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Oscillatory alignment phenomena in Rydberg-atom–rare-gas collisions

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Retention of orbital alignment during near-resonant energy transfer collisions of rare-gas projectiles with excited alkaline-earth-metal atoms is explored theoretically for scattering of Xe from Rydberg states of Ca. For such collisions, conventional interpretations of alignment phenomena, which are based on potential curves for a transient molecule thought to form during the collision, are not relevant. Theoretical partial magnetic sublevel cross sections for Ca**$(4s17d\ ^1D_2 \rightarrow 4s18p\ ^1P_1)$ transitions confirm the existence of alignment effects, as demonstrated experimentally by Spain *et al.* [J. Chem. Phys. **102**, 9532 (1995)], at a mean relative velocity of 914 m/s. Theory further predicts heretofore unobserved oscillatory structures in these cross sections as a function of relative velocity and that these oscillations depend strongly on the initial magnetic quantum number of the Rydberg electron. [S1050-2947(98)50301-0]

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The recent interest in the role of orbital alignment and orientation in collisions of incident electrons or atoms with target atoms or molecules [2] stems from the detailed insights such studies provide into fundamental mechanisms that control the dynamics and changes in properties of the colliding particles as a result of their encounter [3]. Pulsed-laser-excitation crossed-beam experiments by Leone and collaborators [4] have demonstrated pronounced alignment effects in near-resonant electronic energy-transfer collisions of rare-gas atoms with Ca atoms that are initially aligned in a *low-lying excited state*. The central issue in such studies is whether orbital alignment is retained during the collision—i.e., whether the excited electron ''remembers'' the shape of its initial state. Interpretation of data from these experiments in terms of transient quasimolecular electronic states thought to form as the orbital of the excited electron temporarily couples to the internuclear axis (''orbital following'' and ''locking'' models [5]) has illuminated the symmetry properties of the (van der Waals) potential curves that govern such collisions and, more generally, the role of curve crossings and quasimolecule formation in atom-atom scattering.

The centrality of this molecular interpretation to understanding collisional alignment effects raises a provocative question: *do alignment phenomena occur under conditions that preclude quasimolecule formation?* Such conditions obtain if the target atom is initially in a Rydberg state: the comparatively low velocity and extremely diffuse probability distribution of a Rydberg electron render a molecular (Born-Oppenheimer) description inappropriate to such a collision [13]. Scattering from an initially aligned *Rydberg* atom, therefore, cannot be analyzed meaningfully in terms of (adiabatic) molecular potential curves [6]; alignment effects, if present at all, must arise from some other mechanism. We have investigated this question for Ca**-Xe collisions *using a quantum-mechanical theory that explicitly excludes quasimolecule formation*. Our findings not only confirm recent observations of alignment effects in these collisions at a single relative velocity distribution [1], but also predict heretofore unseen oscillations as the velocity is varied—structures that depend strongly on the initial and final magnetic quantum numbers of the Rydberg electron.

We solve the scattering problem using the quantal impulse approximation (IA) within the quasi-free-electron (QFE) model. The IA treats the Rydberg electron, the Ca^+ core, and the rare-gas perturber as independent particles in an effective three-body collision [7,8]. The QFE model neglects core-electron and core-perturber interactions, which have been shown to be much less important than the electron-perturber interaction for the near-resonant transitions of interest here [9]. In this model, the collision, which takes place very far from the core (e.g., the $17d$ radial probability density peaks near $500a_0$), occurs through the interaction of the projectile with a nearly free Rydberg electron. The extremely diffuse Rydberg-electron charge cloud is unaffected by the perturber except when the electron undergoes a transition $\alpha = (n,\ell,m) \rightarrow \alpha' = (n',\ell',m')$. The role of the core in IA theory is to support these initial and final bound states of the Rydberg electron.

The theoretical quantity most closely allied to the experimental data of Leone and co-workers [4] is the partial magnetic sublevel cross section $\sigma^{|m|}(v_{\rm rel})$ for initial relative Ca**-Xe velocity $v_{\rm rel}$. This quantity is the sum over final quantum numbers m' of all state-to-state cross sections $\sigma_{\alpha\rightarrow\alpha'}(v_{\rm rel})$ for a given initial m. The sensitivity of these cross sections to $|m|$ is a measure of the strength of alignment effects; if they are independent of $|m|$, no such effects are present, and all information regarding initial-state alignment was lost during the collision [3]. The fundamental IA-QFE scattering amplitude for transition $\alpha \rightarrow \alpha'$ with accompanying change in relative momentum $\boldsymbol{K} \rightarrow \boldsymbol{K}'$ can be written (in atomic units) as [8]

$$f(\boldsymbol{K}',\alpha' \leftarrow \boldsymbol{K},\alpha) = -\mu f^{(e)}(Q) \langle \alpha' | e^{i\boldsymbol{Q}\cdot\boldsymbol{r}} | \alpha \rangle, \qquad (1)$$

where μ is the reduced mass of the Ca-Xe system, $\boldsymbol{Q} \equiv \boldsymbol{K} - \boldsymbol{K}'$ is the momentum transfer, the matrix element is the transition form factor, and $f^{(e)}(Q)$ is the electron–rare-gas amplitude. Because of the very small binding energy of the Rydberg electron (e.g., 52.5 meV for the $17d$ state), the

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electron-scattering amplitude can be accurately represented using modified effective range theory as [10]

$$f^{(e)}(Q)\approx -A-\frac{1}{4}\pi\alpha_p Q, \tag{2}$$

where the Xe scattering length [11] is $A=-6.50a_0$ and the static polarizability is $\alpha_p=27.0a_0^3$ [12]. We write the state-to-state cross section $\sigma_{\alpha\to\alpha'}(v_{\rm rel})$ as an integral over momentum transfer [13] from $Q_{\rm min}=|K-K'|$ to $Q_{\rm max}=|K+K'|$,

$$\sigma_{\alpha\to\alpha'}=\frac{2\pi}{K^2}(2\ell+1)(2\ell'+1)\mu^2 \times\int_{Q_{\rm min}}^{Q{\rm max}} f^{(e)}(Q)^2[g_{\alpha,\alpha'}(Q)]^2 Q\,dQ, \tag{3}$$

where

$$g_{\alpha,\alpha'}(Q)=\sum_\lambda d_\lambda(\ell' m',\ell m)P_\lambda^{m-m'}(\cos\theta_Q) \times\int_0^\infty R_{n',\ell'}(r)j_\lambda(Qr)R_{n,\ell}(r)r^2 dr. \tag{4}$$

The angular-momentum coefficient

$$d_\lambda=(-1)^{(\ell+\ell'+\lambda)/2}(2\lambda+1) \times\left[\frac{(\lambda-m+m')!}{(\lambda+m-m')!}\right]^{1/2}\begin{pmatrix}\ell & \ell' & \lambda\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell & \ell' & \lambda\\ m & m' & m'-m\end{pmatrix} \tag{5}$$

allows (for $d\to p$ transitions) only $\lambda=1,3$. The integral in Eq. (3) must explicitly take account of the dependence on Q of the Legendre polynomial in the factor $g_{\alpha,\alpha'}(Q)$. This dependence arises because the angle θ_Q is determined by K, by Q, and by the exit-channel relative momentum $K'=(K^2-2\mu\Delta\epsilon)^{1/2}$,

$$\cos\theta_Q=\frac{Q^2+K^2-K'^2}{2KQ}, \tag{6}$$

where the energy defect $\Delta\epsilon$ for the $17d\to18p$ transition is $1.69\ {\rm cm}^{-1}$. [This complication did not arise in previous applications of the IA to Rydberg-atom–rare-gas collisions, which sought only *level-to-level* $(n,\ell\to n',\ell')$ cross sections, i.e., sums of the state-to-state cross sections over m and m' [14].] The radial functions of the Rydberg electron $R_{n,\ell}(r)$ must reflect the Ca quantum defects ($\delta_{18p}=1.8721$ and $\delta_{17d}=0.9043$) and are generated from the Schrödinger equation for a pure Coulomb potential with eigenenergies $\epsilon_{n\ell}=-1/[2(n-\delta_{n\ell})^2]$, by numerically integrating inward from $4(n-\delta_{n\ell})^2\approx1000a_0$ to the inner classical turning point $r_{n\ell}^{(\rm ctp)}$ and there setting $R_{n,\ell}(r)$ to zero. [The huge mean radii of these states ($\langle r\rangle_{n\ell}\approx400a_0$) compared to the turning points ($r_{n\ell}^{(\rm ctp)}\approx3a_0$) renders the contribution to form-factor matrix elements from $r<r_{n\ell}^{(\rm ctp)}$ negligible.]

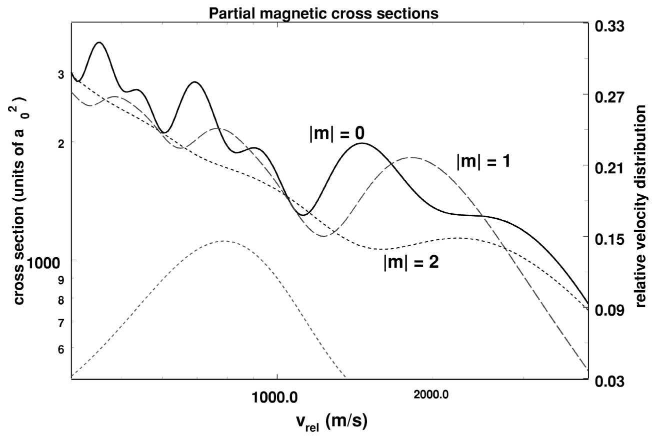

FIG. 1. Partial magnetic $\mathrm{Ca}(17d)+\mathrm{Xe}\to\mathrm{Ca}(18p)+\mathrm{Xe}$ cross sections for $|m|=0$ (solid), 1 (long dash), and 2 (short dash). Also shown is the velocity distribution for the experiment of Spain *et al.* [1,15] (dot-dash curve).

In recent crossed-beam experiments using a new stimulated emission probing technique to identify final electron states, Spain *et al.* [1,15] have measured relative cross sections for the process

$$\mathrm{Ca}^{**}(4s17d\ ^1D_2)+\mathrm{Xe}\to\mathrm{Ca}^{**}(4s18p\ ^1P_1)+\mathrm{Xe} \tag{7}$$

at a single mean relative velocity, 914 m/s (133 meV), which corresponds to the experimental velocity distribution shown in Fig. 1. In Table I we compare their partial magnetic sublevel cross sections (as determined by a least-squares fit to measured alignment cross sections) to our IA-QFE values averaged over the experimental velocity distribution. Both experiment and theory predict clear alignment effects: σ^0 and σ^1, which are of comparable magnitude, are both larger than σ^2.

Going beyond the experiment, we can investigate this phenomenon as a function of $v_{\rm rel}$. Figure 1 shows that pronounced alignment effects occur throughout the range of relative velocities from a few hundred to several thousand m/s. The most distinctive features of $\sigma^{|m|}(v_{\rm rel})$ are the oscillations with $v_{\rm rel}$ and the dependence of these structures on the initial magnetic quantum number $|m|$. These oscillations are superimposed on a smooth decrease in the state-to-state cross sections with increasing $v_{\rm rel}$, a familiar variation that goes as $v_{\rm rel}^{-2}$ at large relative velocities [8,13]. They also survive the additional sum over m in the construction of the $17d\to18p$ level-to-level cross section (not shown).

TABLE I. Relative partial magnetic cross sections (in a_0^2) from experiments of Spain *et al.* [1] and from IA-QFE theory averaged over the experimental velocity distribution and normalized so that $\Sigma_m\sigma^m=2l+1=5$, in accordance with Ref. [1].

$\sigma^{\lvert m\rvert}(v_{\rm rel})$	Theory	Experiment Spain *et al.*[a]
σ^0	1.13	1.13 ± 0.02
σ^1	1.00	1.11 ± 0.02
σ^2	0.93	0.83 ± 0.02

[a]Reference [1].

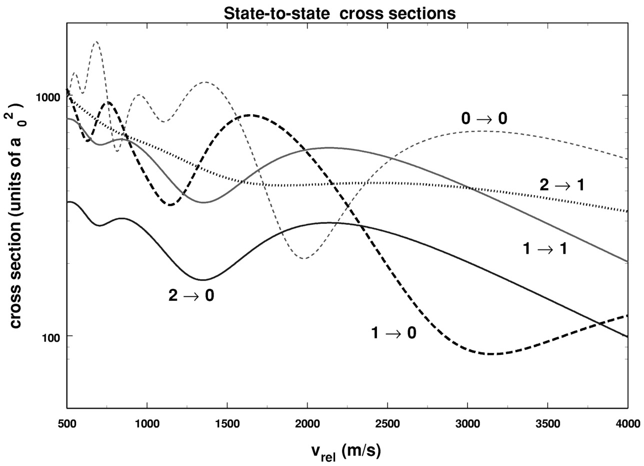

FIG. 2. State-to-state $|m|\rightarrow|m'|$ cross sections for $0\rightarrow0$ (short dash), $1\rightarrow0$ (medium dash), $2\rightarrow1$ (dotted), $1\rightarrow1$ (solid), and $2\rightarrow0$ (thick solid).

The assumptions of the IA-QFE formulation *explicitly preclude scattering via formation of a Ca-Xe quasimolecule*. So unlike, say, the Stueckelberg interference structures familiar from conventional inelastic Rydberg cross sections [16], the oscillations in Fig. 1 cannot possibly arise from avoided crossings. The peaks in these partial cross sections are spaced as $v_{\rm rel}^{-1}$, a pattern reminiscent of structures in the total cross sections for ion-atom scattering via nonadiabatic coupling of quasimolecular states at large internuclear separations [17]. The individual state-to-state cross sections that comprise each $\sigma^{|m|}$ suggest that the angular-momentum properties of the initial and final states of the Rydberg electron play a key role in these structures. The 15 such cross sections for $17d\rightarrow18p$ fall into three classes according to their angular-momentum quantum numbers. As illustrated in Fig. 2, members of each class have a common shape, and the classes can be labeled conveniently by $|m|+|m'|$. The four cross sections with $|m|=\ell$ and $|m|+|m'|=\ell+\ell'$ (e.g., $2\rightarrow1$ in Fig. 2), for which the initial and final electron momenta $\boldsymbol{k}$ and $\boldsymbol{k}'$ are predominantly directed normal to $\boldsymbol{v}_{\rm rel}$, exhibit very weak oscillations. The six with $|m|+|m'|=\ell+\ell'-1$ (e.g., $2\rightarrow0$ and $1\rightarrow1$) manifest common, strongly oscillatory shapes. Finally, the five with $|m|+|m'|\leqslant\ell+\ell'-2$ (e.g., $1\rightarrow0$), for which $\boldsymbol{k}$ and $\boldsymbol{k}'$ are directed mainly along $\boldsymbol{v}_{\rm rel}$, manifest the most pronounced structures, the extreme example of which occurs in $0\rightarrow0$. Examination of other near-resonant $d\rightarrow p$ and $f\rightarrow d$ transitions [18] supports the finding that a primary role in the oscillatory nature of these alignment phenomena is played by the proximity of the initial and final electron momenta to the initial relative velocity vector, the quantization axis for the angular-momentum amplitudes $Y_{\ell}^{m}(\hat{k})$ and $Y_{\ell'}^{m'}(\hat{k}')$ of the asymptotic scattering states.

Provocatively, very similar oscillatory structures were seen in recently calculated partial magnetic cross sections for inelastic scattering of He by Ca atoms *initially in aligned low-lying excited states, for which molecular potential-energy curves do provide a viable scattering mechanism*. Partial magnetic cross sections σ^0 calculated by Hickman *et al.* [19] for the process $\mathrm{Ca}^{**}(4s4f\ ^1F)+\mathrm{He}\rightarrow\mathrm{Ca}^{**}(4p^2\ ^1S)+\mathrm{He}$ exhibit pronounced oscillations, those for σ^1 show weaker structures, and those for σ^2 and σ^3 vary smoothly with $v_{\rm rel}$. Unlike the present IA-QFE study, the calculations of Hickman *et al.* employed fully quantum-mechanical coupled-channel scattering theory using *ab initio* quasimolecular potential curves based on a configuration-interaction description of the system. Hickman *et al.* argue that the oscillations in their cross sections can be understood as interference effects tied to the symmetries of these quasimolecular adiabatic potential curves. But the strong structural similarities between their results for low-lying excited states and those of Fig. 1 suggest a possible common underlying mechanism linked to fundamental angular-momentum properties of the initial and final atomic states. We are currently investigating this interpretation via a parallel semiclassical study of scattering from aligned Rydberg-atom collisions [20]. To conclude, we note that while the present theory and the experiments of Spain *et al.* corroborate the unexpected presence of alignment phenomena in Rydberg-atom–rare-gas collisions, the oscillations in $\sigma^{|m|}(v_{\rm rel})$ await the test of experimental verification.

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