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Scalar scattering of light on the 3p and 3s subshells of the argon atom (Stokes scattering) and anti-Stokes scattering on the excited 4p and 4s states of argon are examined in the Hartree-Fock approximation. The calculation is made in a "velocity" form and in a "length" form. It is shown that the value in the "r" form is 1.5-2 times greater than in the "Δ" form.

1. The Raman effect is one of the fundamental two-photon processes, and to evaluate it requires knowledge of the Green function of an electron moving in the Coulomb field of a nucleus and the self-consistent field of the atomic electrons. The presently available studies of this process are limited mainly to an examination of the Raman effect on the simplest possible object, the hydrogen atom, where, by using integral representations of the Green function, it is possible to obtain an analytic expression for both the bound-bound and the bound-free transitions [1]. The results obtained this way may be used to some extent to study more complicated atoms with the aid of the quantum defect method [2], which is successful for sufficiently high excited levels in the alkali atoms. This method, however, is inadequate for atoms with a large number of electrons in the outer shell and becomes manifestly unsuitable for noble gas atoms, as is indicated by the completely unhydrogenlike behavior of their photoionization cross section [3]. In these atoms it is not possible to replace the complicated self-consistent field in which the excited (or ionized) electron moves with the Coulomb field of a single charge, and the field of the nucleus and the atomic electrons must be taken accurately into account. This is done with the aid of the Hartree-Fock method, which is the best approximation and compatible with the idea of independent motion by the atomic electrons. The purpose of this paper is to apply the Hartree-Fock approximation to the Raman effect on an atom for which the quantum defect method is clearly inadequate and more complex calculations are thus required.

Here it is shown that these calculations are fully capable of being done and allow us to obtain results for a very complex multielectron atom such as argon. The choice of argon is explained by the fact that it has been well studied in atomic spectroscopy and is often used as an object of experimental research.

The calculations were done for the principal electronic transitions, from the outer 3p and 3s subshells into the discrete 4p and 4s states in Stokes scattering and from the 4p and 4s into the 3p and 3s states in anti-Stokes scattering.

2. The Raman effect involves the absorption of a photon with frequency ω_1 , wave vector κ_1 , and polarization \mathbf{e}_1 and emission of a photon with characteristics ω_2 , κ_2 , \mathbf{e}_2 . The atom may then either remain in its initial state (Rayleigh scattering) or go into a discrete excited state. In the latter case the frequency of the emitted photon differs from that of the incident photon by an amount equal to the difference in energy between the initial, E_1 , and final, E_2 , states of the atom. If $\omega_2 > \omega_1$, the scattering is referred to as anti-Stokes scattering, while if $\omega_2 < \omega_1$, it is known as Stokes scattering.

The Raman effect cross section is given by [4]

$$d\sigma = d\sigma^0 + d\sigma^a + d\sigma^s, \quad (1)$$

where

$$d\sigma^0 = \frac{\omega_1 \omega_2^3}{c^4} G_{21}^0 (\mathbf{e}_1 \mathbf{e}_2)^2 d\Omega, \quad d\sigma^s = \frac{1}{10} \frac{\omega_1 \omega_2^3}{c^4} G_{21}^s \left[1 + \frac{1}{3} (\mathbf{e}_1 \mathbf{e}_2)^2 \right] d\Omega, \quad (2)$$

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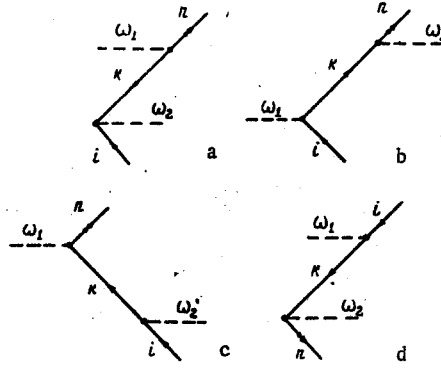


Fig. 1. Diagrams for Stokes Raman effect.

$$d\tau^a = \frac{1}{6} \frac{\omega_1 \omega_2^3}{c^4} G_{21}^a [1 - (e_1 e_2)^2] d\Omega \quad (2)$$

are the scalar, symmetric (quadrupole), and antisymmetric (magnetic) scattering components. The quantities G_{21}^0 , G_{21}^S , and G_{21}^A are related to the scattering tensor, $\alpha_{\lambda\gamma}$ ($\lambda, \gamma = x, y, z$), as follows:

$$G_{21}^0 = \frac{1}{2I_1 + 1} \sum_{M_1 M_2} |\alpha_{21}^0|^2, \quad G_{21}^S = \frac{1}{2I_1 + 1} \sum_{M_1 M_2} \sum_{\lambda_1} |(\alpha_{\lambda_1}^S)_{21}|^2, \quad (3)$$

$$G_{21}^A = \frac{1}{2I_1 + 1} \sum_{M_1 M_2} \sum_{\lambda_1} |(\alpha_{\lambda_1}^A)_{21}|^2.$$

Here α^0 , $\alpha_{\lambda\gamma}^S$, and $\alpha_{\lambda\gamma}^A$ are the irreducible parts of the scattering tensor; summation is over the projection of the momenta, I_1 and I_2 ; c is the speed of light; and, the atomic system of units is used ($\hbar = e = m = 1$).

3. We now consider scattering with the atom undergoing a transition from the ground state Ψ_0 into a discrete state Ψ_n . In this case Stokes scattering occurs since part of the incident photon energy goes into exciting the atom.

In the Hartree-Fock approximation the scattering tensor has the form [5]

$$(\alpha_{\lambda\gamma}^{\text{st}})_{ni} = \sum_{\kappa > F} \left[\frac{\langle n | d_\lambda | \kappa \rangle \langle \kappa | d_\gamma | i \rangle}{\varepsilon_\kappa - \varepsilon_n + \omega_1 + i\delta} + \frac{\langle n | d_\gamma | \kappa \rangle \langle \kappa | d_\lambda | i \rangle}{\varepsilon_\kappa - \varepsilon_i - \omega_1 + i\delta} \right] + \sum_{\kappa \leq F} \left[\frac{\langle n | d_\gamma | \kappa \rangle \langle \kappa | d_\lambda | i \rangle}{\varepsilon_\kappa - \varepsilon_n + \omega_1 - i\delta} + \frac{\langle n | d_\lambda | \kappa \rangle \langle \kappa | d_\gamma | i \rangle}{\varepsilon_\kappa - \varepsilon_i - \omega_1 - i\delta} \right]. \quad (4)$$

Here $\langle n |$ and $| \kappa \rangle$ are the Hartree-Fock electron wave functions.

The summation over κ in Eq. (4), which includes $| \kappa \rangle \langle \kappa |$, and the denominator form the Green function of an electron ($\kappa > F$) or hole ($\kappa \leq F$) in the self-consistent Hartree-Fock field of the atom. Thus, the Raman effect amplitude is determined by the single-electron Green function.

The individual terms, $\alpha_{\lambda\gamma}$, are shown in Fig. 1 as diagrams, where *a*, *b*, *c*, and *d* correspond to the first, second, third, and fourth terms in Eq. (4).

We have used Goldstone diagrams which differ from Feynman diagrams in that they have time ordering of the events shown. In Fig. 1 time increases from left to right.

After separation of the angular parts of Eq. (4) and summation over the projections of the orbital angular momentum of the electrons, *i* and *n*, we have

$$G_{ni}^0 = \frac{1}{9(2I_i + 1)^2} \sum_{ll'} \alpha_i^0 \alpha_{l'}^{0*} \delta_{li} \delta_{l'n},$$

$$G_{ni}^S = \frac{1}{(2I_i + 1)} \sum_{ll'} \sum_{j=0,2} \alpha_i^j \alpha_{l'}^{j*} \left[(2j+1) \begin{Bmatrix} 1 & j & 1 \\ I_i & l & I_n \end{Bmatrix} \begin{Bmatrix} 1 & j & 1 \\ I_i & l' & I_n \end{Bmatrix} - \frac{1}{3(2I_i + 1)} \delta_{li} \delta_{l'n} \right], \quad (5)$$

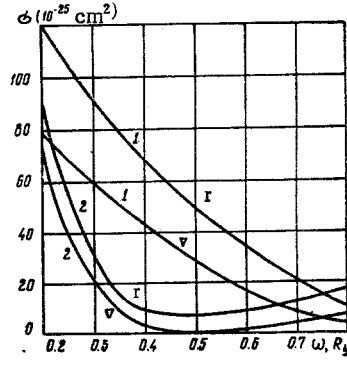


Fig. 2. The anti-Stokes Raman effect cross section: (1) scattering on the 4p state; (2) scattering on the 4s state; (r) length form; (v) velocity form.

$$G_{ni}^a = \frac{3}{(2l_i + 1)} \sum_{ll'} \alpha_i^a \alpha_{i'}^{a*} \begin{Bmatrix} 1 & 1 & 1 \\ l_i & l & l_n \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 1 \\ l_i & l' & l_n \end{Bmatrix},$$

where the tensors α_l^0 , α_l^S , and α_l^a have the form

$$\alpha_{l\kappa}^0 = \alpha_{l\kappa}^S = \sum_{\kappa > F} \langle n \| r \| \kappa \rangle \langle \kappa \| r \| i \rangle \left[\frac{1}{\varepsilon_\kappa - \varepsilon_n + \omega_1 + i\delta} + \frac{1}{\varepsilon_\kappa - \varepsilon_i - \omega_1 + i\delta} \right] + \sum_{\kappa < F} \langle n \| r \| \kappa \rangle \langle \kappa \| r \| i \rangle \left[\frac{1}{\varepsilon_\kappa - \varepsilon_n + \omega_1 - i\delta} + \frac{1}{\varepsilon_\kappa - \varepsilon_i - \omega_1 - i\delta} \right], \quad (6)$$

$$\alpha_{l\kappa}^a = \sum_{\kappa > F} \langle n \| r \| \kappa \rangle \langle \kappa \| r \| i \rangle \left[\frac{1}{\varepsilon_\kappa - \varepsilon_i + \omega_1 + i\delta} - \frac{1}{\varepsilon_\kappa - \varepsilon_n + \omega_1 + i\delta} \right] + \sum_{\kappa < F} \langle n \| r \| \kappa \rangle \langle \kappa \| r \| i \rangle \left[\frac{1}{\varepsilon_\kappa - \varepsilon_i + \omega_1 - i\delta} - \frac{1}{\varepsilon_\kappa - \varepsilon_n + \omega_1 - i\delta} \right]. \quad (7)$$

In Eqs. (6) and (7) $\langle \kappa \| r \| \kappa_2 \rangle$ denotes the reduced matrix element in the form of a "length." The "velocity" form [3] was also used in the calculations.

4. We now determine the cross section for the Raman effect on an excited state. Here both Stokes and anti-Stokes scattering may take place. A long-lived excited state may be produced, for example, by exciting an electron with simultaneous reversal of its spin (triplet states). It is also possible to study metastable states since modern lasers can ensure a high population of excited levels.

In this case it is experimentally easier to observe anti-Stokes scattering with a transition into the ground state and we shall examine this. Then the scattering tensor may be obtained by changing the signs in front of ω_1 in Eqs. (6) and (7).

The coupling between the cross sections for Stokes and anti-Stokes Raman effect determined by the principle of detailed balance does not exist since the relation $M_{in} = M_{ni}^*$ for the Raman effect amplitudes is not fulfilled here according to Eq. (4).

5. Calculations were done for the $3p \rightarrow 4p$, $3s \rightarrow 4s$ transitions in Stokes and the $4p \rightarrow 3p$, $4s \rightarrow 3s$ transitions in anti-Stokes Raman effect on the Ar atom. Of course, it is possible to examine other transitions from the 3p subshell, for example, into the 5p, 6p, and so on, or $3p \rightarrow nf$ ($n = 4, 5, \dots$). Our choice of just the $3p \rightarrow 4p$, $3s \rightarrow 4s$ transition is because these are the principle excitations of both outer subshells. Experimentally they are easier to detect since their excitation energy is greatest. The calculations are done for scalar scattering in which the excited state term must coincide with the ground state term and the electron does not change its quantum number l . Thus, we examine only the monopole excitations $3p \rightarrow 4p$, $3s \rightarrow 4s$. In this case it is necessary to orthogonalize the 4p and 4s functions to the (electron) core function, as opposed to the case of the

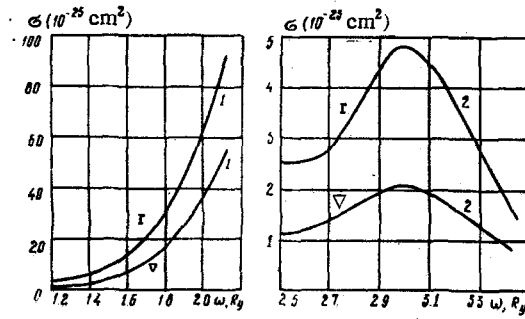


Fig. 3. The Stokes Raman effect cross section: (1) scattering on the 3p subshell; (2) scattering (multiplied by 100) on the 3s subshell; (r) length form; (v) velocity form.

quadrupole transitions ($3p \rightarrow 4f$, $3s \rightarrow 3d$), where the d and f functions are automatically orthogonalized thanks to the angular terms.

The scalar scattering cross section is given in terms of G_{ni}^0

$$d\sigma^0 = \frac{r_e^2}{4} \omega_1 \omega_2^3 G_{ni}^0 (e_1 e_2)^2 d\Omega = \frac{r_e^2}{4} \frac{\omega_1 \omega_2^3}{9(2l_i + 1)^2} \sum_{ii'} \alpha_i^0 \alpha_{i'}^{0*} (e_1 e_2)^2 d\Omega, \quad (8)$$

where r_e is the classical electron radius, and the factor of $1/4$ appears because the energy is measured in Rydbergs. When the incident photons are linearly polarized the scattered light contains two independent components polarized in the $\kappa_2 e_1$ plane and perpendicular to it. The total cross section, integrated over the angle of the emitted photon and summed over the polarizations, has the form

$$d\sigma^0 = \frac{2}{3} \pi r_e^2 \frac{N_i \omega_1 \omega_2^3}{9(2l_i + 1)^2} \sum_{ii'} \alpha_i^0 \alpha_{i'}^{0*}, \quad (9)$$

where N_i is the number of electrons in the i -th subshell.

6. We now discuss those details of the calculation that are of sufficiently general interest.

The wave functions of the excited states were determined in the field of the "frozen" (electron) core with a hole in either the 3p or the 3s subshell, depending on the transition being considered. This is basically an exception to the strict single-particle Hartree-Fock approximation [3]. The denominators in the diagrams of Fig. 1a, b may go to zero for certain energies of the incident quantum. In the case of discrete intermediate states this divergence is eliminated by taking the intrinsic width of the level into account and pertains to resonance fluorescence.

The Raman effect cross section then has sharp maxima and deep (almost to zero, which is attainable if the intrinsic width is neglected) minima. The resonance fluorescence profiles can easily be found since they are determined by the matrix elements of the dipole operator which we have calculated. In the following we shall discuss frequencies ω_1 outside the resonance fluorescence region.

In the continuous spectral region the integration is done with the aid of the formula

$$\int \frac{f(x) dx}{x - a - i0} = P \int \frac{f(x) dx}{x - a} + i\pi f(a). \quad (10)$$

The imaginary part of the Raman effect amplitude is, therefore, the product of the amplitudes for photoionization of the ground and excited states. Neglecting the real part, the Raman effect cross section is given by the product of the photoionization cross sections. The calculations showed, however, that at low energies of the incident photon the imaginary part α_2 is much less than the real part. As the quantum energy is increased the imaginary part begins to increase, sometimes reaching an absolute value of half the real part, and then begins to fall again. α_0 behaves differently. At low energies, $\text{Im} \alpha_0$ exceeds the real part by several times and becomes of equal magnitude at high energies. In the $3s \rightarrow 4s$ transitions the real part of α_1 is greater than $\text{Im} \alpha_1$ at first and then the two parts are equal. Thus, the question of neglecting the real part is very complicated and may be answered only by doing specific calculations.

In the $3p \Rightarrow 4p$ transitions the value of the tensor α_2 is usually greater than α_0 . Then diagram 1b makes the major contribution to α_2 . In it the portion of discrete nd levels is great, in particular, the 3d level, since the matrix element $\langle 4p || r || 3d \rangle$ is large (11.1 in the "length" form) and the difference $\varepsilon_{4p} - \varepsilon_{3d}$ is small.

The fact that the contributions from the discrete and continuous spectra have opposite sign is of special interest. This is caused by a change in the sign of the dipole matrix element $\langle 4p || r || \varepsilon d \rangle$ immediately after the ionization threshold for the 4p state. A second sign change near $\varepsilon = 3.61$ Ry has practically no effect on the contribution to the Raman effect cross section since in this region the matrix elements are two orders of magnitude smaller than near the ionization threshold.

This double sign change leads to two minima in the photoionization cross section of the 4p state. The results of the calculations of the Raman effect are shown in Fig. 2 (anti-Stokes) and Fig. 3 (Stokes). Let us consider the scattering cross section on the 3p subshell. The product $\omega_1 \omega_2^3$ increases as ω_1 is increased. If the scattering tensor also increases, then Stokes scattering occurs and the cross section increases with ω_1 . With anti-Stokes scattering α falls rapidly. As a consequence the cross section also falls.

The nature of the cross section on the 3s subshell is somewhat different. In Stokes scattering the cross section increases slowly, reaching a maximum at $\omega_1 = 3.02$ Ry, and then falls rapidly. In the case of anti-Stokes scattering the cross section decreases rapidly, reaching a minimum at $\omega = 0.4$ Ry, and then begins to rise slowly.

The calculation was done in the "length" r and "velocity" ∇ forms. The cross section in the " r " form was 1.5-2 times larger than in the " ∇ " form in all cases considered. However, it should be noted that the difference between the two forms, as opposed to the single-particle computation of single-photon processes, may be small, although the difference in each diagram it may be very large. This may appear especially clearly when the contributions of the different diagrams are of the same order (but different sign). If the contribution of some diagram dominates or one diagram remains after compensation, the difference between the forms may show up.

It is clear from the diagrams of Fig. 1 that the Raman effect may be regarded as a sort of combination photoionization from the ground and excited states since vertices for these processes are included in the diagrams for combination scattering. For this reason it is to be expected that multielectron correlations, whose contribution to photoionization of the outer shells of noble gas atoms is large [3], should be important in the Raman effect. Here it has been shown that the computational difficulties met in determining the Raman effect cross sections for complex atoms may be overcome. A single-electron Hartree-Fock calculation using the techniques of quantum field theory (perturbation theory, the random phase method with interchange) is the usual first step in the computation. Next, the interelectronic interaction is made more precise since it, as shown in studies of photoionization from outer shells of noble gas atoms [3], may change the cross section by a very large amount. It is natural to expect that multielectron correlations will also be important in the Raman effect cross section. Then more complicated diagrams than those in Fig. 1 will make a serious contribution to the cross section.

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