Excitation of Optically Forbidden States in the Ionization Continuum by Electron Impact

J. AROL SIMPSON, G. E. CHAMBERLAIN, AND S. R. MIELCZAREK
National Bureau of Standards, Washington, D. C.
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The inelastic-electron-scattering resonances in the ionization continuum of He, Ne, and Ar were recorded as a function of primary energy. The energy resolution was ~0.1 eV, the angular resolution $\Delta\theta$ was $\sim 10^{-2}$ rad about the forward direction, and the primary energy was between 60 and 400 eV. The strength of resonances due to optically forbidden transitions from the ground state compared with those due to optically allowed transitions increases as the energy is reduced, as was expected. A marked difference between ^1D and ^1S behavior exists, and certain resonances, notably that due to the $(3s3p^64p)^1P$ state in Ar, change shape as the energy is reduced. At the highest energies used the resonances due to optically forbidden transitions were still apparent.

IN an earlier publication[1] it was shown that 100eV electrons scattered from rare-gas atoms experienced energy losses which were characteristic of atomic states in the ionization continuum. Both optically allowed and optically forbidden transitions from the ground states to these continuum states were observed. The optically allowed transitions to continuum states discovered by Whiddington and Priestley[2] have been studied in optical-absorption spectroscopy by Madden and Codling[3] and by electron impact by Silverman and Lassettre.[4]

Since the optically forbidden transitions were not seen in earlier electron experiments and are inaccessible to optical experiments, and in view of the lack of data on the dependence of excitation cross sections on electron energy in the range where the Born approximation may be expected to fail, we have measured the characteristic energy-loss spectra of 60 to 400-eV electrons scattered by the lighter rare gases. Emphasis was placed on the behavior of the forbidden transitions as the energy was varied.

To cover this range of impact energies two apparatus were used. Up to 100 eV the apparatus[5] of earlier experiments was employed while above 100 eV a new but essentially similar instrument was used. Both instruments consisted of a monochromator, scattering cell, and electron energy analyzer and had over-all resolution of the order of 0.1 eV and an angular acceptance of ~10 mrad. The targets had thicknesses of the order of 10^{-2} Torr cm. The energy-loss spectra were obtained on an *xy* recorder. The records have been traced for reproduction.

The results for He are shown in Fig. 1 where spectra for energy loss in the range 55 to 65 eV are shown for various impact energies. At the highest impact energy the only prominent peaks correspond to optically allowed excitation of the doubly excited states: $(2s2p)^1P$ at 60.1 eV and the second member of the series at 63.6 eV. This state is a mixture of $2s3p$ and $2p3s$ and has been identified by Madden and Codling[6] as $(sp,23+)$. As the impact energy is decreased the forbidden states $(2p^2)^1D$ at 60.0 eV and $(2s^2)^1S$ at 57.9 eV become increasingly visible on the recordings.

The degree of visibility is difficult to relate to more fundamental quantities. As shown by Fano[7] and Fano

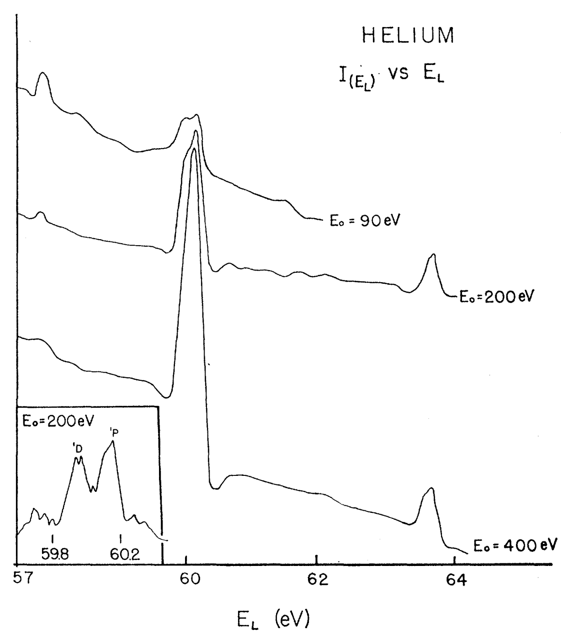

FIG. 1. Electron energy-loss spectra of He between 57- and 65-eV energy loss. The states of interest are $(2s^2)^1S$(57.9 eV), $(2p^2)^1D$(60.0 eV), $(2s2p)\,^1P$(60.1 eV), and $(sp,23+)\,^1P$ at 63.6 eV. Additional states are expected in the 61- to 63-eV region but as yet have not been resolved sufficiently to be identified. Primary energy is shown on curves. The zeros have been suppressed. The insert shows a separation of the ^1P and ^1D levels at a higher resolution and gain in the vicinity of 60-eV energy loss.

[1] J. A. Simpson, S. R. Mielczarek, and J. Cooper, J. Opt. Soc. Am. **54**, 269 (1964).
[2] R. Whiddington and H. Priestley, Proc. Roy. Soc. (London) **A145**, 462 (1934).
[3] R. P. Madden and K. Codling, Phys. Rev. Letters **10**, 516 (1963); J. Opt. Soc. **54**, 268 (1946).
[4] S. M. Silverman and E. N. Lassettre, J. Chem. Phys. **40**, 1265 (1965).
[5] J. A. Simpson, Rev. Sci. Instr. **35**, 1998 (1963).
[6] R. P. Madden and K. Codling, Astrophys. J. **141**, 364 (1965).
[7] U. Fano, Phys. Rev. **124**, 1866 (1961).

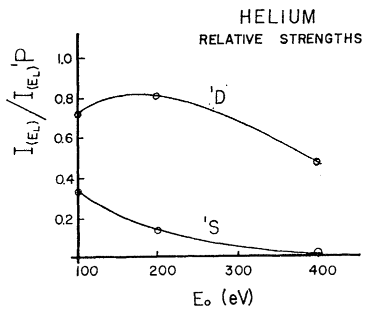

FIG. 2. Relative strengths (see text) of resonances due to forbidden and allowed transitions in He as a function of primary energy.

and Cooper[8] observed autoionizing line shapes are functions of a shape parameter q, width parameter Γ, and a parameter ρ which is a function of the ratio of the minimum cross section to the average cross section across the resonance. In the present experiments the lack of sufficient energy resolution results in an apparent reduction of the line intensity and causes an overlapping of responses to neighboring resonances; consequently it is difficult or impossible to determine the "smooth continuum" which would exist in the absence of resonances. Hence the line-shape parameters cannot be determined and we have defined the "relative strength" of a resonance as the height of the resonance above the local background divided by the height of some resonance which is prominent at the highest energy used.

Figure 2 shows the variation of the strengths of the ^1D and ^1S forbidden transitions in helium relative to the allowed $(2s2p)^1P$. The relative size of the ^1S peak is largest and is still increasing at the lowest energy shown while the ^1D appears to have a broad maximum at $\sim$200 eV.

As far as can be determined the line shapes remain invariant as the energy is varied and agree well with that observed by Madden and Codling for the $(2s2p)^1P$ and $(sp, 23+)^1P$.

The results in neon, Fig. 3, are similar despite the fact that the most prominent series starting at 45.6 eV is an optically allowed inner-shell excitation $(2s^22p^6)^1S \rightarrow (2s2p^6np)^1P$ rather than a double excitation as in He.

As the impact energy is decreased the resonance at 43.7 becomes the most prominent. The strength of this resonance relative to the ^1P at 45.6 eV, shown in Fig. 4, exhibits the same type of variation with energy as does the ^1S relative to the ^1P in helium. This fact leads us to believe that the 43.7-eV resonance is due to the $(2s2p^63s)^1S$ state which would be expected to lie at about this energy.[6] In addition to this resonance a broad loss appears in the 45-eV region which probably corresponds to unresolved states arising from the $(2s^22p^43s3p)^1P$ and $(2s^22p^43s^2)^1D$ configurations.

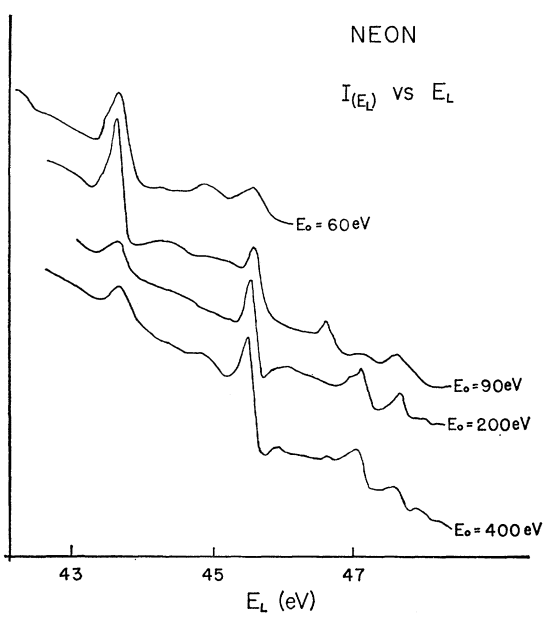

FIG. 3. Electron energy-loss spectra of Ne between 43- and 49-eV energy loss. The states of interest are $(2s2p^63p)^1P$, (45.6 eV) and $(2s2p^63s)^1S$ at 43.7 eV. Unidentified higher members of the series can be seen from 46 eV up. Primary energy is shown on the curves. The zeros have been suppressed.

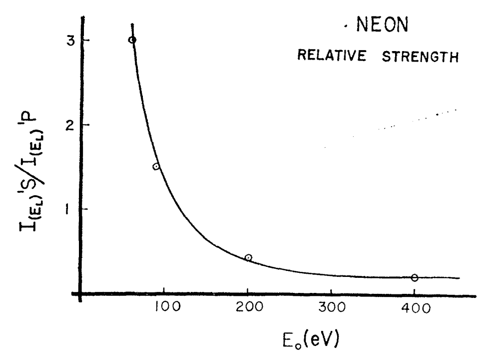

FIG. 4. Relative strength of the ^1S resonance in Ne.

The line shapes remain almost constant throughout the energy range except for a vanishing of the dip following the peak of the $(2s2p^63p)^1P$ resonance.

In argon (Fig. 5) the situation is somewhat different. At high energy the most prominent set of resonances are those seen by Madden and Codling in optical-absorption measurements and which they associate with the $(3s3p^6np)^1P$ states. These resonances are characterized by a decrease in scattered current. This dip is analogous to the dip in the photon absorption. The first member is at 26.72 eV.

As the energy is decreased two additional sets of resonances appear, the first being a downward step in the continuum between 25.2 and 25.3 eV and the second a series of peaks starting at 27.55 eV.

Since in the photon absorption of Ne and Ar the inner-shell excitations are always more prominent than

[8] U. Fano and J. W. Cooper, Phys. Rev. **137**, A1364 (1965).

the double excitations, and in Ne the same is true for the electron experiments we believe the downward step is a consequence of the configuration $3s3p^64s$ which gives rise to both ^1S and ^3S terms. Earlier experiments show that ^3S terms are only weakly observed in forward scattering[9] except very close to threshold. The principal component is thus probably the ^1S term.

The peak at 27.55 eV is then assigned to $(3s3p^63d)^1D$. Calculations by Weiss[10] show that the second member of the ^1S series, $3s3p^65s$, is at almost the same energy. However both the line shape which is different, and the intensity, which is greater than the first member,

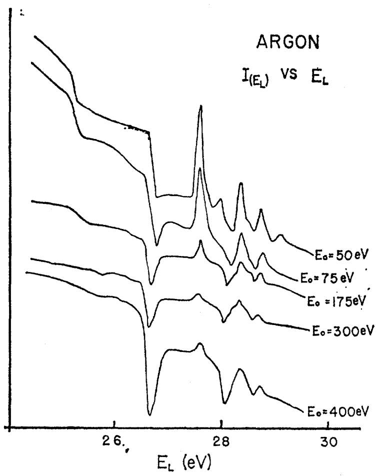

FIG. 5. Electron energy-loss spectra of Ar between 24- and 30-eV energy loss. The states of interest are $(3s3p^64p)^1P$ at 26.7 eV, $(3s3p^64s)^1S$, ^3S at 25.8 eV and $(3s3p^63d)^1D$ at 27.55 eV. Above the second member of the ^1P series at 28.1 eV higher unidentified members of various series can be seen. Primary energy is shown on the curves. The zeros have been suppressed.

strongly suggest that the principal loss does not arise from this ^1S series.

In the case of the most prominent loss spectrum in argon the line shape undergoes a marked change as the energy is decreased, starting as almost a pure dip and ending as an edge with perhaps a preceding slight rise. This latter form does not appear to match any of the Fano line shapes although it is difficult to guess where the "smooth continuum" might be in the absence of the resonances due to the discrete states. It appears

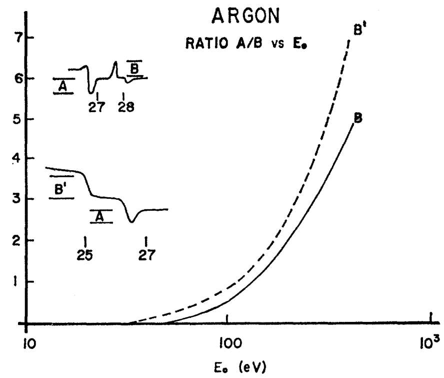

FIG. 6. Semilog plot of inverse of the relative strengths of the optically forbidden resonances in Ar as a function of primary energy.

that only detailed calculations or higher experimental energy resolution can resolve this apparent disagreement. The varying line shape makes the determination of the relative strength of the resonances difficult since we lack a well-defined height for the ^1P loss. Figure 6 shows the inverse of the relative strengths of the forbidden resonances under the assumption that, since the dip corresponds to the optical line shape, the depth of the dip is an index of the strength of the ^1P resonance. It is interesting to note that the semilog plot of Fig. 6 approaches at higher energies the straight line to be expected[11] for the ratio of $^1P/^1S$ cross sections of the nonresonant type.

One feature in common to all the data is that at the highest energy used, 400 eV, the loss spectra still exhibit losses due to optically forbidden transitions. Hence, in the case of discrete states in the continuum, conditions necessary for the so-called "optical approximation" to be valid are not satisfied for forward scattering until the impact energy is in excess of 400 eV. In the case of argon this is almost 20 times the excited state energy. Of the forbidden excitations, those to ^1D states remain more prominent than do those to ^1S states at the higher impact energies.

[9] J. Arol Simpson and S. R. Mielczarek, J. Chem. Phys. **39**, 1606 (1963).
[10] A. Weiss (private communication).
[11] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, London, 1958), p. 145.