Study of excitation transfer Li(3D → 3P) occurring in optical collisions with rare gas atoms experimentally

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Abstract. By selective optical excitation of collision pairs and observation of the reemitted fluorescence information is obtained on the role of the molecular channels involved in inelastic collisions. As an example case we have studied experimentally the Li(3D → 3P) excitation transfer in Li(3D)X systems with X = Ne, Ar by means of the optical collision process Li(2P) + X + hv → LiX(3D) → Li(3P, 3D) + X where LiX(3D) collision molecules dissociate into Li(3P, 3D) atoms following laser excitation hv of Li(2P) + X pairs. For this purpose we measured the Li 3P/3D population ratio by the fluorescence from these levels as a function of the laser detuning ∆ν from the Li(2P → 3D) transition and the rare gas pressure, and determined from this the 3P/3D excitation ratio B(∆ν) for single collision conditions. The experiments were performed using two step cw laser excitation of gaseous mixtures Li+ + Ne or Li+ + Ar. This reflects different dissociation probabilities from the 3D excited states that are initially prepared by blue wing or red wing excitation, respectively. The results are qualitatively discussed in terms of new ab initio potentials for the two systems.

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1 Introduction

In recent years an increasing number of optical collision experiments involving atoms at thermal energies for the study of inelastic processes like depolarisation and excitation transfer have been reported. In such experiments collision pairs (collision molecules) are selectively laser excited during collisions and the population distribution among the dissociated excited states is probed. Basically, by the choice of the laser frequency and due to the Franck-Condon principle the optical transition occurs at well defined distances between pairs of interatomic potentials. Thus optical collisions provide an excellent method to study the detailed dynamics of the collision following excitation and to probe sensitively the interatomic potentials involved.

So far, most optical collision spectra $M + X + hv \rightarrow M^* + X$ have been obtained with metal atom-rare gas systems and with the optical transitions starting from the ground states of $M$. By this means particularly the collision-induced fine-structure transitions and depolarisation of Na(3P) atoms has been intensively studied in cell experiments [1,2] and more recently in beams [3,4]. The very detailed information obtained from the beam experiments was analysed by means of quantum coupled channels methods [5] and yielded an almost complete picture of the detailed collision dynamics. Also recently, for the first time experimental polarisation dependent excitation spectra for excited-state Mg* + X optical collisions have been presented [6,7].

In the following we report on an optical collision experiment for the study of the 3D → 3P excitation transfer in lithium due to collisions with rare gas atoms Li(3D) + X → Li(3D, 3P) + X. For this process, total cross-sections are known from the literature [8–10], that however represent only averages of contributions from the different molecular channels 3DA* → 3P, A. To obtain channel specific information we have therefore set up an experiment, that is based on the following optical collision process

$$Li(2P) + X + hv \rightarrow Li(3P, 3D) + X.$$
profiles information on nonadiabatic couplings specific to the different transfer channels is obtained.

The present optical collision studies at Li(2P)X differ from those at the above mentioned NaX systems in several respects. First, the optical transitions start from excited atoms other than from the groundstate. Second, the spin-orbit interaction is unimportant in the excited Li states, and besides the Δ states of Li(3D)X are involved in the nonadiabatic couplings governing the 3D → 3P transfer process. Last not least, due to the large Li(3D–3P) term separation (357 cm⁻¹) the transfer probabilities are expected to be much smaller than those for the Na(3Pj) fine structure transfer. Experimentally, this might imply severe requirements to the detection sensitivity of the Li(3P) population.

The present work was much motivated by new ab initio potential calculations for LiNe [12] and LiAr [13], that can be sensitively probed by the optical collision spectra for the excitation transfer in principle. Very encouraging were also concurrent quantum calculations of cross-sections for the individual 3DA⁺ → 3ΠA transfer channels [17] using coupling matrix elements from ab initio methods [18], that facilitated at least a qualitative understanding of the experimental results. Last not least, experimental excitation spectra LiX(2P,A → 3D,A⁺) recently reported [15,20] as well as measurements of integral Li(3D → 3P) transfer probabilities performed at these systems [14] permitted realistic estimations of fluorescence signal levels to be expected for given excitation and detection geometry.

2 Experiment

2.1 General experimental method

The present experimental studies are based on two step cw laser excitation of gaseous mixtures of Li+X at temperatures around 600 K. The experimental scheme can be generally understood with reference to Figure 1, representing interaction potentials for the LiNe system. In this scheme laser 1 (pump laser) excites Li atoms to the 2P state, where they subsequently collide with X atoms forming collision molecules LiX(2P,A) and a second laser (scan laser) excites these further into the higher LiX(3D,A⁺) states. According to the potentials, 3DΣ, 3Π, Σ, Π states of LiX(3D,A⁺) are excited selectively at blue wing or red wing detunings respectively of the scan laser from the Li(2P–3D) transition. The subsequent dissociation LiX(3D,A⁺) → Li(3D,3P) produces atomic Li(3D,3P) population, which is monitored by fluorescence emission on the transitions Li(3D–2P) λ = 610 nm and Li(3P–2S) λ = 323 nm. To obtain dissociation probabilities for individual dissociation channels from the experiment, it is essential that single collision conditions are fulfilled as good as possible. Clearly, subsequent collisions of excited Li(3P,3D) atoms before spontaneous decay would redistribute the 3P and 3D population initially present after dissociation of the LiX(3D,A⁺) collision pairs and consequently destroy channel specific information.

In such an experiment extremely small fluorescence rates, particularly at 323 nm, are to be expected for two reasons. Primarily, this results from a very small collisional 3D → 3P transfer probability 10⁻³–10⁻⁴ observed [14] together with the small Einstein coefficient A₃P→2S = 1.17 × 10⁶ s⁻¹ of the 323 nm line. Secondly this is due to extremely small off resonant excitation rates of the Li(3P,3D) atoms resulting from two requirements: (1) rare gas number densities have to be restricted to typically 10¹⁰–10¹¹ cm⁻³ to keep secondary collision rates below 0.1 times the radiative decay rate from the 3D state. (2) also the Li(2P) atom density N₂P has to be limited, because of energy pooling collisions Li(2P) + Li(2P) → Li(3P,3D) + Li(2S), that produce undesired extra Li(3P,3D) excitation at rates proportional to N₂P. From these reasons a 323 nm real signal below typically 10 cps with about the same amount of energy pooling background is observed with the fluorescence detection system used (see Sect. 2.2) at scan laser detunings above 20 cm⁻¹ from the 2P–3D resonance. An additional difficulty arises due to reabsorption of the 323 nm radiation from Li₂S groundstate atoms. This however can be eliminated to large extent by means of the calibration method of relative 323 nm detection sensitivity described in Section 3.

![Figure 1. Interaction potentials for the LiNe system [12] and general experimental scheme for the study of the optical collision process Li(2P) + Ne + hν → Li(3D,3P) + Ne.](image-url)