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Systematics in Rydberg-state excitations for ion-atom collisions

B. Andresen
Chemistry Laboratory III, H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

K. Jensen, N. B. Petersen, and E. Veje
Physics Laboratory II, H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

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Rydberg-state excitations in Ne^+,Mg^+-He collisions have been studied in the projectile energy range 10–75 keV by means of optical spectrometry in a search for systematic trends. The relative excitation cross sections for levels of a Rydberg-term series are found to follow a general $(n^*)^p$ behavior (n^* being the effective quantum number) with $p \lesssim -3$ varying with collision energy and particles, regardless of whether the excited-state population results from direct excitation, single-electron transfer, or double-electron transfer. At higher collision energies $p \simeq -3$ as predicted by theory. Polarization of the emitted line radiation indicates that there is no general rule for the relative excitation of the different magnetic substates of the same level. A statistical distribution of excitation is found for levels within the same term when the fine-structure splitting is small.

I. INTRODUCTION

We are at present performing systematic studies of Rydberg-state excitation phenomena in ion-atom collisions in the projectile energy range 10–100 keV by means of optical spectrometry. As part of this program we recently investigated projectile Rydberg-state excitations in the collisions Be^+-He and Mg^+-He.[1] The almost linear dependence of the relative excitation cross sections on the effective quantum number n^* in a log-log plot observed there for a wide variety of states prompted us in the present study to look for a similar behavior in other collisions.

The projectile excitations studied in Ref. 1 involve direct excitation of Be^+ and Mg^+, which have normal terms of the form $1s^2nl$ and $1s^22s^22p^6nl$, respectively. Such terms are well described by *LS* coupling, and no configuration mixing with complex terms exists. Here we report experimental data for charge transfer into excited states of neutral magnesium (Mg I) in the Mg^+-He collision. In Mg I the ground-state configuration is $1s^22s^22p^63s^2\,{}^1S_0$, and the excited levels are fairly well described by *LS* coupling. However, for some of the excited states, mixtures of the normal configurations of type $3s\,nl$ with those of the complex valence-shell configurations of type $3p^2$ and $3p3d$ occur. This configuration mixing is a general feature for all systems of two electrons outside a closed core, and it makes it difficult to obtain a reliable set of branching ratios necessary for the evaluation of excitation cross sections. Furthermore, it may cause ambiguities in the interpretation of a possible unsystematical behavior of the excitation cross sections. Experimental observations of configuration mixing in Mg I have been reported by Risberg,[2] and Froese Fischer[3] has performed multiconfiguration Hartree-Fock computations of oscillator strengths in Mg I, which in some cases indicated quite large amounts of configuration mixing. Thus care must be exercised in the interpretation of the measurements.

Whereas excitation functions for the Mg^+-He collision appear to be almost without structure,[1] earlier studies[4] showed extensive oscillations for Ne^+-He. Since it is of interest to compare the mean values of oscillating cross sections (averaged over a projectile velocity region covering some oscillations) with corresponding cross sections from collisions showing negligible structure, we decided to include the Ne^+-He collision in the present study. No interaction with doubly excited levels occurs in singly excited, neutral helium (He I), which simplifies interpretation of these data.

In addition to the effective quantum-number dependence we also report on variations with the magnetic quantum number and the total angular momentum quantum number for our new measurements. In a future article we plan to present a more comprehensive investigation of the *l* dependence in atomic collision excitation cross sections.

II. EXPERIMENTAL AND DATA ANALYSIS

Excitation functions, polarizations, and relative emission cross sections were measured in the Ne^+-He and Mg^+-He collisions in the projectile energy range 10–75 keV. The accelerator has been described previously.[5] Two monochromators were used as photon analyzers, a McPherson model 2051, $f/8.7$, working in the wavelength region 200–1200 nm, equipped with an EMI 9659 QB photomultiplier, and a McPherson model 218, $f/5.3$, 200–600 nm, with an EMI 6256 SA photomultiplier. Both monochromators underwent a quantum-efficiency calibration on relative scales by using an Optronic model 245C lamp, as well as a low-current carbon arc, as standards of spectral irradiance in connection with a $BaSO_4$ screen. The calibration procedure has been described[6] together with the procedure for determining the instrumental polarization. The calibrations obtained by using the two different standards of spectral irradiance agreed well with each other. Procedures for data taking and reduction have been described earlier.[1]

A complete set of transition probabilities,[7] obtained from a numerical calculation in the Coulomb approximation, was used to calculate branching ratios necessary for the transformation of emission cross sections into apparent excitation cross sections for magnesium. As mentioned in the Introduction, configuration mixing is known to occur in Mg I, and this limits the validity of the Coulomb approximation. However, that set of transition probabilities[7] is at present the only complete set available, and we felt it better to use a set with internal consistency than to pick a few transition probabilities of higher accuracy from other sources, even though the set[7] may be systematically in error. The branching ratios used in evaluating the Mg I data are given in Table I, so that the results on Mg I presented in Sec. III can be corrected when better transition probabilities become available. In the evaluation of the helium excitation data branching ratios were calculated from transition probabilities given by Wiese *et al.*[8]

III. RESULTS AND DISCUSSION

A. Relative excitations of magnetic substates of the same level

Polarization P of emitted line radiation is in the present experimental geometry[1,6] related to the relative populations of the various magnetic substates of the upper level of the transition through the relations (we here follow the notation of Fano and Macek[9]),

$$P = 3h A_0^{\text{col}} / (4 + h A_0^{\text{col}}) \tag{1}$$

and

$$A_0^{\text{col}} = \frac{\sum_{m_i} [3 m_i^2 - j_i(j_i+1)] \sigma(m_i)}{j_i(j_i+1) \sum_i \sigma(m_i)} , \tag{2}$$

where h depends only on the angular momenta of the initial and final states of the transition studied,

TABLE I. Branching ratios used in the evaluation of the Mg I excitation data.

Transition observed Wavelength (nm)	Lower term	Upper term	Branching ratio
470.3	$3p\,^1P$	$5d\,^1D$	0.478
435.2	$3p\,^1P$	$6d\,^1D$	0.710
416.7	$3p\,^1P$	$7d\,^1D$	0.778
405.8	$3p\,^1P$	$8d\,^1D$	0.800

and $\sigma(m_i)$ indicates the partial cross section for excitation of the state $|j_i m_i\rangle$ with angular momentum quantum number j_i and magnetic quantum number m_i.

In the Mg^+-He collision leading to excited, neutral Mg we generally found the line polarizations to be positive but very close to zero. For a few illustrative examples see Fig. 1. This indicates that the alignment factor A_0^{col} is negative, since $h < 0$ for the cases studied,[9] and of small magnitude. In fact, $-0.1 < A_0^{\text{col}} < 0$ in most cases. This is qualitatively in agreement with the findings in the direct excitation study of the Be^+, Mg^+-He collisions,[1] where we also generally found $A_0^{\text{col}} < 0$, but where A_0^{col} varied monotonically with the azimuthal quantum number of the running electron and reached values close to its lower limit, -1, indicating a preferential population of states with numerically small values of the magnetic quantum number. As can be seen from Eq. (2), $A_0^{\text{col}} = -1$ only when the only nonvanishing $\sigma(m_i)$ is for $m_i = 0$

The $3s\,^1S$-$3p\,^1P$ Mg I line shows a negative polarization, corresponding to a positive alignment factor, or in other words, that the states with the magnetic quantum number equal to $+1$ or -1 are

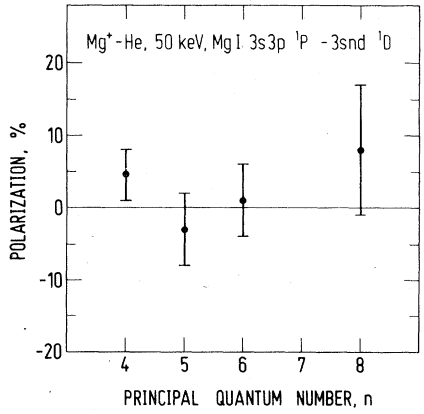

FIG. 1. Polarization of the optical line radiation $3p\,^1P$-nd$\,^1D$, Mg I from the Mg^+-He collision at 50 keV as function of the principal quantum number n.

populated preferentially. The energy dependence of the Mg I polarizations is very slight in all cases.

In the Ne$^+$-He collision the polarizations appear to change quite irregularly with projectile energy, and the structure in polarization does not follow the structure in total level excitation cross sections; see Fig. 2. A_0^{col} is generally negative for the Ne$^+$-He collision and numerically smaller than the corresponding values reported in the Be$^+$, Mg$^+$-He collisions.[1]

Thus, negative as the conclusion may be, no systematic behavior is found for the relative excitation of substates of the same level, and the monotonic dependence of the alignment factor on the azimuthal quantum number shown in Fig. 5 of Ref. 1 is not generally supported.

B. Relative level excitations within the same term

The multiplet radiation from the $3d\,^3D_{3,2,1}$ and $4d\,^3D_{3,2,1}$ terms to the $3p\,^3P_{2,1,0}$ term in Mg I could be partly resolved, and from relative line strengths in the *LS* coupling approximation given by Condon and Shortley,[10] the relative emission cross sections of the $3,4d\,^3D_{3,2,1}$ levels could be determined. In both cases, the cross-section ratios for the levels with $J=3,2$, and 1 were found to equal the statistical weight ratios 7:5:3 within the experimental uncertainties (~10%). It may be mentioned that if cascading levels within the same upper term are populated statistically, the cascade contributions will not cause a relative redistribution between different levels within the same lower term, and therefore, the ratios of relative excitation cross sections will equal the corresponding emission cross-section ratios in such cases.

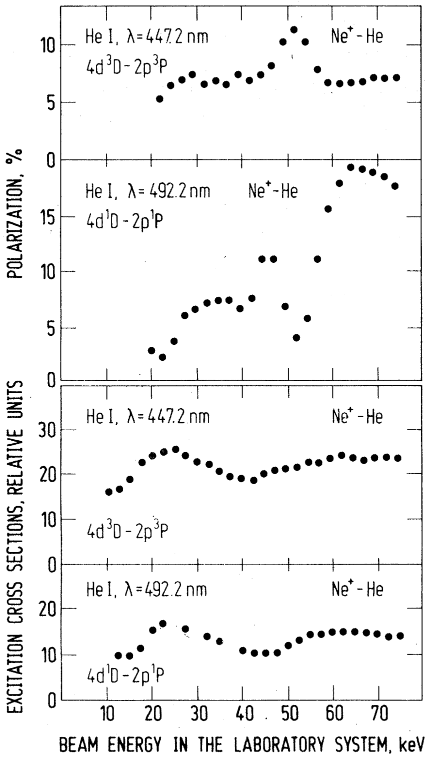

FIG. 2. Polarizations (upper part of the figure) and excitation cross sections (lower part of the figure) for the $4d\,^{1,3}D$, He I levels in the Ne$^+$-He collision as functions of the projectile energy in the laboratory system.

In the Ne$^+$-He collision the different levels within the Ne III $3p\,^5P_{3,2,1}$ term appear to be populated statistically, and we have previously found in the Mg$^+$-He collision[1] that also the $3p\,^2P_{3/2,1/2}$ levels in Mg II have a cross-section ratio equal to the statistical weight ratio, 2:1. In Mg I, Mg II, and Ne III the fine-structure splitting is small. Therefore, the potential-energy curves for levels of the same final term will run close together, and the interactions with other terms will be similar, so that the resulting excitation cross sections for levels of the same term will take on values proportional to the statistical weights of the levels.

In the Ne$^+$-Ne collision, on the other hand, the excitation of Ne I levels seems to have some *J* dependence,[11] and the fine-structure splitting in neutral neon is quite large. Hence, the potential-energy curves of levels belonging to the same configuration are well separated, and they may interact with different strength with other potential-energy curves, giving rise to cross-section ratios which differ from the statistical weight ratios. This explanation of fine-structure effects is in line with the prediction of spin-polarization effects in the H$^+$-Kr and the H$^+$-Xe collisions.[12]

C. Relative term population as a function of the effective quantum number

Figure 3 shows relative excitation cross sections for the Mg I $nd\,^1D$ terms in Mg$^+$-He collisions and the He I $nd\,^{1,3}D$ terms in Ne$^+$-He collisions together with several previously published results.[1,13-17] The cross sections are plotted in a log-log plot as a function of the effective quantum number n^*, defined by

$$E_n = \frac{-Z_c^2 \mathcal{R}}{(n^*)^2}\,, \tag{3}$$

where E_n is the energy of the *n*th state, $\mathcal{R}$ is the Rydberg constant, and Z_c is the total charge of the core.

For the Mg$^+$-He collision, the excitation functions have the same energy behavior, so that the general picture of Rydberg-state excitation is invariant to changes in projectile energy in the energy region studied. This is demonstrated in Fig.

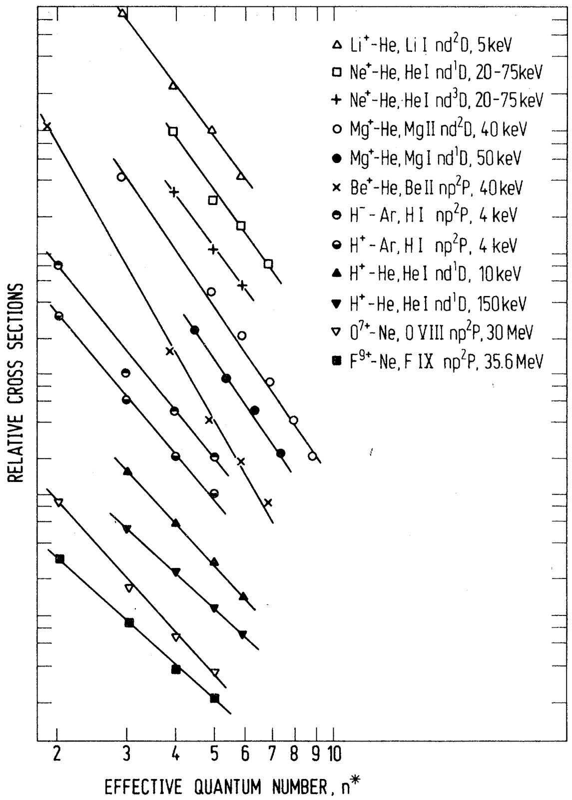

FIG. 3. Relative excitation cross sections as functions of the effective quantum number n^* for a variety of collisions. References to previously published works may be found in Table II.

4, where the relative cross sections for the $nd\,{}^1D$ Mg I terms, measured at 25, 50, and 75 keV, are shown as a function of the principal quantum number. In contrast to this, the Ne⁺-He collision displays extensive oscillatory structure (cf. Fig. 2). This is shown in Fig. 5, which gives the $ns\,{}^1S$ He I level cross sections at 20, 50, and 75 keV. For that reason, the He I data of Fig. 3 are mean values over the energy interval 20–75 keV, which in all cases covers enough structure of the excitation functions to make the average values meaningful.

The early work of Oppenheimer[18] predicts that the cross section for capture from a Rydberg state of one atom into a Rydberg state of principal quantum number n of He⁺ will behave as n^{-3} for s states and large velocities. The data presented in Fig. 3, where the logarithm of the relative excitation cross sections of terms of the same Rydberg series is seen to decrease almost linearly with the logarithm of the effective quantum number, indicates the same kind of $(n^*)^p$ behavior, even for non-s states, at intermediate projectile energies, and regardless of whether the excited-state population results from direct excitation (Be II, Mg II, He I singlets), single-electron transfer (Li I, Mg I), or double-electron transfer (He I triplets). Furthermore, no dependence of slope upon the azimuthal quantum number of the running electron is found.[1] In Table II we list the slopes p of the straight lines in Fig. 3 which are least-squares fits to the experimental points.

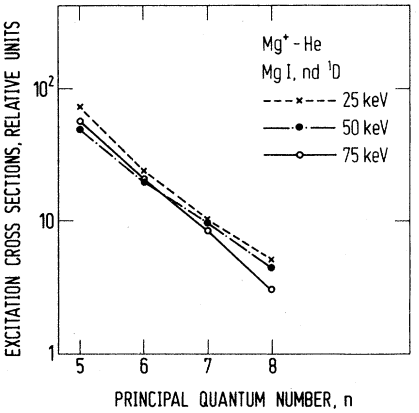

FIG. 4. Relative excitation cross sections for the $nd\,{}^1D$, Mg I levels in the Mg⁺-He collision at 25-, 50-, and 75-keV projectile energy as functions of the principal quantum number n.

Several arguments can be put forth why excitation, capture, and ionization cross sections in general should decrease as n^{-3}. The most convincing ones are based on the fact that high-lying Rydberg-state wave functions have an $n^{-3/2}$ normalization at the origin where the initial-state wave function is centered, so that the interaction element $\langle n|V|i\rangle$ is proportional to $n^{-3/2}$, the square of which determines the relative cross

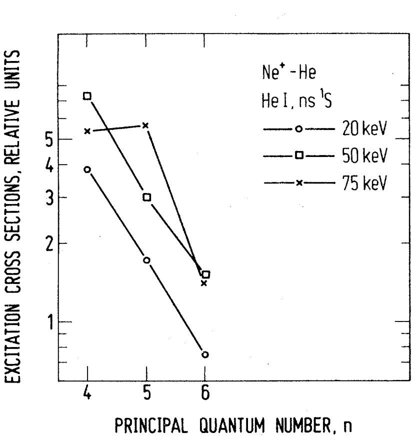

FIG. 5. Relative excitation cross sections for the $ns\,{}^1S$, He I levels in the Ne⁺-He collision at 20-, 50-, and 75-keV projectile energy as functions of the principal quantum number n.

TABLE II. Power p in the n^* dependence of the excitation cross sections included in Fig. 3.

Number	Collision	Level	Lab. energy (keV)	p	Ref.
1	Li^+-He	Li I $nd\ ^2D$	5	−4.3	15
2	Ne^+-He	He I $nd\ ^1D$	20–75	−4.3	This work
3	Ne^+-He	He I $nd\ ^3D$	20–75	−4.4	This work
4	Mg^+-He	Mg II $nd\ ^2D$	40	−4.7	1
5	Mg^+-He	Mg I $nd\ ^1D$	50	−4.8	This work
6	Be^+-He	Be II $np\ ^2P$	40	−5.5	1
7	H^--Ar	H I $np\ ^2P$	4	−4.0	16
8	H^+-Ar	H I $np\ ^2P$	4	−3.8	17
9	H^+-He	He I $nd\ ^1D$	10	−3.4	13
10	H^+-He	He I $nd\ ^1D$	150	−2.9	13
11	O^{7+}-Ne	O VIII $np\ ^2P$	30 000	−3.5	14
12	F^{9+}-Ne	F IX $np\ ^2P$	35 600	−2.9	14

section. The problem got a more firm base with May's derivation of some important sum rules for hydrogenic wave functions,[19] e.g.,

$$\sum_{l=0}^{n-1}\sum_{m=-l}^{l}|f_{nlm}(\vec{q})|^2=\frac{2^6\pi}{a_0^5n^3}\,[q^2+(a_0n)^{-2}]^{-4}\,, \tag{4}$$

where a_0 is the Bohr radius and $f_{nlm}(\vec{q})$ is the Fourier transform of the hydrogen wave function ϕ_{nlm},

$$f_{nlm}(\vec{q})=\int \phi_{nlm}(\vec{r})e^{i\vec{q}\cdot\vec{r}}d\vec{r}\,. \tag{5}$$

With these sum results he was able to calculate the cross section for charge transfer $H^+ + H(n_1l_1m_1) \rightarrow H(n_2l_2m_2)+H^+$ from term n_1, averaged over l_1 and m_1, to the term n_2, summed over l_2 and m_2, which in the Brinkman-Kramers approximation[19,20] is

$$\sigma(\langle n_1\rangle|n_2)=\pi a_0^2\,\frac{2^{18}p^8}{5n_1^5n_2^3} \times\left[p^4+2p^2\left(\frac{1}{n_1^2}+\frac{1}{n_2^2}\right)+\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)^2\right]^{-5}. \tag{6}$$

$p=\hbar v/e^2$ is the dimensionless speed of the incident proton. Equation (6) is seen to have the expected n_2^{-3} dependence aside from higher-order p/n terms. Unfortunately no such simple equation results if the velocity is too low for the Brinkman-Kramers approximation to hold or if one keeps l_1 or l_2 fixed.[21] The counterpart of Eq. (4), summing only over m, is[19]

$$\sum_{m=-l}^{l}|f_{nlm}(\vec{q})|^2=\frac{2^5\pi^2a_0^3n^4(2l+1)}{(z^2+1)^4}\,\frac{(n-l-1)!}{(n+l)!} \times\left(\frac{2z}{z^2+1}\right)^{2l}\left[T_{n-l-1}^{l+1/2}\left(\frac{z^2-1}{z^2+1}\right)\right]^2, \tag{7}$$

with $z=na_0q$ and $T_i^{\alpha}(x)$ being the Gegenbauer polynomial. For large z the Gegenbauer polynomial $T_{n-l-1}^{l+1/2}((z^2-1)/(z^2+1))$ reduces to $\binom{n+l}{n-l-1}$, so that the right-hand side of Eq. (7) is proportional to $n^{-3}(2l+1)/(l+\frac{1}{2})!$, thus recovering the n^{-3} behavior even for single levels.

In the Born approximation for charge transfer into high-lying Rydberg states it turns out that at very high energies the second Born term dominates over the first Born term. Although there is still some controversy over the energy dependence of the two terms, both decrease as n^{-3} for large n and large velocity.[22] Collisions at the energies tabulated in Table II should be well described by the first Born term alone, but even if they were not, the n dependence would not be affected. The calculations of May[19,21] and Oppenheimer[18] use what has become known as the Brinkman-Kramers approximation,[23] which is the first Born approximation in which the internuclear potential has been eliminated from the interaction potential. This further approximation greatly simplifies evaluation of the Born integral but also produces a cross section up to several times too large. Fortunately, however, Jackson and Schiff[24] have obtained results which indicate that the ratio of the Brinkman-Kramers to the Born cross section is almost independent of the final state so that it is safe to use the former method in the present analysis.

Of all the collisions of Table II only the last four are energetic enough to permit the use of the Brinkman-Kramers approximation. All these are seen to have p reasonably close to -3. Note that the detected products of collisions 11 and 12 are truely hydrogenic systems. Collisions 9 and 10, which only differ in energy, show a slight increase in $|p|$ as we go towards the lower limit of the Brinkman–Kramers approximation, an effect that is more pronounced in collisions 1–8. If in 4 and 6 we sum the cross sections over all l at a given n, p is changed to -4.6 and -4.3, respectively. The steeper slopes for the low-velocity collisions is probably due to the formation of molecular complexes which are sufficiently long-lived that the outer electrons can rearrange themselves in the new field. This will favor adiabatic behavior and hence preferential population of low-lying states over and above what the normalization constants dictate. It is remarkable, however, that one still finds the cross sections proportional to a power of n^*, and that this behavior continues all the way down to the closed shell. The collision energy range studied experimentally here is the difficult intermediate one, not quite high enough to permit analytical conclusions from the Brinkman-Kramers approximation, and not low enough for calculations involving only a few states.

A field closely related to this one is the study of radiative lifetimes of highly excited atoms. Here as well do the sum rules and limiting behaviors of Rydberg states apply, since the lifetime is inversely proportional to the corresponding excitation cross section by microscopic reversibility and hence should increase[25] as $(n^*)^3$. The measured radiative lifetimes τ of the s and d Rydberg levels of Na I for $n = 5$–13 are found[26] to follow a $\tau \propto (n^*)^p$ form very closely with $p = 2.87$ and 3.00, respectively. Radiative decay is a fast process compared to the collision excitations described above. Therefore the transition probability is determined solely by the wave-function normalization and is not complicated by the varying distance of closest approach, molecular-orbital formation, and close-coupling effects of atomic collisions, so that $|p|$ is closer to 3 than in Table II.

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