaged spectra. Such an approach would allow data with a much lower noise content, more suitable for normalization to an absolute scale, to be obtained.

Note added in proof. The authors have just learned of the existence of calculated values for the minima and maxima in Ar ($K_{min}=1.2_5$ and $K_{max}=1.7_5$) which include some correlation effects. S.I. Sheftel, Ph. D. thesis (Ioffe Physical Technical Institute, Leningrad, U.S.S.R., 1974).

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