# Rayleigh and Raman scattering by hydrogen and caesium

H R Sadeghpour and A Dalgarno

Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, USA

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Abstract. An inhomogeneous differential equation method is used to calculate the Rayleigh and Raman scattering cross sections for atomic hydrogen and atomic caesium as functions of wavelength below and above the ionization limits. The profile of the scattering cross section near the 6s-6p resonance of atomic caesium is determined by including an energyindependent radiative width in the scattering formula. The effect of replacing the electric dipole operator by a modified form that takes account of the polarization of the core by the valence electron is explored.

#### 1. Introduction

Rayleigh and Raman scattering are important phenomena in the study of solids, liquids and gases. In gases, Rayleigh scattering is a source of extinction in planetary and stellar atmospheres and Raman scattering is a source of emission. Both are two-photon processes in which an incident photon is scattered. In Rayleigh scattering the scattered and incident photons have the same frequency and the process is elastic. In Raman scattering, the frequencies differ and the process is inelastic.

Raman scattering may be a useful diagnostic probe of plasmas containing sources of ultraviolet radiation because it converts the incident ultraviolet photons into photons of longer wavelength that may be more readily detectable. Recently Raman scattering has been identified as a source of emission in symbiotic stars (Schmid 1989, Schmid and Schild 1990). Features at 683.0 nm and 788.8 nm in the spectrum of the star He 2-38 have been attributed to Raman scattering of the resonance lines of  $O^{5+}$  at 103.2 nm and 103.8 nm by atomic hydrogen in an inelastic event, terminating in the 2s level.

Two-photon processes were first described by the Kramers-Heisenberg formula (Kramers and Heisenberg 1925) which expresses the scattering in terms of an expansion over the complete set of intermediate discrete and continuum states of the atomic or molecular system. The formula has been used by Saslow and Mills (1969), Isliker *et al* (1989) and Nussbaumer *et al* (1989) to calculate the Raman cross section for scattering from the 1s to the 2s state of atomic hydrogen. The Rayleigh scattering cross section has been calculated by Gavrila (1967) with a procedure specific to atomic hydrogen that employs an analytic representation of the Coulomb Green function implicit in the Kramers-Heisenberg formula.

An alternative general procedure was used by Tannor and Heiler (1982) in which the emission spectrum is written as the Fourier transform of an autocorrelation function (cf Dalgarno 1966). The procedure avoids the infinite summation of the Kramers-Heisenberg formula but requires instead the numerical solution of a time-dependent Schrödinger equation. It provides the spectra at all frequencies in a single calculation, but is inconvenient in the case of a Coulomb interaction. We employ here another method, based on the differential equation technique of Dalgarno and Lewis (1955) which also avoids the infinite summation. It involves the direct solution of an equation in which the frequency is a parameter and Raman and Rayleigh scattering cross sections can be calculated exactly for any atomic and molecular system characterized by a central field. The method has been used previously in calculations of multiphoton ionization (Aymar and Crance 1980, 1981). We present scattering cross sections for atomic hydrogen and caesium and we discuss the structure of the response wavefunctions that arise in the application of the method.

## 2. Formulation

Suppose  $\omega$  and  $\omega'$  are the initial and final photon energies respectively and  $\varepsilon_a$  and  $\varepsilon_b$  are the initial and final photon polarization vectors. Then the differential cross section for Rayleigh or Raman scattering of photons into the solid angle  $d\Omega$  by an atom in initial state with eigenfunction  $|a\rangle$  and eigenvalue  $E_a$  into the final state with eigenfunction  $|b\rangle$  and eigenvalue  $E_b$  is given by

$$\frac{\mathrm{d}\sigma(\omega)}{\mathrm{d}\Omega} = (\frac{1}{137})^4 \omega \omega'^3 |(\hat{\boldsymbol{\varepsilon}}_a \cdot \hat{\boldsymbol{\varepsilon}}_b)^2 \boldsymbol{M}_{ab}(\omega)|^2 a_0^2 \tag{1}$$

where  $\omega - \omega' = E_b - E_a$  and

$$\boldsymbol{M}_{ab}(\boldsymbol{\omega}) = \sum_{t} \left( \frac{\langle \boldsymbol{a} | \boldsymbol{r} | t \rangle \langle t | \boldsymbol{r} | b \rangle}{E_{a} + \boldsymbol{\omega} - E_{t} - i\Gamma_{t}/2} + \frac{\langle \boldsymbol{a} | \boldsymbol{r} | t \rangle \langle t | \boldsymbol{r} | b \rangle}{E_{a} - \boldsymbol{\omega}' - E_{t}} \right)$$
(2)

in which  $|t\rangle$  is an intermediate state eigenfunction with eigenvalue  $E_t$  and  $\Gamma_t$  is the decay width of the state  $|t\rangle$ . The total scattering cross section is obtained by integrating over the solid angle and summing over the polarization directions as

$$\sigma(\omega) = \frac{8\pi a_0^2}{3(137)^4} \omega \omega'^3 |\mathbf{M}_{ab}(\omega)|^2$$
(3)

where the frequencies are in atomic units.

We introduce the response wavefunctions

$$\chi_a(\omega, \mathbf{r}) = \sum_t \frac{|t\rangle \langle t|\mathbf{r}|a\rangle}{E_a + \omega - E_t}$$
(4*a*)

and

$$\chi_b(\omega, \mathbf{r}) = \sum_t \frac{|t\rangle \langle t|\mathbf{r}|b\rangle}{E_b - \omega - E_t}.$$
(4b)

Then

$$\boldsymbol{M}_{ab}(\boldsymbol{\omega}) = \langle b | \boldsymbol{r} | \chi_a(\boldsymbol{\omega}, \boldsymbol{r}) \rangle + \langle \chi_b(\boldsymbol{\omega}, \boldsymbol{r}) | \boldsymbol{r} | \boldsymbol{a} \rangle.$$
<sup>(5)</sup>

Expressions (4a) and (4b) are equivalent to the differential equations

$$(H - E_a - \omega)\chi_a(\omega, \mathbf{r}) = -\mathbf{r}|a\rangle \tag{6a}$$

$$(H - E_b + \omega)\chi_b(\omega, \mathbf{r}) = -\mathbf{r}|b\rangle.$$
(6b)

To solve (6a) and (6b) we write

$$\chi_{ab}(\omega, \mathbf{r}) = \frac{u_{a,b}(\mathbf{r})}{\mathbf{r}} Y_{lm}(\hat{\mathbf{r}}).$$
(7)

If the initial and final states are s states of zero orbital angular momentum and V(r) is a central field potential,  $u_a(r)$  and  $u_b(r)$  are solutions of the radial equations

$$-\frac{1}{2}\frac{d^2}{dr^2}u_a(r) + \left(\frac{2}{r^2} + V(r) - E_a - \omega\right)u_a(r) = -r^2|a\rangle$$
(8a)

$$-\frac{1}{2}\frac{d^2}{dr^2}u_b(r) + \left(\frac{2}{r^2} + V(r) - E_b + \omega\right)u_b(r) = -r^2|b\rangle$$
(8b)

satisfying the boundary conditions  $u_{a,b}(r) \rightarrow r^2$  as  $r \rightarrow 0$ ,  $u_b(r) \rightarrow 0$  as  $r \rightarrow \infty$  for all frequencies and  $u_a(r) \rightarrow 0$  as  $r \rightarrow \infty$  for all frequencies less than the ionization limit,  $E_a + \omega < 0$ . For frequencies in the continuum,  $u_a(r)$  satisfies the outgoing wave boundary condition

$$u_{a}(r) \xrightarrow[r \to \infty]{} - \left(\frac{2\pi}{k}\right)^{1/2} \langle \phi_{E1}(r) | r | a \rangle \exp[i(kr + \eta_{1} + \xi)]$$
(9)

where  $E = E_a + \omega = k^2/2$ ,  $\eta_1(k)$  is the full Coulomb phaseshift corresponding to l = 1,  $\xi$  is the contribution from the accumulation of phase of the valence electron in the presence of any short-range non-Coulombic potential field, and where  $\phi_{E1}(r)$ , satisfying  $[H - E]\phi_{E1}(r) = 0$ , is regular at the origin and behaves asymptotically as  $k^{-1/2} \sin(kr + \eta_1 + \xi)$ .

The solution  $\chi_a(\omega, r)$  is singular for frequencies  $\omega$  equal to an eigenfrequency of the atom. For  $\omega = E_c - E_a$ , we may replace (6a) by

$$(H - E_a - \omega)\chi_c(\omega, r) = -r|a\rangle + \langle c|r|a\rangle|c\rangle$$
(10)

which eliminates the term t = c from the summation. It can then be added back to the summation as the explicit term

$$\frac{\langle a|\mathbf{r}|c\rangle\langle c|\mathbf{r}|b\rangle}{E_a + \omega - E_c - i\Gamma_c/2}.$$
(11)

The set of solutions  $u_{ab}(r)$  in (8) were obtained by solving an integral equation involving the Green function (cf Arfken 1985).

#### 3. Results and discussion

#### 3.1. Scattering by hydrogen

As a test of the numerical procedure, the static polarizability of atomic hydrogen which is given by

$$\alpha = -\frac{2}{3} \langle u_a | r | a \rangle \tag{12}$$

at  $\omega = 0$  was calculated. The result 4.499 9998  $a_0^3$  agrees to seven figures with the exact value 4.5  $a_0^3$ . A similar calculation was performed for the  $2p\pi$  state of hydrogen with

the result 155.999 993  $a_0^3$  compared to the exact value of 156  $a_0^3$  (Dalgarno and Stewart 1957).

As a further test of the method, we have calculated the Rayleigh and Raman scattering cross sections for atomic hydrogen. We list in table 1 the Rayleigh cross sections at several wavelengths. The values agree closely with those derived from the tabulation of  $\omega^2 M_{ab}(\omega)$  by Gavrila (1967) who calculated  $M_{ab}(\omega)$  using an analytical representation of the Green function. For example, at  $\omega = 2$  au, we obtain for  $\omega^2 |M_{ab}(\omega)|^2$  a value of 1.105 au while Gavrila obtained a value of 1.104 au.

Raman scattering cross sections from the 1s to the 2s state of hydrogen have been calculated and presented in graphical form by Saslow and Mills (1969) and Nussbaumer *et al* (1989), who evaluated the explicit summations in equation (2). Our cross sections are in agreement with their results. We list in table 1 cross sections at several wavelengths, including those identified by Nussbaumer *et al* (1989) as of astrophysical interest.

## 3.2. Scattering by caesium

We have applied the method to atomic caesium in the approximation that caesium can be described as a single electron moving in an effective potential V(r). For V(r)we adopted the parametric model potential of Greene (1990). The static polarizability we obtain is 438.6  $a_{0}^{3}$ , in agreement with the value calculated by Greene (1990). If we take account of the adiabatic polarization of the Cs<sup>+</sup> core by the electric field of the valence electron (Hameed *et al* 1968, Caves and Dalgarno 1972, Zhou and Norcross 1989) by replacing the dipole operator -er by

$$d = -er\left(1 - \frac{\alpha_{\rm c}}{2r^3}\left[1 - \exp(-r/r_{\rm c})^3\right]\right)$$

where  $\alpha_c$  is the polarizability of Cs<sup>+</sup> and  $r_c$  is a cut-off radius (Greene (1991), we obtain a value of 405.3  $a_0^3$  for the static polarizability of Cs. It agrees closely with the

Wavelength (nm)	Rayleigh $\sigma$ (cm <sup>2</sup> )	Raman $\sigma$ (cm <sup>2</sup> )
103.2	$1.82 \times 10^{-23}$	$3.66 \times 10^{-24}$
103.8	$4.25 \times 10^{-24}$	$1.48 \times 10^{-24}$
113.6	$4.32 \times 10^{-24}$	$4.81 \times 10^{-26}$
102.5	$3.57 \times 10^{-20}$	$4.73 \times 10^{-21}$
101.8	$2.50 \times 10^{-23}$	$1.83 \times 10^{-24}$
101.2	$7.87 \times 10^{-24}$	$3.11 \times 10^{-25}$
100.6	$3.64 \times 10^{-24}$	$5.59 \times 10^{-26}$
99.5	$9.97 \times 10^{-25}$	$7.40 \times 10^{-27}$
95.5	$3.62 \times 10^{-26}$	$1.21 \times 10^{-25}$
94.3	$1.04 \times 10^{-24}$	$6.14 \times 10^{-28}$
93.5	$3.05 \times 10^{-24}$	$6.64 \times 10^{-26}$
92.5	$4.93 \times 10^{-24}$	$2.00 \times 10^{-25}$
91.5	$3.75 \times 10^{-25}$	$2.57 \times 10^{-26}$
91.3	$1.60 \times 10^{-23}$	$1.29 \times 10^{-24}$

**Table 1.** Rayleigh and Raman cross sections for ground state hydrogen atoms as functions of wavelength  $\lambda$ .

empirical value of 404.1  $a_0^3$  (Dalgarno and Davison 1967), the measured value of 402±8  $a_0^3$  (Molof *et al* 1974) and the model potential value of 400.6  $a_0^3$  calculated by Zhou and Norcross (1989). The difference between the model potential values of Greene (1990) and Zhou and Norcross (1989) arises largely from the different forms adopted for the dipole operator and is not due to relativistic effects.

The response functions  $u_a(r)$  and  $u_b(r)$  for Rayleigh scattering by the 6s state of caesium at a frequency of  $\omega = 0.07$  au, above the 6p resonance, is shown in figure 1(a). Both are dominated by the contribution from the virtual 6p excitation and are similar in shape to the 6p wavefunction. Because of the different values of the energy denominator, the rotating wavefunction  $u_a(r)$  is large and mostly negative and the counter-rotating wave  $u_b(r)$  is small and mostly positive.



Figure 1. (a) The caesium Rayleigh scattering response functions  $u_a(r)$  and  $u_b(r)$  at a photon frequency  $\omega = 0.07$  au. (b) As in (a) for Raman scattered photons at  $\omega = 0.09$  au.

Figure 1(b) illustrates the Raman response function for the scattering from the 6s to 7s state of Cs at a frequency of  $\omega = 0.09$  au. They are similar to the Rayleigh functions except that, because of the changed denominator, the counter-rotating function is larger than in the case of Rayleigh scattering and is largely negative.

Figures 2(a) and 2(b) present results for  $\omega = 0.099$  76 au, blue-shifted just outside the natural linewidth of the Cs(7p) resonance. The functions  $u_a(r)$  in both Rayleigh and Raman scattering have the appearance of a distorted 7p wavefunction and have large amplitudes. By comparison  $u_b(r)$  is small.

Rayleigh cross sections for the 6s state and the Raman scattering cross sections from an initial 6s state to the 7s final state are illustrated in figure 3(a). The first



Figure 2. (a) The Rayleigh scattering response functions  $u_a(r)$  and  $u_b(r)$  at an incident photon frequency of  $\omega = 0.09976$ , near the 7p resonance frequency. (b) As in (a) for Raman scattering of photons into the Cs(7s) state.



Figure 3. (a) The Rayleigh 6s-6s cross section as a function of incident photon frequency (in  $cm^{-1}$ ) in Cs. The first peak is the 6p resonance profile. The broken curve refers to calculations using the modified dipole operator. (b) The Raman 6s-7s cross section in Cs as a function of incident photon frequency (in  $cm^{-1}$ ). The 6p peak is missing because it cannot be accessed by the inelastic process.

resonance structure in figure 3(a) corresponding to the 6s-6p transition does not appear in figure 3(b) because the 6p state lies below the 7s final state.

In the neighbourhood of an absorption line, the detailed shape of the resonance profile depends critically on the behaviour of the real and imaginary components of the transition matrix element  $M_{ab}(\omega)$ . We have calculated the 6s-6p resonance profile by including an energy-independent radiative width ( $\Gamma$ ) in equation (2). The cross section derived from only the real part of  $M_{ab}(\omega)$  vanishes near the line centre (Dalgarno 1963) but the inclusion of the imaginary part produces the expected Lorentzian profile in figure 4.



Figure 4. The square of the real part (broken curve), the imaginary part (dotted curve) and the total  $|M|^2$  (full curve). The profile is dominated by the imaginary component of M.  $\omega_0 = 0.052$  671 au is the 6s-6p transition frequency.

## 4. Summary

We have calculated the resonant and non-resonant cross sections for elastic and inelastic scattering of photons from hydrogen and caesium atoms by solving an inhomogeneous differential equation. The results for hydrogen are in agreement with the exact results of Gavrila (1967). No comparison data are available for caesium. Based on the calculation of Cs(6s) static polarizability, we conclude that the Cs cross sections calculated using the modified form of the dipole operator are correct to within a few per cent. The resonant profile of a typical absorption line, the 6s-6p transition of caesium, was calculated and it was pointed out that the profiles of the real and imaginary parts of the scattering matrix elements are drastically dissimilar.

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