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Evidence for autoexcitation producing inner-shell vacancies in slow ion-atom collisions

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A previous experimental study of Ar L-vacancy production in slow $Ar^+ + SiH_4$ collisions is reanalyzed to provide evidence for the dielectronic process of (inverse) autoexcitation, which removes an electron from a deep inner shell by interaction with another electron decaying from an upper level. Analytic models are evaluated to treat alternative cases where two electrons are transferred at a curve crossing and between parallel potential curves. The theoretical results confirm the experimental observation that the Ar L-vacancy production increases with decreasing energy.

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In the past few years considerable interest has been devoted to dynamic electron-correlation effects that occur in energetic ion-atom collisions [1,2]. These effects are produced by mutual interactions of two electrons whose description leads beyond the independent-particle model. Hence, the electron-electron interaction causes two-electron processes that are referred to as dielectronic processes [3]. A characteristic dielectronic process is *autoexcitation* [2], where one electron is transferred to a deeper lying level, while another electron is excited to a higher-lying (Rydberg) level. Autoexcitation is similar to autoionization, where one electron is transferred to a deeper lying level, while the second electron is ejected into the continuum.

Both autoexcitation and autoionization may occur in separated atoms as well as in collision systems [4]. In a separated atom, autoexcitation gives rise to the stationary phenomenon of configuration mixing, which manifests itself by its effects on the associated state energies. In time-dependent collision systems the process of autoexcitation can be observed in a more direct manner; e.g., by verifying the population of high Rydberg states after the collision. Examples for autoexcitation occurring during the collision are the process of correlated double capture [5] and correlated transfer excitation [6]. Recently, a further example for autoexcitation has been studied in the postcollision region [7]. These phenomena have in common that they involve electron-correlation effects inducing transitions to high Rydberg states.

The autoexcitation event may be inverted in time, giving rise to a specific dielectronic process where an electron from a higher-lying level is deexcited, transferring its excess energy to another electron, which, in turn, is removed from a deeply lying shell [2]. Hence, this process of inverse autoexcitation, also denoted dielectronic excitation [8,9], involves a mechanism producing vacancies in a rather deep inner shell. (Hereafter, as no conflict in notations occurs, the process of inverse autoexcitation is also referred to as autoexcitation.) The remarkable feature of the autoexcitation process is its dominance at very low collision energies at which other mechanisms fail to produce inner-shell vacancies.

First experimental indications for autoexcitations producing of inner-shell vacancies, have been provided by Afrosimov *et al.* [10], studying the system $N^+ + Ar$ at relatively low projectile energies near 20 keV. The authors postulated the initial production of two vacancies in the molecular orbital associated with the Ar L shell and a subsequent two-electron transition involving vacancy production in an outer shell and the K shell of nitrogen. Similarly, DuBois, Stolterfoht, and Schneider [11], who studied the Ar+Si system, considered double-vacancy production in the Si L shell followed by a two-electron transition creating a vacancy in the L shell of the heavier collision partner, argon. It should be noted, however, that the interpretation of the experimental observations [10,11] has not been verified theoretically.

The study of the Ar+Si system has been motivated by related work about ion-solid collisions involving Ar^+ incident on crystalline Si. At incident energies as low as a few keV, Witmaak [12] had observed a significant Ar L-vacancy production whose interpretation remained a long-standing mystery. New interest in the field was created since much attention has recently been devoted to the interaction of slow, highly charged ions with solid surfaces where "hollow" atoms are produced [8,13]. These studies have clearly exhibited the need for conclusive evidence regarding the process of autoexcitation.

In this Rapid Communication, it is shown that Ar L-vacancy production in the Ar+Si system [11] is caused by the process of inverse autoexcitation. This is done by means of model calculations describing dielectronic processes in slow ion-atom collisions. First-order perturbation theory and the semiclassical approximation (SCA) are utilized to evaluate analytic formulas suitable to estimate the autoexcitation process. Two extreme cases are treated: (i) transitions near a curve crossing in accordance with the Landau-Zener model [14] and (ii) transitions between potential curves of constant-energy difference.

The experiment by DuBois, Stolterfoht, and Schneider [11] has been performed to study both Ar L- and Si L-vacancy production in the collision system Ar+Si. Figure 1(a) shows the associated molecular-orbital (MO) diagram based on previous Hartree-Fock calculations [15]. Experimental results for 7- to 40-keV $Ar^+ + SiH_4$ collisions are shown in Fig. 2, where the cross-section ratios for Ar L- to Si L-vacancy production are depicted [11].

Different mechanisms may be responsible for the Ar L-vacancy production in $Ar^+ + SiH_4$ collisions [16]. It is found, however, that the related one-electron processes are very unlikely at collision energies below about 50 keV [15,16]. For instance, it can be estimated by means of Demkov's formula [17] that the probability for single-vacancy transfer from the 6σ MO to the 4σ MO is $\sim 10^{-12}$ at 40 keV. Furthermore, this probability decreases significantly with decreasing projectile energy. These findings are in obvious disagreement with the experimental data, which increase with decreasing energy (Fig. 2). Hence, it appears reasonable to search for other Ar L-vacancy production mechanisms such as two-electron events.

The dielectronic process of inverse autoexcitation occurs after the promotion of two electrons via the 6σ MO (i.e., the $4f\sigma$ MO in the diabatic notation) and their loss by couplings to other high-lying MO's. Hence, in the outgoing part of the collision, two vacancies return via the 6σ orbital, which correlates with the $2p$ orbital of Si. At about 1 a.u. resonance conditions are created for autoexcitation where, simultaneously, the two vacancies are filled by transitions of an electron from high-lying MO's and an electron from the 4σ or 1π MO [Fig. 1(a)]. These latter MO's correlate with the $2p$ orbital of Ar into which one vacancy is finally guided.

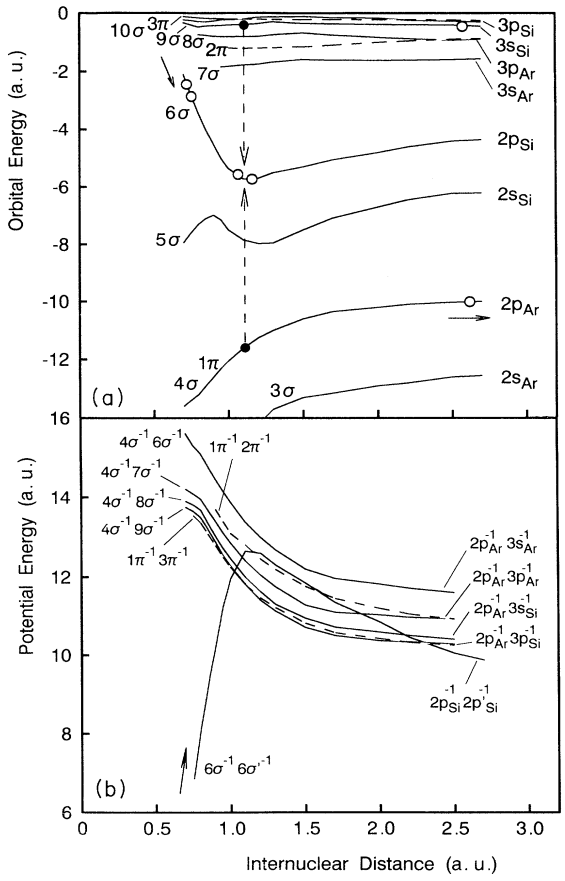

FIG. 1. Molecular-energy diagrams for the system Ar+Si determined from previous Hartree-Fock calculations [15]. In (a) molecular-orbital (MO) energies are given. In (b) are shown potential energies obtained as a negative sum of the MO energies for the two associated vacancies. The "initial" energy curve attributed to the configuration $6\sigma^{-1}6\sigma'^{-1}$ was corrected with respect to relaxation effects, see text.

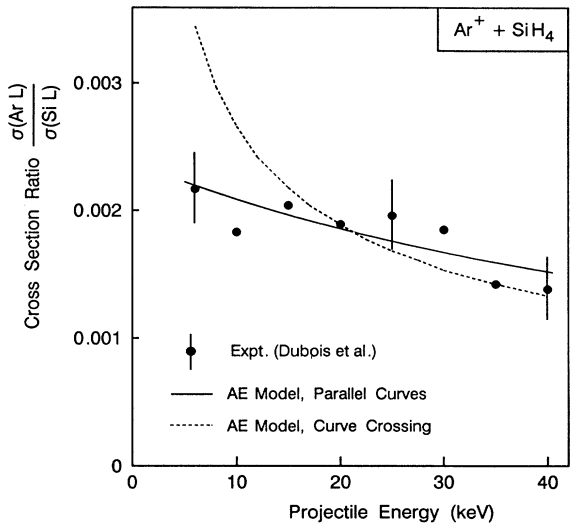

FIG. 2. Cross-section ratio for Ar to Si L-shell-vacancy production in $Ar^+ + SiH_4$ collisions measured by DuBois, Stolterfoht, and Schneider [11]. The experimental data are compared with theoretical results from the present autoexcitation (AE) models assuming curve crossing (dotted line) and parallel curves (solid line).

To verify finer details of the resonance conditions, which are involved in the process of autoexcitation, it is useful to consider the potential curves shown in Fig. 1(b). The "initial" configuration is $6\sigma^{-1}6\sigma'^{-1}$, whose potential curve was corrected for orbital relaxation effects, i.e., it was shifted by a constant energy due to the increase of the binding of the second electron after removal of the first one. It is seen that near 1 a.u. the resonance condition for autoionization manifests itself by crossings of the initial $6\sigma^{-1}6\sigma'^{-1}$ curve with a series of "final" curves attributed to $4\sigma^{-1}n\sigma^{-1}$ $(n \geq 6)$ and $1\pi^{-1}n\pi^{-1}$ $(n \leq 2)$. Also, within an interval from 1.0 a.u. to ~ 1.5 a.u., it is seen that the initial curve runs parallel to the final curves. Hence, it is expected that transitions between parallel and crossing potential curves are important for the Ar L Auger-electron production in the Ar+Si system.

In the following, first-order perturbation theory is applied to evaluate processes of autoexcitation that are produced by electron-electron interaction. The first-order approach is likely to be justified, as the electron-electron interaction is relatively weak. Atomic units will be used throughout. Assuming a unit occupation of the initial state, the time-dependent occupation coefficient for the final state is obtained as (see, e.g., [2])

$$d_f(t) = i \int_{t_0}^{t} V_{if}(t') \exp\left[-i \int_{t_0}^{t'} \Delta E(\tau) d\tau\right] dt' , \qquad (1)$$

where V_{if} is the coupling matrix element, also denoted dielectronic in the following, and ΔE is the energy difference between the initial and final state whose in-

teraction starts at time t_0. The transition probability from the initial to the final state is given by $P=|d_f(t\rightarrow\infty)|^2$.

The main task in analyzing autoexcitation is the determination of the dielectronic matrix element V_{if}, which describes the two-electron transition produced by the electron-electron interaction:

$$V_{if}=\left\langle \varphi_f^1\varphi_f^2 \left| \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} \right| \varphi_i^1\varphi_i^2 \right\rangle , \tag{2}$$

where φ_i^μ and φ_f^μ are, respectively, the initial and final states of the electron labeled $\mu=1$ or 2. If one of the electrons is transferred to a final Rydberg state n, the matrix element (2) is to be weighted by the factor $Z_{\text{eff}}n^{-3/2}$, where Z_{eff} is the effective nuclear charge of the system [7]. To evaluate V_{if}, different cases are to be distinguished. In separated atoms, both electrons remain at one nuclear center. It has been pointed out previously [2] that the one-center matrix element is rather constant with values near a few 10^{-2} a.u. This information is useful for a fair estimate of one-center autoexcitation.

Less information is available about two-center autoexcitation where one or two electrons are exchanged between the collision partners. Grozdanov and Janev [18] have shown that the two-center matrix element varies exponentially within the asymptotic region of large internuclear distances ($R\alpha\gg1$), i.e.,

$$V_{if}(R)=ke^{-\alpha R} , \tag{3}$$

where k and α are approximately constant. Here, the primary interest concerns the two-center autoexcitation where only one electron is exchanged. In this case it is expected that the exponent α in Eq. (3) is similar to that known for one-electron capture. For inner-shell charge transfer one may set

$$\alpha=0.86\frac{\sqrt{2B_i}+\sqrt{2B_f}}{2} , \tag{4}$$

where B_i and B_f are the binding energy of the transferred electron in the initial and final states, respectively (see [15] and references therein). Only little is known about the constant k. For $R\alpha\lesssim1$ the two-center wave functions overlap appreciably so that the corresponding matrix element is expected to merge into that for one center. Hence, for an order-of-magnitude estimation, one may set $ke^{-1}\approx5\times10^{-2}$ a.u., so that $k\approx0.2$ a.u. However, since detailed information is missing about the parameter k, it will be used as a fit parameter in this work.

The following analysis treats specific cases that are described in more detail elsewhere [9]. First, it is assumed that the potential curves cross at $R_c=R(t=0)$ and the interaction matrix element is constant within the coupling region, i.e., $V_{if}=V_{if}(R_c)$. These conditions are the same as those incorporated into the Landau-Zener formula [14], so that only the final result is given here, yielding the transition probability for a number N_f of final states

$$P=2\pi\frac{N_f|V_{if}(R_c)|^2}{v_R F(R_c)} . \tag{5}$$

It implies the truncated Taylor expansion $\Delta E(t)=td\Delta E/d\tau=tv_R F(R_c)$, where R is the internuclear distance, v_R is the radial velocity, and the "force" $F(R_c)=d\Delta E/dR$ is a measure for the relative inclination of the potential curves. Expression (5) is an accurate approximation to the Landau-Zener formula for small perturbations $2\pi|V_{if}(R_c)|^2\ll v_R F(R_c)$, characteristic for the electron-electron interaction.

Second, it is assumed that the energy difference of the potential curves remains constant, i.e., $\Delta E=\Delta E(t_0)$ and the coupling matrix element depends exponentially on R, in accordance with Eq. (3). The truncated Taylor expansion $R=R_0+v_R t$ is utilized, where $R_0=R(t_0=0)$ is the lower limit of the coupling region. Then, it follows that

$$d_f(t)=V_{if}(R_0)i\int_0^t e^{-\alpha v_R t'}e^{-i\Delta E t'}dt' , \tag{6}$$

which can be solved analytically:

$$|d_f(t)|^2=\frac{|V_{if}(R_0)|^2}{(\Delta E)^2+(\alpha v_R)^2}[1+e^{-2\alpha v_R t} -2e^{-\alpha v_R t}\cos(\Delta E t)] . \tag{7}$$

This expression describes damped oscillations (i.e., quantum beats) typical for two-state interactions. For the number N_f of final states one obtains the transition probability (at $t\rightarrow\infty$)

$$P=\frac{N_f|V_{if}(R_0)|^2}{(\Delta E)^2+(\alpha v_R)^2} . \tag{8}$$

It should be pointed out that this result is rather different from that given by Demkov [17], i.e., $P=\exp[-\pi\Delta E(\alpha v_R)^{-1}]$, which has been derived using assumptions similar to those for Eq. (8). The essential difference lies in the initial conditions. The autoexcitation model is based on $V_{if}(R_0)\ll\Delta E$. On the contrary, in Demkov's model $V_{if}(R_0)\gg\Delta E$ so that, initially, the diabatic states are fully mixed and the system is started in one of the associated adiabatic states.

Figure 2 shows the comparisons of the experimental data with the results of the present autoexcitation models. The dotted line represents the calculations by Eq. (5) based on the curve crossing model. Crossings involving the final configurations $4\sigma^{-1}n\sigma^{-1}$, with $n=7$ to 9, were used to determine the parameter $F(R_c)=10.5$ a.u. The radial velocity was estimated to be $v_R=0.7v$ where v is the incident velocity. The value $N_f|V_{if}(R_c)|^2=3.1\times10^{-4}$ a.u. was obtained by arbitrarily fitting the theoretical curve to the experimental data between 20 and 40 keV. Hence, in that range good agreement is achieved between theory and experiment. However, at lower energies, it is seen that the theoretical results do not reproduce the experimental data. The agreement between experiment and theory is significantly improved as the model, based on parallel potential curves, is utilized. The theoretical results from Eq. (8) are represented by the solid line in Fig. 2. In the calculations, the value of $\alpha=3.15$ a.u. was obtained from Eq. (4) and $\Delta E=0.6$ a.u. was determined as the mean value of the energy differences between the initial and final states near the in-

ternuclear distance of ~ 1.2 a.u. [Fig. 1(b)]. As before, $N_f|V_{if}(R_0)|^2 = 8\times 10^{-4}$ a.u. was determined from the fit to the experimental data.

In the previous analysis, each model implies an adjustable parameter whose value was determined to achieve agreement between theory and experiment. Setting $R_c = 1.05$ a.u. and $N_f = 5$ [Fig. 1(b)] for the curve crossing model, one can estimate by means of Eq. (3) that $N_f|V_{if}(R_c)|^2 = 2.5\times 10^{-4}$, which is consistent with the fit value given above. Furthermore, to analyze the model based on parallel curves, it appears reasonable to set $R_0 \approx R_c$. With this assumption, it appears difficult to explain the relative large fit value given above. It is noted, however, that the number of final states increases significantly for parallel curves due to adjacent Rydberg states. (Also, N_f is enhanced for open shells produced after multiple removal of outer-shell electrons during the collision.) Nevertheless, the absolute values for the transition probability suggest that the curve crossing mechanism is more important than that involving the coupling of the "parallel" states. On the other hand, as noted from Fig. 2, the energy variation of the transition probability supports the parallel-state coupling mechanism. In any case, the latter mechanism is dominant when a curve crossing is missing [Fig. 1(b)]. Hence, at this point, it is anticipated that both mechanisms play a certain role in slow Ar+Si collisions.

In conclusion, the present models confirm that autoexcitation provides a mechanism producing vacancies in deep inner shells when other processes become inactive. It appears safe to conclude for projectile energies lower than 40 keV that the experimental observation of Ar L-vacancy production in $Ar^+ + SiH_4$ collisions is attributed to autoexcitation. Further theoretical work is needed to gain more information about the dielectronic matrix elements, which are essential to verify the dominance of the different mechanisms considered in this work.

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