Mixing and quenching of the Cs $5D_J$ states induced by collisions with caesium ground-state atoms*

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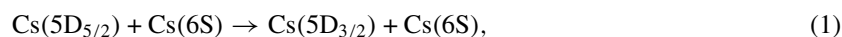Institute of Physics, Bijenicka 46, 10000 Zagreb, Croatia

Abstract. Applying the cw laser absorption and fluorescence method the cross sections for the fine-structure mixing and quenching of the caesium $5D_J$ states have been measured in pure caesium vapour. Caesium atoms were optically excited to the $5D_{5/2}$ state via the quadrupole-allowed $6S_{1/2} \rightarrow 5D_{5/2}$ transition. The ground-state caesium density N_0, obtained from the absorption at the pumped quadrupole transition, and the fluorescence intensity I_{689} of the sensitized $5D_{3/2} \rightarrow 6S_{1/2}$ emission were measured simultaneously in the range $3 \times 10^{14} \text{ cm}^{-3} \leqslant N_0 \leqslant 1 \times 10^{16} \text{ cm}^{-3}$ at constant temperature $T = 585$ K. It was found that the quantity N_0^2/I_{689} exhibited a parabolic dependence on N_0, confirming that the quenching of the Cs $5D_J$ states is due to collisions with Cs ground-state atoms, not molecules. The coefficients of the second-order polynomial fitted through the measured data yielded the cross sections $\sigma_{5/2 \rightarrow 3/2} = (57 \pm 19) \times 10^{-16} \text{ cm}^2$ and $\sigma_D = (35 \pm 10) \times 10^{-16} \text{ cm}^2$ for the Cs $5D_J$ fine-structure mixing and quenching, respectively, due to collisions with caesium ground-state atoms. Using recently calculated Cs* + Cs potentials we performed an analysis which shows good agreement between the measured values and the theoretical predictions.
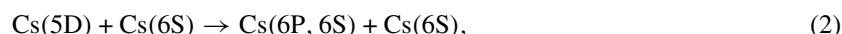
1. Introduction

Investigations of collisionally induced excitation energy transfer (EET) occurring in excited atomic vapours play an important role in understanding the dynamics of inelastic collisions in gases. The theoretical determination of the cross section for a particular EET reaction relies on the accurate knowledge of the potentials between collision partners. Therefore, comparison of the calculated and experimentally obtained cross section values constitutes a very sensitive test of our knowledge of the potentials between the atoms or molecules involved in the collisions. Due to their simple hydrogen-like structure, alkali atoms are relatively simple to treat theoretically. In addition, their resonance lines are in the spectral region easily attainable by dye-lasers and solid-state laser diodes. Therefore, a great deal of the investigation of the EET processes was (Krause 1975), and still is, related to alkali atoms. Experimentally, determination of the EET cross sections essentially involves the determination of the ground-state atom number density and the ratio of the population densities in those excited atom states participating in the particular process. Though this may sound a very simple task to accomplish, it is rarely so. First, the determination of the ground-state densities is often erroneous. The lifetimes of the considered excited states enter the evaluation of the excited-state population ratio. Since the experiments are seldom performed in conditions where the lifetimes can be considered to be natural, the situation is further complicated by having to determine the effective (due to radiation trapping effects) lifetimes. Once effective lifetimes are involved, the diffusion

* Dedicated to Professor Boran Leontic on the occasion of his 70th birthday.

of the excited atoms out of the excitation volume has to be considered, ending up with the need to determine the spatial distributions of the excited atoms. All the quantities mentioned act as sources of serious error in the experimentally obtained cross sections. Therefore, it usually takes several experiments, performed independently by different groups of authors, to establish reliable cross section values for any particular EET process. The EET reactions considered here, i.e. the fine-structure mixing,

$$Cs(5D_{5/2}) + Cs(6S) \rightarrow Cs(5D_{3/2}) + Cs(6S), \tag{1}$$

and quenching,

$$Cs(5D) + Cs(6S) \rightarrow Cs(6P, 6S) + Cs(6S), \tag{2}$$

of the caesium $5D_J$ states due to collisions with Cs ground-state atoms, are no exception.

The first estimate of the cross section for the process (1) was made by Wu and Huennekens (1984), who reported the fine-structure mixing cross section to be $<2 \times 10^{-16}$ cm^2. The experiment was performed at caesium ground-state densities ranging from 8×10^{16} to 1.4×10^{17} cm^{-3}. Under such conditions complete mixing between $5D_J$ states, which are only 100 cm^{-1} apart, should occur, and the $5D_{5/2}$ to $5D_{3/2}$ state population ratio should approach the thermal equilibrium value of ≈ 1.1. Nevertheless, the authors found that the population ratio was approximately equal to two and independent of the caesium ground-state density in the range investigated. This finding implied either a very small fine-structure mixing cross section or the presence of a caesium atomic or molecular quenching process with large cross section. The authors Wu and Huennekens (1984) decided in favour of the former explanation.

One year later Davanloo *et al* (1985) published the first quantitative results for the Cs $5D_J$ mixing and quenching cross sections. They performed measurements at constant caesium ground-state density ($p_{Cs} = 0.13$ Torr, corresponding to $N_{Cs} = 2.6 \times 10^{15}$ cm^{-3} and $T = 485$ K according to Taylor and Langmuir (1937) and Nesmeyanov (1963)) and obtained the value $\sigma_{5/2 \rightarrow 3/2} = (17 \pm 10) \times 10^{-16}$ cm^2 for process (1). However, to fit their data they needed to take a quenching process into consideration, which they implied was of the form given by expression (2). The corresponding cross section, derived from the total 5D state collisional quenching rate of $(4.7 \pm 1) \times 10^5$ s^{-1} reported by Davanloo *et al* (1985), amounts to $(47 \pm 10) \times 10^{-16}$ cm^2.

A few years later, Keramati *et al* (1988) re-investigated these mixing and quenching processes of the Cs $5D_J$ states. They found the fine-structure mixing cross section $\sigma_{5/2 \rightarrow 3/2} = (70 \pm 28) \times 10^{-16}$ cm^2, which was obtained under the assumption that the quenching due to process (2) is negligible since it requires conversion of almost 3000 cm^{-1} of internal energy into kinetic energy. Keramati *et al* (1988) allowed for the existence of $5D_J$ state quenching by caesium molecules, but that contribution was eventually also neglected due to the low Cs$_2$ density in their experiment.

More recently, Sasso *et al* (1992) studied the processes at hand once more. They performed two experiments, one in a cw and the other one in a pulsed regime. In the cw experiment the caesium ground-state density was varied in the range from 1.1×10^{15} to 1.1×10^{16} cm^{-3} at constant vapour temperature $T = 601$ K. The cross sections obtained in this part of the measurements were $\sigma_{5/2 \rightarrow 3/2} = (31 \pm 10) \times 10^{-16}$ cm^2 and $\sigma_{3/2} = (23 \pm 16) \times 10^{-16}$ cm^2, for the mixing of the $5D_J$ levels and quenching of the $5D_{3/2}$ level, respectively. To improve the accuracy of the values obtained, the datum obtained in the previous experiment (Wu and Huennekens 1984) at much higher vapour density ($N_{Cs} \approx 10^{17}$ cm^{-3}) was expressed in terms of the intensity ratio measured by Sasso *et al* (1992) and added to the data field to be fitted. This combined set of data yielded the cross section values $\sigma_{5/2 \rightarrow 3/2} = (33 \pm 9) \times 10^{-16}$ cm^2 and $\sigma_{3/2} = (26 \pm 12) \times 10^{-16}$ cm^2. From the shape of the functional dependence of the intensity ratio measured in the cw experiment the authors concluded that the quenching of the

5D state was caused by collisions with caesium ground-state atoms. The pulsed part of the experiment of Sasso *et al* (1992) was performed in the temperature range from 480 to 637 K, covering the caesium density range between 2.3×10^{15} and 1.6×10^{17} cm^{-3}. The fine-structure mixing and quenching cross sections were found to be $\sigma_{5/2 \to 3/2} = (55 \pm 25) \times 10^{-16}$ cm^2 and $\sigma_D = (30 \pm 3) \times 10^{-16}$ cm^2. In the pulsed experiment individual quenching rates of the $5D_J$ levels could not be resolved, and the reported σ_D value represents the mean value $(\sigma_{3/2} + \sigma_{5/2})/2$ of the quenching cross sections of the $5D_J$ sublevels. The atomic nature of the 5D level quenching was confirmed by pulsed measurements too. Taking into account the results of both cw and pulsed experiments, Sasso *et al* (1992) reported the best cross section values to be $\sigma_{5/2 \to 3/2} = (36 \pm 8) \times 10^{-16}$ cm^2 and $\sigma_D = (30 \pm 3) \times 10^{-16}$ cm^2.

The above history of the investigations of the mixing and quenching processes of Cs $5D_J$ states shows that in spite of being studied many times, none of the results was completely confirmed by later re-measurement. The question of $5D_J$ quenching alone is quite interesting since it recurs throughout the sequence of experiments in an 'exists–exists-not' manner.

As mentioned before, the results in this field of investigation (EET processes) are regarded as reliable when they have been confirmed independently by different groups of authors. To that end we decided to re-investigate processes (1) and (2) experimentally. In our recent paper (Movre *et al* 1999) we have mentioned the preliminary cross section values ($\sigma_{5/2 \to 3/2} = (45 \pm 15) \times 10^{-16}$ cm^2, $\sigma_D = (30 \pm 10) \times 10^{-16}$ cm^2) for the processes considered here. These values, based on the scant set of measured data, showed fair agreement with the results of Sasso *et al* (1992). Here, we present the method and the results of the completed extensive measurements of the processes at hand. Cw laser radiation was used to excite the caesium vapour, while the quantities relevant for the cross section determination (ground and excited state populations) have been obtained by laser absorption and fluorescence measurements. The cross section determination procedure differs from those used previously by other authors. It relies upon simple fluorescence intensity measurements and a very accurate determination of the ground-state atom density, while radiation trapping and diffusion effects are completely avoided.

Sasso *et al* (1992) offered a theoretical explanation for the quenching process (2). Using the theoretical potential curves for the Cs* + Cs system (Krauss and Stevens 1990) they concluded that the collisional depopulation of the 5D states occurs through a highly repulsive Cs(6P)+Cs(6S) potential and that the most likely candidate is the $2\,^3\Sigma_u^+$ state. This conclusion was based upon knowing the $2\,^3\Sigma_u^+$ potential to a limited extent and its extrapolation down to shorter distances. In this manner an estimate for the gas-kinetic cross section of the order of 80×10^{-16} cm^2 was obtained. We have calculated the contribution to the cross section due to the mechanism they proposed, and obtained a value which is six orders of magnitude smaller than the measured one. Regarding their explanation to be unsatisfactory, in the present work we propose other mechanisms which give much better agreement with the measured cross section.

2. Experiment

The results presented in this paper for the mixing and quenching of the Cs $5D_J$ states have been obtained using the experimental arrangement described in our recent paper (Movre *et al* 1999) on Cs 6P fine-structure mixing and quenching by ground-state caesium atoms, and all experimental details can be found there.

In brief, the measurements were performed in a glass cell, covering the caesium density range between 3×10^{14} and 5×10^{16} cm^{-3}. The excitation of the caesium ground-state atoms was achieved by a dye laser tuned to the stronger hyperfine (hf) component of the quadrupole-

allowed $6S_{1/2} \rightarrow 5D_{5/2}$ transition (wavelength 685 nm). The determination of the cross sections for the $5D_J$ mixing and quenching required measurements of the caesium population in the ground state and excited 5D state. The caesium ground-state density was obtained from measurements of the peak absorption coefficient of the 685 nm line. The excited 5D state population was monitored by measuring the sensitized fluorescence of the collisionally populated 5D substrate, which was observed side-on by the monochromator.

3. Mixing and quenching of the Cs $5D_J$ states

3.1. Rate equations and method

The partial term scheme of caesium is depicted in figure 1(a), where the relevant radiative and collisional transition rates involved in the population and depopulation of the Cs $5D_J$ states are indicated. The states $6S_{1/2}$, $6P_{1/2}$, $6P_{3/2}$, $5D_{3/2}$, and $5D_{5/2}$ have labels 0–4, respectively. The radiative and collisional mixing rates for $m \rightarrow n$ transitions ($m = 3, 4$; $n = 0$–4) are denoted by A_{mn} and R_{mn}, respectively, while Q_m labels the quenching rate for a particular m state. The rates R_{nm} due to collisions with the ground-state atoms are of the form $N_0 v_{Cs-Cs} \sigma_{mn}$. At this point, we do not define the character of quenching, i.e. we do not define the final state for the outgoing rates Q_m, which can be due to collisions with either the caesium atoms or caesium molecules. In the conditions of the present experiment, the radiative $5D \rightarrow 6P$ transition was not trapped and the corresponding A_{mn} rates are equal to the natural radiative rates. Using the published data for the quadrupole (Niemax 1977) and dipole (Hansen 1984) oscillator strengths, we calculated the following values for the radiative rates A_{mn}: $A_{30} = 23.0$ s^{-1}, $A_{40} = 26.8$ s^{-1}, $A_{31} = 9.0 \times 10^5$ s^{-1}, $A_{32} = 1.0 \times 10^5$ s^{-1} and $A_{42} = 7.2 \times 10^5$ s^{-1}.

The rate equations for the steady-state populations created in the $5D_J$ levels following the $5D_{5/2}$ state excitation can be expressed in the following matrix form:

$$\begin{pmatrix} -(A_{31} + A_{32} + R_{34} + Q_3) & R_{43} \\ R_{34} & -(A_{42} + R_{43} + Q_4) \end{pmatrix} \times \begin{pmatrix} N_3 \\ N_4 \end{pmatrix} = \begin{pmatrix} 0 \\ -\rho B_{04} N_0 \end{pmatrix}. \tag{3}$$

Here, ρ is the laser spectral power density and B_{04} is the Einstein absorption coefficient for the $0 \rightarrow 4$ quadrupole pump transition. In the above system of equations the quadrupole radiative rates A_{30} and A_{40} are not included since they are negligible in comparison with the total depopulation rates for the $5D_J$ states.

According to results reported by Sasso *et al* (1992), the cross sections for the quenching of the $5D_J$ sublevels are close in value (see the introduction). Therefore, we can assume that $Q_3 \approx Q_4 \equiv Q_D$. Furthermore, from the principle of detailed balancing, it follows that the ratio $R_{34}/R_{43} = 1.18$ at the experimental temperature $T_0 = 585$ K. Thus the system of equation (3) yields the following expression for the population density of the $5D_{3/2}$ state:

$$N_3 = \frac{\rho B_{04} \sigma_{43} v_{Cs-Cs} N_0^2}{A_{42}[A_{3P} + (1.18 + \frac{A_{3P}}{A_{42}})R_{43} + \frac{A_{3P}+A_{42}}{A_{42}}Q_D + \frac{2.18}{A_{42}}R_{43}Q_D + \frac{1}{A_{42}}Q_D^2]}, \tag{4}$$

where $A_{3P} = A_{31} + A_{32}$.

We define the quantity $F = N_0^2/I_{689}$, where I_{689} denotes the measured fluorescence intensity of the sensitized quadrupole line. F is expressed in the units cm^{-6} aui^{-1}, where aui stands for arbitrary unit of intensity. Since $I_{689} \propto h\nu_{30} A_{30} N_3$, from equation (4), it follows that

$$F = \frac{N_0^2}{I_{689}} = K \left(A_{3P} + 2.57 R_{43} + 2.39 Q_D + \frac{2.18}{A_{42}} R_{43} Q_D + \frac{1}{A_{42}} Q_D^2 \right), \tag{5}$$

where the explicit values for the radiative rates given earlier have been taken into account, and K labels a proportionality constant.
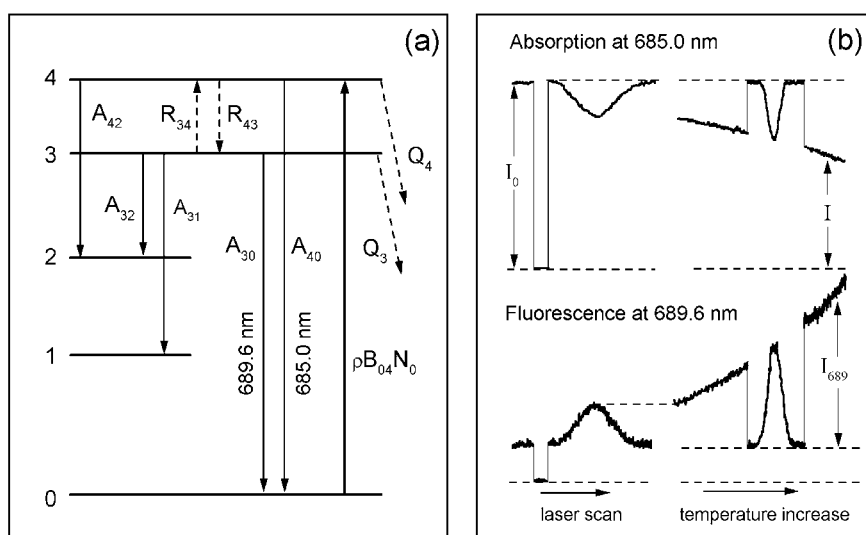
Figure 1. (*a*) Partial term scheme of caesium, including the radiative (*A*) and collisional (*R*) rates relevant for the population and depopulation of the Cs $5D_J$ states. The states $6S_{1/2}$, $6P_{1/2}$, $6P_{3/2}$, $5D_{3/2}$ and $5D_{5/2}$ are denoted as states 0–4, respectively. (*b*) Absorption at pump $6S_{1/2} \rightarrow 5D_{5/2}$ quadrupole transition (upper traces) and the fluorescence of the sensitized $5D_{3/2} \rightarrow 6S_{1/2}$ quadrupole line (lower traces). The left-hand traces were obtained during the pump laser scan over the transition. The right-hand traces represent peak absorption and fluorescence signals monitored during the temperature increase. Occasional scans over the pump line were made in order to control the stability of the pump laser frequency.

If the quenching is due to collisions with molecules, than the quenching rate is proportional to the ground-state molecular density and in turn proportional to the square of the atomic density. Consequently, in this case $F(N_0)$ would exhibit the form of a fourth-order polynomial with argument N_0.

If the quenching of the 5D states is atomic, than the quenching rate $Q_D = \sigma_D v_{Cs-Cs} N_0$, and the quantity F can be represented by a second-order polynomial:

$$F(N_0) = a_0 + a_1 N_0 + a_2 N_0^2. \tag{6}$$

By comparing equations (5) and (6) we obtain

$$a_0 = K A_{3P}, \tag{7}$$

$$a_1 = \frac{a_0}{A_{3P}}(2.57\sigma_{43} + 2.39\sigma_D)v_{Cs-Cs}, \tag{8}$$

and

$$a_2 = \frac{a_0}{A_{3P}}(2.18\sigma_{43}\sigma_D + \sigma_D^2)\frac{v_{Cs-Cs}^2}{A_{42}}. \tag{9}$$

Relation (7) defines the value and the dimension of the proportionality constant, $K = a_0/A_{3P}$ (expressed in units of cm^{-6} s aui^{-1}), which has been substituted in relations (8) and (9). The coefficients a_1 and a_2 are given in cm^{-3} aui^{-1} and aui^{-1}, respectively.

Using the values A_{3P} and A_{42} given previously, and the mean Maxwellian relative velocity $v_{Cs-Cs} = \sqrt{8kT/\pi\mu_{Cs-Cs}}$, which at our experimental temperature $T = 585$ K amounts to 4.315×10^4 cm s^{-1}, we obtain the following solution to the system of equations (8) and (9):

$$\sigma_D = 9.57\frac{a_1}{a_0}\left[1 - \sqrt{1 - 4.11\frac{a_0 a_2}{a_1^2}}\right] \tag{10}$$

$$\sigma_{43} = 8.90 \frac{a_1}{a_0} \left[1.3 \times 10^{-2} + \sqrt{1 - 4.11 \frac{a_0 \, a_2}{a_1^2}} \right]. \tag{11}$$

In the above relations the cross sections are expressed in cm^2.

In the present experiment, we have measured the quantity F as a function of the ground-state number density N_0. The values of F were determined from the simultaneous measurements of I_{689} and N_0. By examining its functional dependence we found that it exhibits a polynomial form defined by equation (6), showing that the quenching of 5D states is due to collisions with Cs atoms. The second-order polynomial fit through the measured $F(N_0)$ data yields the values of the coefficients a_0, a_1 and a_2, which enable the determination of the cross sections σ_D and σ_{43} according to equations (10) and (11).

3.2. Measurements and results

Because of the detection limits of our apparatus we were able to monitor the 5D populations only by measuring the fluorescence of the quadrupole lines. Since the fluorescence at the wavelength of the pumped quadrupole transition was blended by the strong scatter of laser light, our measurements were restricted to recording the sensitized fluorescence from the collisionally populated 5D substate. The Cs quadrupole lines lie at the edge of the DCM gain profile and we used the $6S_{1/2} \rightarrow 5D_{5/2}$ rather than $6S_{1/2} \rightarrow 5D_{3/2}$ excitation, because of the significantly greater dye-laser gain at the wavelength of the former transition.

Typical signals obtained in this part of the experiment are shown in figure 1(*b*). The peak absorption coefficient of the pump line (the stronger hf component of the 685 nm line) was measured simultaneously with the fluorescence intensity of the sensitized Cs quadrupole line at 689 nm, while the Cs ground-state number density was varied by changing the temperature of the metal bath. In this manner the caesium density in the fluorescence cell was varied between 3×10^{14} and 1×10^{16} cm^{-3} at the cell temperature $T_0 = 585$ K. For the measurements at lower number densities the maximal pump power density (power 50 mW, beam diameter 1 mm) was used. As shown by Vadla (1988), at higher densities such pumping can produce a significant population ($\sim 10^{11}$ cm^{-3}) in the resonance 6P states. In order to avoid trapping of the $5D \rightarrow 6P$ radiation, the measurements at higher densities were performed applying the pump power reduced step by step down to 10 mW.

Figure 2(*a*) shows the dependence of the measured fluorescence signal I_{689} (in aui) on caesium number density N_0. The N_0 data were obtained from a series of measurements using a single, double and triple pass of the absorption beam through the cell. The data measured at low N_0 values are more numerous than shown, but for visual clarity they are not depicted. During the experiment, the pump power as well as the cell window transparency were controlled. The transparency T of a single cell window was extracted from the data obtained by the absorption of the white light beam passing through both cell windows. The window transparency is not necessarily a simple function of density as shown in figure 2(*a*). However, all measurements presented here were made in continuously temperature-rising runs and, therefore, effects such as hysteresis were avoided. The T curve in figure 2(*a*) represents the transparency normalized by its value at the beginning of the heating sequence. The measurements were restricted to caesium number densities up to at most 1×10^{16} cm^{-3}, because at higher densities the transparency decreases significantly and becomes inhomogeneous across the window surface.

Using the data given in figure 2(*a*) we calculated $F(N_0) = N_0^2/I_{689}$ (I_{689} being corrected for the cell window transparency), and the results are shown in figure 2(*b*). The associated error bars include the uncertainties of the fluorescence signals and the ground-state densities added in quadrature.
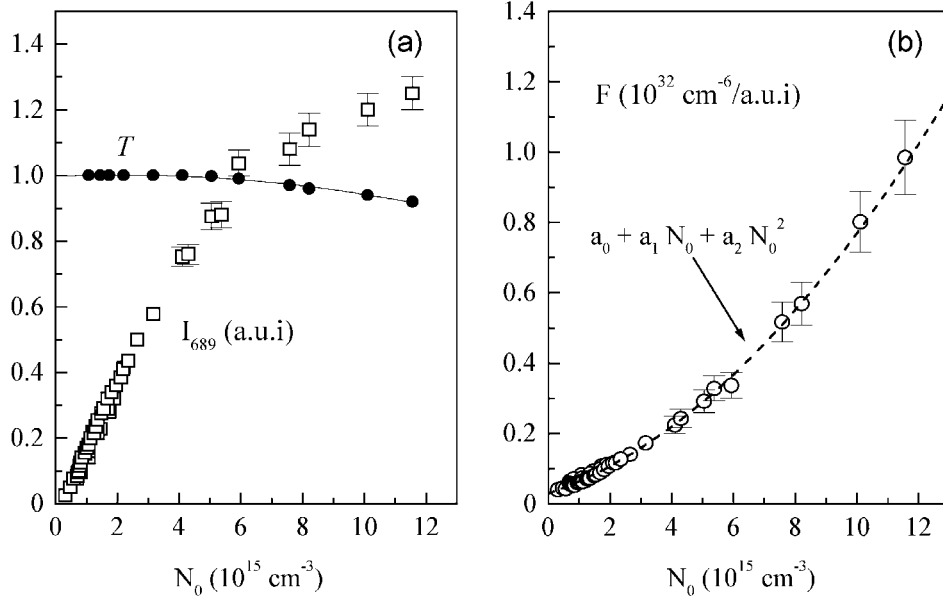
Figure 2. (*a*) The measured fluorescence signal I_{689} (in arbitrary units of intensity) of the Cs 689.7 nm line and the transparency T of the cell windows as a function of the caesium ground-state atom number density N_0. (*b*) The quantity F, defined as the N_0^2 to $I_{689.7}$ ratio, shown as a function of the caesium ground-state number density N_0. The dashed curve represents the best second-order polynomial fit through the data. Where not shown, the error bars are of the size of the symbols.

Fitting the data depicted in figure 2(*b*) to a fourth-order polynomial, which would correspond to the case of molecular quenching, does not make much sense. All obtained polynomial coefficients are quite arbitrary in value (with standard errors between 100 and 200%), with a_4 being non-physical (negative) in addition. The data analysis shows that $F(N_0)$ can be truly represented by a second-order polynomial. Based upon the results of these fitting procedures, we conclude that the quenching rates are proportional to N_0, i.e. that the quenching of the 5D states is due to collisions with caesium atoms, not molecules.

The second-order polynomial fit through the $F(N_0)$ data weighted by the corresponding errors yields the following values for the polynomial coefficients: $a_0 = (3.0 \pm 0.4) \times 10^{30}$ (cm^{-6} aui^{-1}), $a_1 = (3.0 \pm 0.4) \times 10^{15}$ (cm^{-3} aui^{-1}) and $a_2 = 0.44 \pm 0.07$ (aui^{-1}). Using these values and equations (10) and (11) we obtained the cross sections

$$\sigma_D = (35 \pm 10) \times 10^{-16} \text{ cm}^2, \tag{12}$$

and

$$\sigma_{43} = (57 \pm 19) \times 10^{-16} \text{ cm}^2. \tag{13}$$

The declared uncertainties of the cross sections are the standard errors obtained by taking into account the inaccuracies of the polynomial coefficients a_0, a_1 and a_2 used in the evaluation. The results obtained here are listed in table 1 together with the results of previous investigations.

Our preliminary values for the investigated cross sections (Movre *et al* 1999) are within the error bars of the present results. The difference in mean values is caused by the fact that in the present measurements coefficient a_0 is determined far more reliably; namely, its value is sensitive to how closely we approach the origin with the measured data and how numerous the

Table 1. Cross sections for the fine-structure mixing and quenching of the Cs $5D_J$ states induced by collisions with ground-state caesium atoms.

Temperature (K)	$\sigma_{5/2\to3/2}$ (10^{-16} cm^2)	σ_D (10^{-16} cm^2)	References
473–648	<2	—	Wu and Huennekens (1984)
485	17 ± 10	47 ± 10	Davanloo *et al* (1985)
425	70 ± 28	—	Keramati *et al* (1988)
480–637[a]	55 ± 25[a]	30 ± 3[a]	Sasso *et al* (1992)
601[b]	31 ± 10[b]	23 ± 16[b]	—
601[c]	33 ± 9[c]	26 ± 12[c]	—
—	36 ± 8[d]	30 ± 3[d]	—
585	57 ± 19	35 ± 10	This work, experiment
585	<44	29	This work, theory

[a] Pulsed experiment, $\sigma_D = (\sigma_{3/2} + \sigma_{5/2})/2$.
[b] Cw experiment, $\sigma_D = \sigma_{3/2}$.
[c] Cw experiment combined with additional data point taken from the work of Wu and Huennekens (1984).
[d] Best values of the combined cw and pulsed experiments.

data are in this low-density limit. In that regard, the quality of the present set of experimental data is markedly improved compared to the preliminary one.

4. Theory

The dynamics of the collision is a complex problem not only because of the large number of electronic states that may be involved but also due to the sensitivity to details of the potential curves. In addition, the knowledge of various coupling matrix elements is required. For the full theoretical treatment of the cross sections measured in the present experiment a minimal number of the electronic states includes those asymptotically correlating to the lowest S + P and S + D asymptotes. Krauss and Stevens (1990) have calculated non-relativistic adiabatic potential energy curves of Cs$_2$ that correlate to the ground S+S and first excited S+P asymptote, while Spies (1990) has calculated in addition those correlating to the lowest S + D asymptote. He also treats the spin–orbit coupling among the states pertaining to S+P and S+D asymptotes. To the best of our knowledge, no radial- or rotational-coupling matrix elements are available in the literature.

Given the above, even in the case of all required coupling matrix elements being available, the full quantum mechanical treatment of the problem would be very complicated. However, an approximate semiclassical treatment based on the avoided crossings present in the calculated adiabatic curves correlated to the 6S + 6P and 6S + 5D asymptotes is possible.

The adiabatic electronic states of the molecule form a useful basis for the formulation of the thermal-energy collision problem. In the molecular adiabatic picture, the semiclassical expression for the cross section for a given transition from an initial adiabatic channel α to a final channel β is

$$\sigma_{\alpha\to\beta}(E) = 2\pi \int_0^\infty b \, P_{\alpha\to\beta}(E, b) \, db, \tag{14}$$

where E is the kinetic energy of the relative motion in the entrance channel and the probability of the process for impact parameter b is $P_{\alpha\to\beta}(E, b)$. The cross section for a transition from a group of initial states i pertaining to an asymptotic energy level with a statistical distribution

of Zeeman sublevels and degeneracy g_i to a group of final states f is defined as

$$\sigma_{i\to f}(E) = \frac{1}{g_i}\sum_{\alpha,\beta}\sigma_{\alpha\to\beta}(E), \tag{15}$$

where α (β) labels a nondegenerate molecular state component of the initial (final) asymptotic energy level. In our case $g_i = 2g_1g_2$ where g_1 and g_2 are the respective ground- and excited-state atomic degeneracies.

The observed rate coefficient for the collision in a cell is

$$k_{i\to f}(T) = \langle v\sigma_{i\to f}(E)\rangle, \tag{16}$$

where v is the relative collision velocity and the brackets $\langle\,\rangle$ imply a thermal average. For a Maxwellian energy distribution this formula can be conveniently expressed as

$$k_{i\to f}(T) = \bar{v}(kT)^{-2}\int_0^\infty \sigma_{i\to f}(E)E\exp(-E/kT)\,\mathrm{d}E, \tag{17}$$

where $\bar{v} = (8kT/\pi\mu)^{1/2}$ is the mean relative velocity of the two colliding atoms and μ is the reduced mass. An effective (thermal) cross section $\sigma_{i\to f}(T)$ for a given temperature T may be defined by

$$k_{i\to f}(T) = \bar{v}\sigma_{i\to f}(T). \tag{18}$$

Within a particular symmetry (gerade or ungerade) we consider all the potential curves which are correlated with the various initial and final states. For given E and b parameters we count avoided crossings met on the way inward (decreasing R) and outward (increasing R). The passage at each avoided crossing n between two curves γ and γ' redistributes the populations W_γ, $W_{\gamma'}$ with a probability $P^n(E,b)$:

$$\begin{pmatrix}\tilde{W}_\gamma\\\tilde{W}_{\gamma'}\end{pmatrix} = \begin{pmatrix}1 - P^n(E,b) & P^n(E,b)\\P^n(E,b) & 1 - P^n(E,b)\end{pmatrix}\begin{pmatrix}W_\gamma\\W_{\gamma'}\end{pmatrix} \tag{19}$$

where $\tilde{W}_\gamma$ and $\tilde{W}_{\gamma'}$ are the populations after passage of the avoided crossing.

In the simple two-channel model the transition probability $P^n(E,b)$, which estimates the population transfer from one molecular curve to another one in the vicinity of an avoided crossing, is given by the Landau–Zener (LZ) formula:

$$P_{\mathrm{LZ}} = 2\mathrm{e}^{-A}(1 - \mathrm{e}^{-A}), \tag{20}$$

where

$$A = 2\pi V_x^2/(\hbar v_x D_x) \tag{21}$$

and V_x, v_x and D_x are, respectively, the coupling matrix element, velocity and slope difference of the (diabatic) potential curves at the crossing point R_x of the two curves.

Sasso *et al* (1992) considered how the 5D level (atomic) quenching can come about. They concluded that it must occur through a highly repulsive potential curve of the 6S + 6P manifold, and that the most likely candidate is the $2\,^3\Sigma_u^+$ state. This conclusion was based upon knowing the $2\,^3\Sigma_u^+$ potential to a limited extent (Krauss and Stevens 1990) and its extrapolation down to shorter distances, yielding a gas-kinetic cross section of the order of 80×10^{-16} cm^2, not inconsistent with the quenching cross section of $\sim 30 \times 10^{-16}$ cm^2 reported by Sasso *et al* (1992). In fact, according to the calculations by Spies (1990), $2\,^3\Sigma_u^+$ and $3\,^3\Sigma_u^+$ exhibit an avoided crossing at about $12.7a_0$ (see figure 3(*a*)) and the calculation taking account of the LZ parameters of the crossing yields a disappointingly small cross section of 6×10^{-22} cm^2. Therefore we propose other mechanisms which account for the measured cross section much better. According to Spies (1990), there is a crossing of $2\,^3\Sigma_u^+$ and $2\,^3\Pi_u$
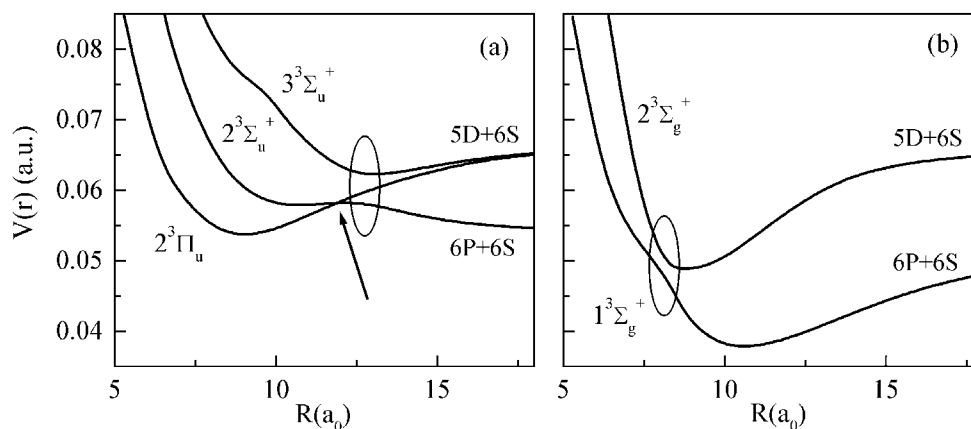
Figure 3. Several non-relativistic potential curves for Cs_2 calculated by Spies (1990). (*a*) The encircled area marks the avoided crossing of two ungerade $^3\Sigma_u^+$ curves and the arrow indicates the crossing of $2\,^3\Sigma_u^+$ and $2\,^3\Pi_u$ curves. As shown in the present work, the former yields a negligible contribution to the quenching cross section $\sigma(5D \rightarrow 6P)$ while the latter is found to be responsible for the collisional transition due to spin–orbit interaction. (*b*) The marked avoided crossing of two gerade $^3\Sigma_g^+$ curves also contributes substantially to the quenching cross section $\sigma(5D \rightarrow 6P)$.

potentials at $R = 11.9a_0$. The calculation which takes into account spin–orbit coupling between these two states results in a contribution to the cross section $\sigma_u = 13 \times 10^{-16}$ cm^2. Moreover, the $1\,^3\Sigma_g^+$ potential in the gerade manifold exhibits an avoided crossing with the $2\,^3\Sigma_g^+$ potential (see figure 3(*b*)). The radial coupling between these potentials yields the cross section $\sigma_g = 16 \times 10^{-16}$ cm^2. The total cross section $\sigma_u + \sigma_g$ reasonably matches the experimental value of $(35 \pm 10) \times 10^{-16}$ cm^2.

In order to estimate the fine-structure mixing cross section for the lowest D state, we have analysed potential curves for 40 electronic states pertaining to the $6S_{1/2} + 5D_J$ asymptotes, calculated by Spies (1990). We have identified several avoided crossings which could contribute to the corresponding cross section. Within the $\Omega = 2_g$, 1_g, 1_u and 0_u^+ manifolds there are avoided crossings at $R_x = 8.5$, 16.3, 12.6 and 13.8a_0, respectively. Summing up their gas-kinetic cross sections (πR_x^2) weighted by corresponding statistical factors ($1/g$, where $g = 2g_1g_2$, while g_1 and g_2 are the respective ground- and excited-state atomic degeneracies) we have estimated the upper bound for the $\sigma(5D_{5/2} \rightarrow 5D_{3/2})$ to be about 44×10^{-16} cm^2, which falls within the error bar of our experimental finding.

5. Discussion

The analysis of the previous (Wu and Huennekens 1984, Davanloo *et al* 1985, Keramati *et al* 1988) mutually inconsistent data for the collisional depopulation cross section of the Cs $5D_J$ states led Sasso *et al* (1992) to the conclusion that the quenching of the Cs 5D state is caused by atomic collisions. These authors (Sasso *et al* 1992) also concluded that the discrepancies mentioned among the results of earlier work were caused either by neglecting the quenching effects, or by the misleading conclusion that the quenching originates from collisions with caesium molecules. Their cw experiment was performed by pumping the Cs $5D_{5/2}$ state and observing the fluorescence at $5D_J \rightarrow 6P_J$ transitions. These measurements, combined with one datum published previously (Wu and Huennekens 1984), yielded the mixing cross section

$\sigma_{43} = (33\pm9)\times10^{-16}$ cm^2 and the atomic-quenching cross section $\sigma_D = (26\pm12)\times10^{-16}$ cm^2 for the state 5D$_{3/2}$. In the pulsed experiment, Sasso *et al* (1992) measured the time-resolved fluorescence of the sensitized quadrupole transition 5D$_{3/2} \rightarrow$ 6S$_{1/2}$, following the direct laser excitation of the 5D$_{5/2}$ level from the ground state. These pulsed measurements showed that the quenching is atomic, since the effective lifetimes of the Cs 5D$_J$ states were linear in atomic number density. The cross sections obtained in the pulsed experiment were $\sigma_{43} = (55 \pm 25) \times 10^{-16}$ cm^2 and $\sigma_D = (30 \pm 3) \times 10^{-16}$ cm^2 (total quenching cross section for the 5D level). The pulsed and cw results for the quenching cross section obtained by Sasso *et al* (1992) are in good agreement, while the pulsed result for the mixing cross section is about 70% higher than that obtained in the cw regime and lies much closer (30% lower) to the value obtained by Davanloo *et al* (1985). Based on the results of both the cw and the pulsed experiments, Sasso *et al* (1992) declared the best cross section values to be $\sigma_{43} = (36 \pm 8) \times 10^{-16}$ cm^2 and $\sigma_D = (30 \pm 3) \times 10^{-16}$ cm^2.

Our results clearly confirm the findings of Sasso *et al* (1992) regarding the quenching mechanism for the 5D$_J$ states. Our quenching cross section σ_D of $(35 \pm 10) \times 10^{-16}$ cm^2 is in acceptable agreement with both σ_D values reported by Sasso *et al* (1992). The present result for the mixing cross section $\sigma_{43} = (57 \pm 19) \times 10^{-16}$ cm^2 is in very good agreement with the σ_{43} value obtained by pulsed measurements reported by Sasso *et al* (1992), and somewhat higher, but still within the combined experimental uncertainties, than the value of their cw experiment.

In principle, the atomic quenching of the 5D states can be caused either by the intermultiplet process Cs(5D)+Cs(6S) $\rightarrow$ Cs(6P)+Cs(6S), or by the quenching process Cs(5D)+Cs(6S) $\rightarrow$ Cs(6S) + Cs(6S). The latter process seems to be less probable because of the large energy difference between the initial and final states. However, our analysis has shown that the avoided crossing of $2\,^3\Sigma_u^+$ and $3\,^3\Sigma_u^+$ potentials (the mechanism previously proposed by Sasso *et al* (1992) as the most likely one to cause the quenching) yields a negligible contribution to the quenching cross section. Based on the analysis of the potential curves calculated by Spies (1990) we have proposed different mechanisms for the quenching of the 5D state, which yield the cross section of 29×10^{-16} cm^2, that agree with the experiment much better. We have demonstrated the importance of the spin–orbit coupling, which at the crossing of the non-relativistic $2\,^3\Sigma_u^+$ and $2\,^3\Pi_u$ potentials produces almost half of the calculated cross section. We have also shown that the avoided crossing of the $1\,^3\Sigma_g^+$ with the $2\,^3\Sigma_g^+$ potential is responsible for the remaining contribution. As for the 5D fine-structure mixing cross section, we were able to compute the upper limit of 44×10^{-16} cm^2, which is in reasonable agreement with the value observed experimentally.

6. Conclusion

EET processes involving the caesium atoms excited to the 5D$_J$ states and colliding with the caesium ground-state atoms or molecules have been investigated. In particular we obtained the cross section for the 5D$_J$ fine-structure mixing,

$$\sigma_{5/2\rightarrow3/2} = (57 \pm 19) \times 10^{-16} \text{ cm}^2$$

and the cross section for the *J*-nonselective intermultiplet mixing of the 5D and 6P states

$$\sigma_D = (35 \pm 10) \times 10^{-16} \text{ cm}^2.$$

We have found that collisions with caesium ground-state atoms, and not molecules, causes the quenching of the 5D state. Our experimental results confirm the results of Sasso *et al* (1992) regarding the cross section values as well as the nature of the quenching of the 5D state. Our

theoretical analysis shows that spin–orbit and radial coupling mechanisms equally contribute to the observed quenching cross section of the 5D state.

For a treatment of the collision dynamics that would go beyond the scope of the present paper, a further theoretical investigation of the Cs_2 collisional complex would be needed. That should include not just improvement of the existing potentials but also the various coupling elements, subjects that remain open for future study.

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