Comment on "Entropy lowering in ion-atom collisions"

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(Received 27 July 2005; published 18 January 2006)

The recent experimental result by Nguyen *et al.* [Phys. Rev. A **71**, 062714 (2005)] on the ratio of cross sections for charge exchange processes $\mathrm{Rb}^{+}+\mathrm{Rb}(5s)\rightarrow\mathrm{Rb}(5p)+\mathrm{Rb}^{+}$ and $\mathrm{Rb}^{+}+\mathrm{Rb}(5p)\rightarrow\mathrm{Rb}(5s)+\mathrm{Rb}^{+}$ is quantitatively derived from simple considerations within the general framework of the quasimolecular theory. Contrary to the expectations, applicability of the Demkov model for charge exchange with small energy defect is not shattered.

DOI: 10.1103/PhysRevA.73.016702 PACS number(s): 34.10.+x, 34.20.−b, 34.70.+e, 34.50.Pi

Contrary to its title, the recent paper by Nguyen *et al.* [1] deals not with issues of statistical physics, but is devoted to the elementary ion-atom charge exchange processes

$$\mathrm{Rb}^{+}+\mathrm{Rb}(5s)\rightarrow\mathrm{Rb}(5p)+\mathrm{Rb}^{+}, \tag{1}$$

$$\mathrm{Rb}^{+}+\mathrm{Rb}(5p)\rightarrow\mathrm{Rb}(5s)+\mathrm{Rb}^{+}. \tag{2}$$

By carefully using the state-of-the-art magneto-optical trap recoil ion momentum spectroscopy (MOTRIMS) technique the authors came to the major experimental result of the study: the ratio of the cross sections for the two channels of interest, Eqs. (1) and (2), is obtained as

$$\frac{\sigma_{5s-5p}}{\sigma_{5p-5s}}=2.96\pm0.24. \tag{3}$$

The subsequent discussion stresses that this result is beyond capability of the well-known two-state Demkov [2] model that is designed to consider processes of charge exchange with a small defect of energy Q. The reasoning for the apparent failure of the Demkov model was based on the observation that the latter gives cross sections as a strong function of the magnitude of the Q value, but is independent of its sign, in an apparent contradiction with the result (3). The qualitative explanation suggested by the authors [1] indicates that the incoming Rb(5*s*) state almost exclusively feeds the Rb(5*p*) state, while the incoming (higher lying) Rb(5*p*) state feeds *both* the Rb(5*s*) *and* the (yet more higher lying) Rb(4*d*) exit channels. Thus the accompanying transitions to the excited Rb(4*d*) state are deemed to be crucial for explaining the experimental finding (3). The two-state model is allegedly unable to describe such a complexity.

The objective of the present Comment is to demonstrate how the experimental result (3) is quantitatively obtained from simple dynamical analysis without any calculations, see formula (6) below. The treatment is based, in particular, on the Demkov model without resort to transitions into Rb(4*d*) state. The derivation is rooted in the general framework of the quasimolecular theory for slow atomic collisions (see, for instance, Refs. [3,4]).

I start with the trivial observation that the process (1) is characterized by the total cross section that is a sum of partial cross sections. The latter ones correspond to definite value of the final magnetic quantum number m_l of the product Rb(5*p*) atom:

$$\sigma_{5s-5p}=\sum_{m_l=-l}^{m_l=l}\sigma_{5s-5p_{m_l}}, \tag{4}$$

where the orbital momentum l is equal to 1 in the case of interest. Similarly, the process (2) is characterized by three partial cross sections $\sigma_{5p_{m_l}-5s}$. The measured cross section is apparently defined in the standard manner as a result of averaging over initial m_l substates,

$$\sigma_{5p-5s}=\frac{1}{2l+1}\sum_{m_l=-l}^{m_l=l}\sigma_{5p_{m_l}-5s}, \tag{5}$$

The next observation is that the two-state Demkov model describes transitions between the quasimolecular states with the same projection Λ of the electronic orbital momentum on the internuclear axis. The transition is induced by rearrangement of separated atom orbitals into molecular orbitals as the internuclear separation R decreases; it amounts to radial coupling of quasimolecular states. In the pattern of quasimolecular potential curves the relevant feature is characteristic (exponential) repulsion between potential curves as R decreases and the one-center atomic orbitals start to appreciably overlap. The achievement by Demkov [2] was to indicate that just this type of transitions defines cross section of charge exchange with small energy defect for slow collisions. This general conclusion was supplemented by exact solution of an appropriate model with a simple analytical expression for the transition probability; however, this formula is not needed in the analysis below.

In the case of interest there are essentially two Σ potential curves [5] correlated to initial and final states in reactions (1) or (2). The transitions between these curves can be described by the Demkov model. The probability of transition does not

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depend on the direction of the process, (1) or (2). This feature was cast in Ref. [1] as independence on the sign of the energy defect Q. In fact this is a very general property linked to the detailed balance relation $k_a^2\sigma_{a\to b}=k_b^2\sigma_{Tb\to Ta}$. In the experiment [1] the collision energy was chosen as 7 keV, while the energy defect Q for the processes (1) or (2) is around 0.05 a.u. Therefore the difference between the momenta in incident and outgoing channels k_a and k_b is negligible and the cross sections for the direct $(a\to b)$ and time-reversed $(Tb\to Ta)$ processes are essentially equal.

In addition to Σ potential curves, there are also Π curves correlated to Rb($5p$) states in the separated atom limit. The charge exchange process in principle might occur through transitions between ingoing Π and outgoing Σ quasimolecular potential curves (or vice versa). Such transitions are induced by the rotation of the quasimolecular axis. For low collision velocity they are well known to be strongly suppressed compared to the Demkov-type radial-coupling-induced transitions.

To summarize the picture, only $\Sigma-\Sigma$ charge exchange transitions are appreciable while $\Sigma-\Pi$ transitions are negligible. This means that each sum in Eqs. (4) and (5) effectively contains only one term and this term is the same in both the sums. The only difference between the expressions (4) and (5) is in statistical factor

$$\frac{\sigma_{5s-5p}}{\sigma_{5p-5s}} = 2l+1 = 3, \qquad (6)$$

that is in perfect agreement with the experimental finding (3). It is not influenced by the transitions to higher lying Rb($4d$) state, although signature of these transitions was separately observed in experiments [1].

It is worthwhile to indicate that in addition to the charge exchange there are also depolarization processes that are collision-induced transitions between different m_l substates of the Rb($5p$) atom. These occur at substantially larger internuclear separations than R domain important for the charge exchange processes and hence have much larger cross sections. The depolarization processes are responsible for redistribution of the population between Σ and Π quasimolecular states. This "one-center" redistribution does not change the present result being absorbed by summation in formulas (1) and (2).

In conclusion, it is worthwhile to note that identification of excitation and deexcitation collisions, respectively, with entropy lowering and increase is incorrect in the rigorous theoretical sense and has not heuristic power to help intuition.

This work was carried out during author's visit to Max Plank Institute for Physics of Complex Systems, Dresden. The hospitality of this Institute is gratefully acknowledged.

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[5] I imply here potential curves of the same symmetry, *gerade* or *ungerade*.