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To cite this article: I E McCarthy et al 1978 J. Phys. B: Atom. Mol. Phys. 11 3299

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Comparison of (e, 2e), photoelectron and conventional spectroscopies for the Ar II ion

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- Received 27 April 1978

Abstract. States of the Ar II ion whose eigenvectors contain large components of singlehole configurations are observed in the (e, 2e) and (γ , e) reactions on the Ar I atom. The cross section is regarded as being proportional to the spectroscopic factor, that is the state expectation value of the single-hole configuration in the eigenvector. Spectroscopic factors obtained from these reactions for $\frac{1}{2}$ + states are compared with those obtained by diagonalising an effective Hamiltonian in a model space, with radial matrix elements determined by fitting spectra for bound states. (e, 2e) and conventional spectroscopy are compatible and provide complementary information about structure. Simple analysis of the present (γ , e) data does not lead to compatible information on spectroscopic factors.

1. Introduction

In conventional atomic and molecular spectroscopy the energy eigenvalues of the Hamiltonian are determined from the energies of emitted or absorbed photons. Cross sections for reactions in which a target system is ionised can, in principle, give information about the eigenvectors of the Hamiltonians for the target and the ion, provided the reaction mechanism can be sufficiently well described. Both the (e, 2e) and photoionisation (γ , e) reactions have been used to obtain such structure information, but detailed agreement has not been obtained for information from these two different methods.

Correct reproduction of information relevant to eigenvectors is a strong indication of the validity of the description of a reaction, at least in a limited range.

The spectroscopic factors for states of the argon ion with total angular momentum $J = \frac{1}{2}$ and parity π positive have been obtained from (e, 2e) reaction theory applied to experiments (McCarthy and Weigold 1976, to be referred to as I). These are compared with similar information obtained from photelectron spectroscopy (Spears *et al* 1974). The spectroscopic factor for a single-hole configuration in a state is the state expectation value of that configuration.

0022-3700/78/0019-3299 \$02.00 © 1978 The Institute of Physics

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The present work obtains the same spectroscopic factors from a diagonalisation of the Hamiltonian matrix in which the radial integrals are treated as parameters and are adjusted so that the eigenvalues fit as closely as possible the energy levels of positive parity states determined from photon emission and absorption. The calculation parallels one due to Luyken (1972).

The $\frac{1}{2}$ + structure of the argon ion is chosen because it is simple in the sense that only four states are seen with significant strength in the (e, 2e) and (γ , e) reactions. Yet it is sufficiently complex to provide a test of the spectroscopy.

Sections 2 and 3 introduce the notation, define the spectroscopic factors and review (e, 2e) and (γ , e) spectroscopy. Section 4 gives details of the present calculation. Section 5 gives a possible collective interpretation of the states of the argon ion excited in (e, 2e) reactions.

2. (e, 2e) spectroscopy

A matrix representation for the Hamiltonian is obtained in terms of an independentparticle model basis ϕ_{α} , $\alpha = (N, J, M)$, where N is a radial quantum number and J, M characterise the angular momentum state. An eigenvector Ψ_i is given by the expansion

$$\Psi_i = \sum_{\alpha} a_{i\alpha} \phi_{\alpha}. \tag{1}$$

In a convenient basis ϕ_{α} is a Slater determinant of single-particle functions ψ_{μ} , $\mu = (n, j, m)$.

In (e, 2e) spectroscopy the momenta k_A , k_B of two coincident emerging electrons are measured following an ionising collision initiated by an electron of momentum k_0 . In the experimental geometry that has proved adequate for spectroscopy the polar angles θ of k_A and k_B , measured from k_0 , are equal and fixed at about 45°, the energies of the two electrons are equal, and the azimuth of one of the detectors is varied to determine a cross section profile as a function of the recoil momentum q for each state of the ion.

$$\boldsymbol{q} = \boldsymbol{k}_0 - \boldsymbol{k}_{\mathrm{A}} - \boldsymbol{k}_{\mathrm{B}}.\tag{2}$$

Different states of the ion are resolved by the kinetic energy loss between initial and final states.

The expression for the amplitude that is used in the interpretation of an experiment in which the ion is left in a state f is

$$M_{f} = K \int d^{3}r'_{1} \int d^{3}r'_{2} \int d^{3}r_{1} \int d^{3}r_{2}(1 - P_{12})\chi_{A}^{(-)*}(r'_{1})\chi_{B}^{(-)*}(r'_{2})\Psi_{f}^{\dagger}(\xi)$$

$$\times t(r'_{1}, r'_{2}, r_{1}, r_{2})\Psi_{T}(r_{2}, \xi)\chi_{0}^{(+)}(r_{1})$$
(3)

where K is a kinematic factor and P_{12} is the exchange operator.

The essential assumption to be tested is that t is a two-body operator, independent of the ion coordinates ξ . In order to determine the momentum profile it is necessary to determine the distorted waves (continuum orbitals) $\chi^{(\pm)}$ from an optical model and to make an assumption for the form of t. There is strong evidence (Camilloni *et al* 1978) that the free Coulomb t matrix is a sufficient approximation for the two-body operator t. However, the two-body force assumption results in the structure appearing in (3) only in the form of the target-ion overlap $\langle \Psi_f | \Psi_T \rangle$. We use the form (1) for the target structure and a basis $\phi'_{\mu\beta}$ for the ion, in which single-hole orbitals ψ^{\dagger}_{μ} are coupled to target configurations ϕ_{β} in such a way that the ion state Ψ_f always has the total angular momentum and parity specified by a set of quantum numbers λ .

$$\Psi_f = \sum_{\mu\beta} t^{(f)}_{\mu\beta} \phi'_{\mu\beta} \tag{4}$$

$$\phi'_{\mu\beta} = C_{\mu\lambda\beta}\psi^{\dagger}_{\mu}\phi_{\beta}.$$
⁽⁵⁾

Here $C_{\mu\lambda\beta}$ is a Clebsch–Gordan coefficient and sums over projection quantum numbers are implied in the notation.

When a large fraction of the reaction strength for states with quantum numbers λ is in the continuum of the ion, it is best to evaluate the overlap directly by Green's function methods (Williams *et al* 1977). However, in the present case we deal with bound-state configurations.

If the Hartree-Fock configuration ϕ_0 dominates the expansion (1) of the target ground state Ψ_T , then the overlap is

$$\langle \Psi_f | \Psi_{\rm T} \rangle = \sum_{\mu} t_{\mu 0}^{(f)} \psi_{\mu}^{\dagger} \tag{6}$$

where the sum runs only over different radial quantum numbers in the orbital set μ . The optimum single-particle potential is the one in which only one term in this sum is significant. In our example of the $\frac{1}{2}$ + structure of the argon ion this is the 3s orbital. The (e, 2e) cross section is then proportional to the spectroscopic factor

$$S_{\mu}^{(f)} = (t_{\mu 0}^{(f)})^2 \tag{7}$$

which is simply the square of the coefficient of the single-hole state in the expansion (4) of the ion eigenvector Ψ_f . The shape of the momentum profile is characterised by the orbital ψ_{μ} .

It has been demonstrated (I) that the Hartree-Fock potential is optimum in this sense, and that the Hartree-Fock configuration is sufficient to describe the argon target. There are two reasons for this. Firstly the experimental momentum profile is not distorted from its 3s form as it would be if there were significant contributions to $\langle \Psi_f | \Psi_T \rangle$ from excited target configurations. These would give terms in (3) characterised by a different orbital (e.g., 3d). A more strict test of the target Hartree-Fock assumption is satisfaction of the spectroscopic sum rule for ion eigenstates with the same quantum numbers λ ,

$$\sum_{f} S_{\mu}^{(f)} = 1 \tag{8}$$

which is obtained from the normalisation and closure relations for $\phi'_{\mu\beta}$ and Ψ_f .

Present (e, 2e) experiments do not measure absolute cross sections. Argon cross sections for $\frac{1}{2}$ + states are compared with those for $\frac{1}{2}$ - and $\frac{3}{2}$ -. Since there is only one of each of the latter (corresponding to 3p orbitals with spin-orbit splitting at about 15.76 eV), we normalise the cross sections so that their spectroscopic factors are one. With this normalisation the sum of the spectroscopic factors for the observed $\frac{1}{2}$ + states is indeed found to be one.

We take the spectroscopic factor for the lowest $\frac{1}{2}$ + state at 29.24 eV as our chief point of comparison for spectroscopies. The (e, 2e) value (I) is $S_{3s}^{29.24} = 0.58 \pm 0.06$.

The (e, 2e) reaction identifies the following further $\frac{1}{2}$ + states by their momentum profiles (energy levels are given in eV with spectroscopic factors in parentheses): 38.6(0.23), 41.2(0.13), 43.4(0.06), 48(small), 51(small). The ionisation threshold for Ar II is at 43.4 eV. Therefore about 94% of the $\frac{1}{2}$ + strength is in bound states.

3. Photoelectron spectroscopy

The approximation commonly used for an interpretation of the photoionisation (γ, e) reaction with electron energy E' and photon energy E is the dipole model:

$$\sigma(E, E') = 4\pi^2 \alpha E' \left| \langle \Psi_f | \sum_{j=1}^N r_j | \Psi_T \rangle \right|^2.$$
(9)

There are also corresponding approximations involving the velocity and acceleration operators of the electrons. This cross section is not strictly proportional to the spectroscopic factor, but the approximation is often made that it is. The same states of the argon ion are observed in the (γ , e) reaction as in the (e, 2e) reaction. If we make this assumption and use the sum rule (7) we obtain $S_{3s}^{29\cdot24} = 0.81 \pm 0.01$ (Spears *et al* 1974).

4. Diagonalisation of the argon ion Hamiltonian

Using the matrix representation (5) the argon ion Hamiltonian is

$$H = \langle \phi'_{\mu'\beta'} | H | \phi'_{\mu\beta} \rangle. \tag{10}$$

The Hamiltonian H is known in terms of the electromagnetic interactions among the electrons and the nucleus. It includes spin-orbit, spin-spin and spin-other-orbit interactions as relativistic corrections.

The independent-particle basis $\phi'_{\mu\beta}$ spans the whole space including the continuum, so the set *H* of matrix elements is infinite. In practice the basis is truncated to a subset of all the configurations formed by an inert core and several active orbitals. The set of matrix elements in this model space is $H_{\rm M}$.

$$H_{\rm M} = P_{\rm M} \langle \phi'_{\mu'\beta'} | H | \phi'_{\mu\beta} \rangle \tag{11}$$

where $P_{\rm M}$ projects onto the model space.

The model diagonalisation, of course, produces different eigenvalues and eigenvectors from the true ones. This is corrected in the model space by defining a renormalised effective Hamiltonian \overline{H} , which accounts for core polarisation and continuum effects by requiring that the set

$$\vec{H}_{\rm M} = P_{\rm M} \langle \phi'_{\mu'\beta'} | \vec{H} | \phi'_{\mu\beta} \rangle \tag{12}$$

of renormalised matrix elements in the model space produces a finite set of eigenvalues that are as close as possible to the experimental values. The matrix elements for the electrostatic interaction are written in terms of radial integrals

$$R^{k}(n_{a}l_{a}, n_{b}l_{b}; n_{c}l_{c}, n_{d}l_{d}) = e^{2} \int_{0}^{\infty} R_{n_{a}l_{a}}(r_{1})R_{n_{b}l_{b}}(r_{2}) \frac{r_{<}^{k}}{r_{>}^{k+1}}R_{n_{c}l_{c}}(r_{1})R_{n_{d}l_{d}}(r_{2}) dr_{1} dr_{2}$$

while the associated numeric coefficients can be calculated by means of the so called Racah algebra (Racah 1941, 1942, 1943). The radial integrals are treated as parameters in the energy-level fitting procedure.

 F^k and G^k parameters are defined as: $F^k(n_a l_a, n_b l_b) = R^k(n_a l_a, n_b l_b; n_a l_a, n_b l_b)$ and $G^k(n_a l_a, n_b l_b) = R^k(n_a l_a, n_b l_b; n_b l_b, n_a l_a)$.

With the same algebraic techniques the spin-orbit matrix elements are written in terms of the radial integrals (parameters):

$$\zeta(n_{\mathrm{a}}l_{\mathrm{a}}, n_{\mathrm{b}}l_{\mathrm{b}}) = \int R_{n_{\mathrm{a}}l_{\mathrm{a}}}(r)\xi(r)R_{n_{\mathrm{b}}l_{\mathrm{b}}}(r)\,\mathrm{d}r.$$

Apart from those contributions expressed in terms of the ordinary Slater parameters, Luyken (1972) used the two well known effective interactions (Rajnak and Wybourne 1963):

$$\alpha(n_a l_a) L(L+1)$$
 and $\beta(n_a l_a) S(S+1)$.

They have been introduced to take into account the interactions with many farlying configurations. This procedure in which α and β are treated as parameters and the expressions L(L+1) and S(S+1) as coefficients is normally called model interaction.

L and S are the quantum numbers of the final state which means that the parameters α and β contain the effects of excitations of two electrons out of the p orbital as well as out of other active orbitals.

In the present calculation all bound eigenvalues with even parity are fitted by diagonalising submatrices for J = 0.5 to 4.5. Experimental values are those of Minnhagen (1963). The active orbitals used are 3s, 4s, 3p, 3d and 4d. Initial estimates of parameters are obtained by scaling integrals of Hartree-Fock orbitals, determined by Froese Fischer's (1972) program.

All parameters have been listed in table 1. Probably they are defined in the same way as those of Luyken, apart from the *E* parameters (configuration energy). The RMS deviation has been considerably reduced in our calculations by introducing a parameter $\alpha(4s)$. The values under the heading 'Luyken' are the final values obtained by Luyken in his energy-level fit. The third column, labelled 'HF value', gives the values obtained using the Froese Fischer program. The last column gives our final values.

The model space is chosen to include four configurations, so that there are 14, 19, 18, 10 and 4 basis states for J = 0.5, 1.5, 2.5, 3.5 and 4.5, respectively. A total of 60 levels are fitted first, by varying simultaneously 29 of the set of 30 parameters. The parameter $R^{1}(3p, 4s; 3d, 3p)$, being badly determined, has been adjusted in a final independent calculation.

The energy levels are reproduced by the calculation with at least three-figure accuracy. The greatest deviation is 350 cm^{-1} . The number of levels for which the deviation is greater than 200 cm^{-1} is 12. These deviations have a negligible effect on the $\frac{1}{2}$ + eigenvectors.

Parameter	Luyken (1972)	HF value	This work
$\overline{E (3s^2 3p^4 3d)}$	191133(517)		168322(253)
$E (3s^2 3p^4 4d)$	220597(423)		198260(279)
$E (3s^2 3p^4 4s)$	172881(626)		148762(195)
E (3s3p ⁶)	141892(408)		142341(485)
$F_{3d}^2(3p, 3p)$	56300(887)	66425	52861(574)
$F_{4d}^2(3p, 3p)$	55825(650)	68025	55870(772)
$F_{4s}^2(3p, 3p)$	57075(1062)	67825	53000(388)
F^{2} (3p, 3d)	30765(609)	38185	31519(733)
F^{2} (3p, 4d)	12915(599)	8295	12399(711)
G^{1} (3p, 3d)	27555(351)	45510	27859(442)
G^{1} (3p, 4d)	7350(516)	8805	6742(637)
G^{1} (3p, 4s)	3783(714)	4083	3845(191)
G^{3} (3p, 3d)	18130(1005)	26705	18281(1252)
G^{3} (3p, 4d)	10364(735)	5390	9679(893)
$\zeta_{3d} (3p, 3p)$	1003(117)	957	1130(139)
ζ_{4d} (3p, 3p)	1148(146)	996	1090(182)
ζ_{4s} (3p, 3p)	1048(148)	995	1055(181)
ζ (3d, 3d)	6.1(55)	12.6	18.8(61)
ζ (4d, 4d)	8.3(52)	3.2	20.7(64)
R^2 (3p, 3d; 3p, 4d)	15750(777)	14857	15124(1001)
R^{1} (3p, 3d; 4d, 3p)	16470(267)	19697	16426(328)
R ³ (3p, 3d; 4d, 3p)	21633(1372)	11795	19591(1656)
R ² (3p, 4s; 3p, 3d)	-2975(279)	-6075	-3120(466)
R^1 (3p, 4s; 3d, 3p)	(988)		(1178)
R ¹ (3p, 3p; 3s, 3d)	42858(611)	62078	43690(704)
R ¹ (3p, 3p; 3s, 4d)	29548(774)	27454	28511(956)
α (3d)	54.7(12.7)		78.1(12.7)
α (4d)	28.0(15.1)		18.6(18.5)
α (4s)	0		269(61)
β (3d)	486(76)		279(77)
Δ (RMS)	167		203

Table 1. Parameters and RMS deviations for $3s^23p^43d+3s^23p^44d+3s^23p^44s+3s3p^6$ configurations.

The calculation is illustrated by table 2, which shows the energy-level comparison and the principal components of the eigenvectors for the $\frac{1}{2}$ + states. The first and second columns give, respectively the experimental (E_{ex}) and calculated (E_{calc}) energy levels in cm⁻¹. The third column gives the deviation

$$\Delta = E_{\rm ex} - E_{\rm calc}.\tag{13}$$

In the fourth column we show the separation energy in eV for the states relevant to the (e, 2e) reaction, that is those with a significant contribution from the 3s-hole configuration, denoted $3s^{-1}(^2S)$. The last four columns give the squared coefficients $(t_{\mu\beta}^{(f)})^2$ for the four most important states in each eigenvector, called state expectation values. These numbers sum to one for each eigenvector and for each basis vector state.

The spectroscopic factor in this notation is the state expectation value for the basis state $3s^{-1}(^2S)$. For the 29.24 eV state, $S_{3s}^{29.24} = 0.61$.

Some insight into the validity of an *ab initio* shell-model calculation in the present model space is given by comparing some of the initial values of the Slater integrals obtained from Hartree–Fock orbitals with their effective values determined by fitting **Table 2.** Details of the $J\pi = \frac{1}{2} +$ states of Ar II in the diagonalisation of the Hamiltonian matrix. The column headings are described in the text.

				3		۰ ۱		
$E_{\mathrm{ex}}(\mathrm{cm}^{-1})$	$E_{ m calc}(m cm^{-1})$	$\Delta(\text{cm}^{-1})$	$\epsilon_{\rm s}({ m eV})$		Stat	e probabiliti c s		
205242-97	205245	-2	41.20	$0.75 4d(^{1} D)^{2} S$	$0.20 \ 3s^{-1}(^2S)$	0-05 3d(¹ D) ² S		
199446-54	199311	135		$0.88 4d(^{1}D)^{2}P$	$0.08 4d(^3 P)^2 P$	$0.04 \ 3d(^{3}P)^{2}P$		
189934-55	189809	125		$0.75 4d(^3 P)^2 P$	$0.15 \mathrm{3d}(^{1}\mathrm{D})^{2}\mathrm{P}$	$0.08 4d(^{1}D)^{2}P$	$0.01 \ 3d(^3P)^2P$	
186171-26	186031	140	ė	$0.88 4d(^3 P)^4 P$	0-05 3d(³ P) ⁴ P	$0.03 \ 3d(^{1}D)^{2}S$	$0.02 4d(^{3}P)^{4}D$	
184191-71	184272	-81	38-61	$0.78 4d(^{3}P)^{4}D$	$0.08 \ 3d(^3 P)^4 D$	0-08 3d(¹ D) ² S	$0.02 \ 3s^{-1}(^2S)$	
184093-06	184103	-10	38-58	$0.51 3d(^{1}D)^{2}S$	$0.164d(^{1}D)^{2}S$	$0.15 3s^{-1}(^2S)$	$0.07 4d(^3P)^4D$	
174820-93	174703	118		$0.49 \ 3d(^3 P)^2 P$	$0.37 \ 3d(^{1}D)^{2}P$	$0.13 4d(^3 P)^2 P$		
167307-92	167294	14		0-99 4s(¹ S) ² S	0-01 3d(¹ D) ² S	$0.01 \ 3s^{-1}(^2S)$		
147227-97	147008	220		0-94 3d(³ P) ⁴ P	0.05 4d ⁽³ P) ⁴ P	$0.01 4s(^{3}P)^{4}P$		
144709-91	144742	-32		$0.48 \ 3d(^{1}D)^{2}P$	$0.44 \ 3d(^{3}P)^{2}P$	$0.04 4d(^{1}D)^{2}P$	$0.03 4d(^3 P)^2 P$	
139258-25	139238	20		$(0.98 4 s(^3 P)^2 P)^2$	$0.01 \ 3d(^3P)^2P$			
135601-65	135608	L		$0.99 4s(^{3}P)^{4}P$	0-01 3d(³ P) ⁴ P			
132737-91	132784	-46		0-91 3d(³ P) ⁴ D	$0.09 4d(^3P)^4D$			
108721-47	108719	2	29-24	$0.61 \ 3s^{-1}(^2S)$	$0.32 \ 3d(^{1}D)^{2}S$	$0.07 4d(^{1}D)^{2}S$		

	Eigenvector		
Eigenvalue (eV)	$3s^{-1}(^2S)$	$3d(^{1}D)^{2}S$	$4d(^{1}D)^{2}S$
30.4	0.734	0.533	0.422
38.8	0.494	-0.844	0.207
41.2	0.466	-0.502	-0.883
29.24	0.781	0.569	0.255
38.58	0.385	-0.713	0.420
41.20	0.450	-0.232	-0.861

Table 3. Comparison of eigenvectors for the main states observed by (e, 2e) calculated by fitting (e, 2e) data with a three-term basis and by fitting energy levels with a fourteenterm basis.

energy levels (see table 1, columns 3 and 4). The effective values are always of the same order of magnitude, but differences of about 30% are common. Scaling factors, e.g. those known from analogous spectra, have been used in finding effective values.

5. A collective model sub-basis

A very interesting insight into atomic structure is provided by examining the eigenvectors in the model diagonalisation of the states observed by (e, 2e). Neglecting state probabilities less than about 0.05 (and therefore neglecting the 38.61 eV state), we notice that the three states at 29.24 eV, 38.58 eV and 41.20 eV are all described by a three-term basis $3s^{-1}(^2S)$, $3d(^1D)^2S$ and $4d(^1D)^2S$, so that the structure can be approximately evaluated by diagonalising an effective Hamiltonian in this sub-basis.

The configurations in the sub-basis may be considered in terms of a collective model. The first represents the direct knockout of an electron with orbital quantum numbers $\mu = 3s$ from a target state with quantum numbers $\beta = 0+$. The second and third, respectively, represent the knockout of a 3d and 4d electron from a target state $\beta = 2+$. This can be considered as a vibrational excitation of the target, thus giving a tentative physical explanation for the dominance of these configurations.

If one uses the three-term sub-basis for diagonalisation of the Hamiltonian for these three states then there are six independent matrix elements and six experimentally determined quantities, three eigenvalues and three spectroscopic factors. One therefore has a means of determining approximate experimental values of all the coefficients in the three-term eigenvectors for the three states from the (e, 2e) experiment. This calculation is reported in I. It is compared with the relevant part of the full diagonalisation in table 3. The same phase convention is used for both cases.

6. Comparison and conclusions

We first consider the validity of the assumptions made in using the various spectroscopies as a measure of the structure of the Ar II ion.

The ionisation spectroscopies, (e, 2e) and (γ , e), observe certain states of Ar II, namely those that have a significant component of the 3p-hole or 3s-hole configurations. Use of particular orbitals to form the basis already implies a particular single-particle model. The first great advantage of the (e, 2e) reaction is that it selects a particular orbital set, namely the Hartree–Fock orbitals, by the fact that they give the experimental momentum profiles for 3p and 3s cases.

States with $J\pi$ not equal to the single-hole values $\frac{1}{2} - , \frac{3}{2} - , \frac{1}{2} + may$ be excited either if there are significant components of excited configurations in the Ar I ground state or if the reaction is capable of exciting such configurations in 'two-step' processes in which the distorted waves $\chi^{(\pm)}$ have inelastic as well as elastic components. In the present case both these effects are small. This is shown by the absence of states that can be identified by momentum profiles as having 'forbidden' values of $J\pi$. It is confirmed by the satisfaction of the spectroscopic sum rule. Note that in the case of helium, forbidden states are identified. They give a very sensitive measure of correlations in the helium ground state (Dixon *et al* 1976).

The whole of the $\frac{1}{2}$ + strength of Ar II is identified by (e, 2e). About 6% of it is not identified as a model space state, so it is due to contributions either from the collective *n*d series ($n \ge 5$), or from the continuum, both of which are compatible with the obtained energy value.

Momentum profile shapes have not been observed for the (γ, e) reaction. Because of kinematic restrictions, variation of q requires variation of the incident energy. This means that a very detailed description of the reaction mechanism would be required to obtain reliable confirmation of a particular structure model. It would enhance the use of photoelectron spectroscopy if there were a simple proportionality relationship between spectroscopic factors and cross sections. If there is, then there is a conflict between (γ, e) and (e, 2e), for which $S_{3s}^{29\cdot24} = 0.81 \pm 0.01$ and 0.58 ± 0.06 , respectively. However, the analysis of (γ, e) does not so far have the advantage of a correct description of momentum profiles or the satisfaction of the spectroscopic sum rule that the analysis of (e, 2e) has. The conflict is resolved by the diagonalisation of the effective Hamiltonian, which produces the value $S_{3s}^{29\cdot24} = 0.61$, thus giving further confirmation of the validity of (e, 2e) spectroscopy.

The matrix diagonalisation description of conventional spectroscopy suffers from a disadvantage. It does not attempt to describe all the structure of the ion for a particular $J\pi$, since continuum states are not normally observed. In the case of the $\frac{1}{2}$ + structure of Ar II only about 6% of the strength is not found in the model space, so one would expect close correspondence between the spectroscopic factors and those of (e, 2e). However, since the 6% high-energy strength is forced into the model space states, one must expect spectroscopic factors for the higher-energy states

Eigenvalue (eV)		Spectroscopic factor	
Diagonalisation	(e, 2e)	Diagonalisation	(e, 2e)
29·24 38·58)	29.3 ± 0.1	0.61 0.15)	0·58 ± 0·06
38.61	38.6 ± 0.1	0.02	0.23 ± 0.02
41.20	$ \begin{array}{r} 41.2 \pm 0.2 \\ 43.4 \pm 0.1 \\ 48 \end{array} $	0.20	0.13 ± 0.02 0.06 ± 0.02 small
	51		small

Table 4. Comparison of eigenvalues and spectroscopic factors determined by (e, 2e) and diagonalisation of the effective Hamiltonian.

to be somewhat unrealistically high. This distortion of the eigenvectors would continue down to the lower eigenvectors, but one would not expect it to affect the lowest eigenvector (29.24 eV) very much. Hence the use of this state as our main point of comparison. The detailed comparison of spectroscopic factors for (e, 2e) and the diagonalisation is given in table 4. The discrepancies would of course be reduced by including more terms in the basis.

In view of the limitations of both methods the correspondence of the relevant eigenvector state probabilities for (e, 2e) and the analysis of spectra is very satisfactory. With the availability of cross checks from momentum profiles and the spectroscopic sum rule, one might expect the (e, 2e) values to represent the best estimates of the spectroscopic factors. Photoelectron spectroscopy awaits experiments with varying incident energy and a detailed description of the reaction mechanism before it can provide the same information. The analysis of spectra, of course, gives a much more complete description of the structure of Ar II, since it takes into account many bound states that cannot be observed in the ionisation spectroscopies.

Acknowledgment

One of us (IEMcC) would like to thank Professor Dr J Kistemaker for the hospitality of the FOM Institute, where this work was begun.

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