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Relative level excitation in ion-atom collisions as a function of the orbital-angular-momentum quantum number

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We present experimental data on relative excitation cross sections from the collisions Li^+-He, -Ne, -C_6H_6; Ne^+-, Na^+-, Mg^+-, Mg^{2+}-He; and Mg^+-C_6H_6 at 10–150 keV. The ion-atom data show a preferential excitation of d levels for fixed principal quantum number, whereas no preferential excitation exists in the ion-benzene collisions. The data are compared with various model predictions. The preferential d-level population seems to be a result of the symmetry properties of the transient quasimolecule formed during the collision for projectile velocities of the order of one atomic unit of velocity. It is concluded that neither the Born approximation, the Brinkman-Kramers approach, a statistical population viewpoint, or a velocity-matching viewpoint explains the data satisfyingly well in our energy regime. For $v \gg v_0$ (1 a.u.), $s > p > d > \cdots$.

I. INTRODUCTION AND EXPERIMENTAL

We have earlier[1] performed experimental studies of projectile Rydberg state excitations in the collisions Be^+- and Mg^+-He, 10–75 keV. We found,[1] for fixed value of the principal quantum number n, that for s, p, and d levels the cross sections increase almost as 1:3:5 with increasing value of the orbital angular momentum quantum number l. Then, for f and g levels, the cross sections drop to approximately the same value as for s levels. Blaney and Berry[2] found essentially the same feature for electron transfer into excited s, p, and d levels in lithium in the Li^+-H_2 collision. From two other recent studies[3,4] of charge transfer, Na^+-O_2, -N_2, -CO and Li^+-H_2, at slightly lower energies one can also deduce an s-p-d increase of 1:3:5 or faster. No f or higher levels were measured,[3,4] but f-excitation cross section (needed for cascade corrections) were extrapolated from the trends in the s, p, and d cross sections.[4] In view of our present results this seems a risky procedure.

Since we have no adequate theory to compare with, and also because no qualitative model is available, we have continued our experiments by expanding to other collisions in a search for systematic features. In Table I we list the new systems investigated experimentally and for which we present data here, together with some earlier works, from which similar data can be extracted. A more complete reference list is given by Blaney and Berry.[2]

During the last few years we have performed similar experimental studies of beam-foil excitations[5] and found thay they oscillate as a function of the orbital angular momentum quantum number with maxima at odd values of l $(p, f, \ldots)$ and minima at even l $(s, d, g, \ldots)$. To bridge the gap between atomic collisions and atom-solid interactions, we have studied a few collisions between atomic ions and benzene vapor (C_6H_6). These results will also be presented in this paper.

Our data have all been obtained by use of optical spectrometry, which essentially is the only feasible way to study Rydberg state excitations in atomic collisions. They have all been obtained under single-collision conditions. We have earlier published descriptions of the accelerator,[6] of the quantum

TABLE I. Upper part of the table shows the collisions investigated in this work. Some earlier studies are given in the lower part of the table. Further references to earlier works can be found in Ref. 2.

Collision	Projectile energy (keV)	Levels studied	Reference
Li^+-He	10–100	He I, $n=4$	This work
Li^+-Ne	10–100	Li II, $n=4$	
Ne^+-He	10–100	He I, $n=4$	
Na^+-He	10–100	He I, $n=3,4$	
Mg^+-He	10–100	He I, $n=4$	
Mg^{2+}-He	20–200	Mg II, $n=5-7$	
Li^+-C_6H_6	10–100	Li I, II, $n=4$	
Mg^+-C_6H_6	10–100	Mg II, $n=5-8$	
Be^+-He	10–75	Be II, $n=4-7$	1
Mg^+-He	10–75	Mg II, $n=4-9$	1
Li^+-H_2	2	Li I, $n=3-5$	2
He^+- He Ne Ar Kr Xe	0.3–150	He I, $n=3-5$	11

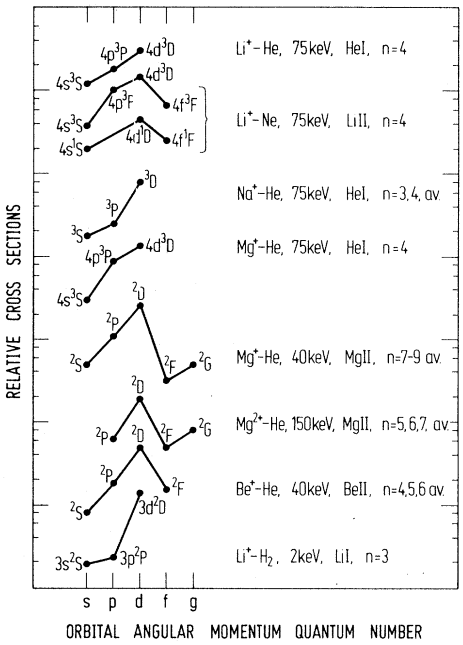

FIG. 1. Relative collisional cross sections in arbitrary units vs orbital angular momentum quantum number for ion-atom collisions. References to previously published data may be found in Table I.

efficiency calibration[7] of the optical system, and of the data treatment.[1] Therefore, such descriptions shall not be repeated here.

In passing, we note that—unfortunately enough—for neutral species the line radiation emitted from levels with $l>2$ is in the low-frequency end of the infrared part of the spectrum where single photon detection is impossible at present. Therefore, though excitation of neutrals is of great theoretical interest, much more information can be gained experimentally from ionic species.

II. RESULTS

In Fig. 1 is shown representative data for relative excitation cross sections versus the orbital angular-momentum quantum number, for fixed principal quantum number, from various ion-atom collisions and from the Li$^+$-H$_2$ interaction. We note that for all processes presented in Fig. 1 the cross sections increase with l for s through d levels and then drop off for f and g levels. Some of the collisions studied show oscillatory structure in total cross sections versus the projectile energy. In such cases the data of Fig. 1 are average results over representative projectile energy intervals.

It is striking to see the very similar behavior regardless of whether the excitation results from direct excitation (e.g., Mg II levels in the Mg$^+$-He collision), electron capture into excited states (Mg II levels in the Mg^{2+}-He collision and Li I levels in the collision Li$^+$-H$_2$), or more involved processes like triplet excitation in Li II and He I, which presumably result from double electron exchange processes due to conservation of total electron spin, rather than from spin-orbit-coupling–induced excitations.

In beam-foil excitations[5] (see Fig. 2) we found levels with odd parity populated preferentially, regardless of projectile.

Finally, Fig. 3 shows data from the collisions Li$^+$, Mg$^+$-C$_6$H$_6$. There is clearly no preferential excitation in these collisions, which are thus intermediate between the ion-atom and beam-foil excitations. This is very reasonable, since benzene with its conjugated ring is expected to behave like a small ultrathin foil when hit centrally, and like an atom when grazed by the projectile.

In Sec. III, four explanations of the ion-atom excitations will be presented and discussed, only one of which is consistent with the data.

III. DISCUSSION

A. Quasimolecular aspects of ion-atom collisions

We have recently explained a general n^r ($r \leq -3$) relationship of the relative excitation of different levels within the same Rydberg level series for a wide selection of processes and collision energies in terms of the atomic wave function amplitudes in the vicinity of the nucleus.[8] A similar explanation of the data of this work does not seem to be feasible, since the wave-function amplitudes in the neighborhood of the nucleus decrease[9] with increasing l, which implies that also the cross sections should decrease monotonically with increas-

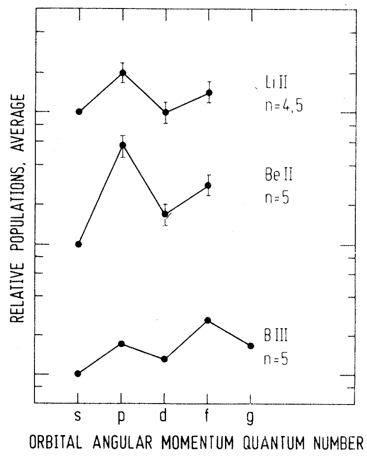

FIG. 2. Relative level populations in arbitrary units vs orbital angular momentum quantum number for beam-foil excitations (Ref. 5).

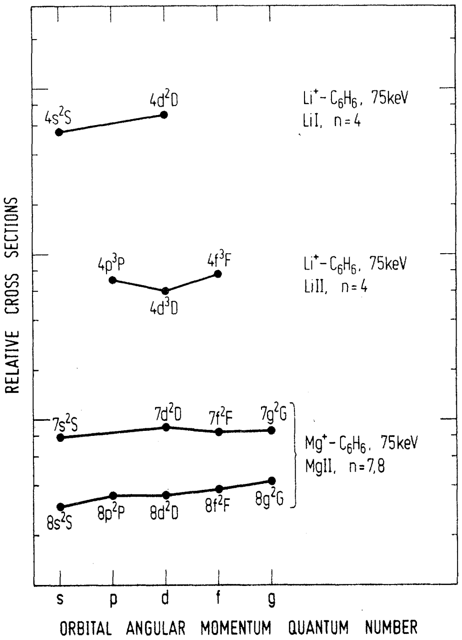

FIG. 3. Relative collisional cross sections in arbitrary units vs orbital angular momentum quantum number for ion-benzene collisions.

ing l. Instead, reasoning taking account of the quasimolecule formed during the collision goes as follows.

In the ion-atom collisions presented here the initial channel is always a Σ term, and a Π and a Δ term will generally cross this Σ term at small internuclear distances. Since our projectile velocities are fairly large, rotational coupling will usually be more important than radial coupling between terms. The incoming channel being a Σ term, it can accommodate no more than two electrons, so that one- and two-electron processes will be strongly favored to multielectron processes, which is also observed in other investigations.[10] Thus, the Π and Δ terms can be populated through rotational coupling, but no terms of higher symmetry are accessible. Upon separation of the atoms, Σ terms can populate levels of all l values, Π terms only non-s-levels, and Δ terms only levels with $l \geqslant 2$. On the other hand, they will preferentially separate into the lowest possible level, i.e., $\Sigma \rightarrow s$, $\Pi \rightarrow p$, and $\Delta \rightarrow d$. This argument makes plausible the observed intensities $s < p < d$, but f, $g < d$.

The two-electron processes resulting in $\Sigma \rightarrow \Pi \rightarrow \Delta$ transitions are clearly related to the quasimolecule formed during the collision. At higher projectile velocities the collision time will be too short to allow two-electron processes, and one might expect p levels with a change in angular momentum of only one, and eventually s levels to be strongest populated in agreement with the Brinkman-Kramers cross section derived in Sec. III C. This is exactly what Muller and de Heer[11] observed in their He^+–inert-gas collisions, and what has also been seen in proton-inert gas[12] and He^+-He collisions.[13]

If p levels are primarily populated through the Π level and d levels through the Δ level, the magnetic substates with numerically large values of m should be strongest populated in the final p and d levels. In our earlier polarization measurements[1] we see just the opposite. However, the final distribution of excitation among the different magnetic substates of the same atomic level occurs at large internuclear distances where the molecular terms merge into atomic ones, and recouplings are likely to change the intensities there. In a recent study[14] of the $(He\text{-}Ne)^+$ collision we observed quite irregular features in our polarization data, indicating the presence of such final-state interactions.

The quasimolecular explanation given above is closely related to the rotational symmetry around the internuclear axis, which makes this axis the axis of quantization, combined with a rotation of this axis, causing rotational coupling. In the Li^+-H_2 collision the axial symmetry is still present to some extent, explaining the similarity between this and the ion-atom collisions, whereas, when benzene is used as target, there is no longer such a symmetry property of the collision. Consequently, there is no longer a rotation of a well-defined axis of quantization, and a collision with benzene should be regarded not as a rotation but rather as a vibration. Thus no preference should occur in excitation processes, as confirmed by experiment (Fig. 3).

B. Statistical weight considerations

In our earlier work[1] on projectile Rydberg state excitations in the Be^+-, Mg^+-He collisions we mentioned that the ratios between cross sections for s, p, and d levels with same n were close to the statistical weight ratios 1:3:5. The decrease for higher l values might be related to the well-known fact[9] that the electron probability density in the vicinity of the nucleus, where the excitation is supposed to take place, for different l levels with same n falls off with increasing l—albeit not so abruptly as displayed in Fig. 1.

An explanation of the data of Fig. 1 in terms of a statistical weight distribution for low l values combined with a decrease for high l values due to the decreasing electron probability density around the nucleus is, however, not applicable because there is no similarity between the systematics shown in ion-atom collisions (Fig. 1) and in ion-benzene collisions (Fig. 3). Were the features of Fig. 1 to be explained from statistical reasons, similar trends must also occur in Fig. 3, since then the excitation depends primarily on properties of the projectile atomic wave function and to a much lesser extent on the nature of the exciter, the target.

C. Predictions of the Born and Brinkman-Kramers approximations

The Born and Brinkman-Kramers approximations are expansions of the transition amplitude in terms of a weak interaction potential. Thus, they are evidently justified for large projectile velocities, but one might also expect this to be the case at lower velocities for excitation of high-lying Rydberg levels to which the coupling elements are small.

Yager and Lane[15] calculated upper and lower bounds to the Born approximation cross sections for the excitation of ground-state He$^+$ ions in collisions with free carbon atoms. At all projectile energies between 0.5 and 6.5 MeV and for all $n=2$ through $n=7$ levels they found that for fixed n excitation happens preferentially to p levels. Such a peaking at p levels is clearly not found in our experiments.

Oppenheimer in his early work[16] treated electron capture by α particles from an atom with a single electron. He found that at high projectile velocity v, capture into s states will dominate since the contributions from levels with $l\neq 0$ vanish more rapidly than those of corresponding s states by a factor v^{-2l}. A more general expression for the total charge exchange cross section from hydrogenic state n_1l_1 to n_2l_2 may be derived from the sum rules for hydrogenic wave functions developed by May.[17] Following his procedure[17] of transforming to the momentum representation, we find in the Brinkman-Kramers approximation[18,19]

$$\sigma(n_1l_1 \,|\, n_2l_2) = (2\pi p)^{-2}\iint \sum_{m_1} |f_{n_1l_1m_1}(\vec{q})|^2 \times \sum_{m_2} |g_{n_2l_2m_2}(\vec{Q})|^2 \, dq_x\, dq_y \,, \tag{1}$$

where we have followed May's notation:

$$f_{nlm}(\vec{q}) = \int \phi_{nlm}(\vec{r})\, e^{i\vec{q}\cdot\vec{r}}\, d\vec{r} \,, \tag{2a}$$

$$g_{nlm}(\vec{q}) = \int r^{-1}\phi_{nlm}(\vec{r})\, e^{i\vec{q}\cdot\vec{r}}\, d\vec{r} \tag{2b}$$

are Fourier transforms of hydrogenic wave functions ϕ_{nlm},

$$p = \hbar v/e^2 \tag{3}$$

is the projectile velocity in atomic units, and

$$q^2 = q_x^2 + q_y^2 + \beta/a_0^2 - (n_1a_0)^{-2} \,, \tag{4a}$$

$$Q^2 = q_x^2 + q_y^2 + \beta/a_0^2 - (n_2a_0)^{-2} \,, \tag{4b}$$

with a_0 being the Bohr radius and

$$\beta = \tfrac{1}{4}p^2[1 + 2p^{-2}(n_1^{-2} + n_2^{-2}) + p^{-4}(n_1^{-2} - n_2^{-2})^2] \,. \tag{5}$$

Introducing the sum rule

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

and

$$g_{nlm}(\vec{q}) = (2a_0n^2)^{-1}(z^2+1)f_{nlm}(\vec{q}) \,, \tag{7}$$

where $T_i^{\alpha}(x)$ is the Gegenbauer polynomial and

$$z = na_0q \,, \tag{8}$$

the cross section [Eq. (1)] becomes

$$\begin{aligned}\sigma(n_1l_1 \,|\, n_2l_2) = {} & (2\pi p)^{-2}(2^{5+2l_1}\pi^2 a_0^3 n_1^4)(2^{3+2l_2}\pi^2 a_0)(2l_1+1)\frac{(n_1-l_1-1)!}{(n_1+l_1)!}(2l_2+1)\frac{(n_2-l_2-1)!}{(n_2+l_2)!} \\ & \times \iint_0^{\infty} (n_1^2a_0^2q^2+1)^{-4}\left(\frac{n_1a_0q}{n_1^2a_0^2q^2+1}\right)^{2l_1}\left[T_{n_1-l_1-1}^{l_1+1/2}\left(\frac{q_x^2+q_y^2+\beta/a_0^2-2(n_1a_0)^{-2}}{q_x^2+q_y^2+\beta/a_0^2}\right)\right]^2 \\ & \times (n_2^2a_0^2Q^2+1)^{-2}\left(\frac{n_2a_0Q}{n_2^2a_0^2Q^2+1)}\right)^{2l_2}\left[T_{n_2-l_2-1}^{l_2+1/2}\left(\frac{q_x^2+q_y^2+\beta/a_0^2-2(n_2a_0)^{-2}}{q_x^2+q_y^2+\beta/a_0^2}\right)\right]^2 dq_x\, dq_y \,.\end{aligned} \tag{9}$$

After some algebra we arrive at

$$\begin{aligned}\sigma(n_1l_1 \,|\, n_2l_2) = {} & \frac{2^{6+2l_1+2l_2}\pi^3}{p^2 a_0^{8+2l_1+2l_2} n_1^{4+2l_1} n_2^{4+2l_2}}(2l_1+1)(2l_2+1)\frac{(n_1-l_1-1)!}{(n_1+l_1)!}\frac{(n_2-l_2-1)!}{(n_2+l_2)!} \\ & \times \int_{\beta/a_0^2}^{\infty} t^{-(6+l_1+l_2)}[1-(tn_1^2a_0^2)^{-1}]^{l_1}[1-(tn_2^2a_0^2)^{-1}]^{l_2}[T_{n_1-l_1-1}^{l_1+1/2}(1-2/tn_1^2a_0^2)]^2[T_{n_2-l_2-1}^{l_2+1/2}(1-2/tn_2^2a_0^2)]^2\, dt \,.\end{aligned} \tag{10}$$

For large p or n_1 and n_2,

$$T^{l+1/2}_{n-l-1}(x) \xrightarrow[x\to 1]{} (n+l)!/2^{l+1/2}(l+\tfrac{1}{2})!\,(n-l-1)!\,,$$

which greatly simplifies the expression

$$\sigma(n_1l_1\,|\,n_2l_2) \approx \frac{2^{14+2l_1+2l_2}\pi^3 a_0^2}{p^{12+2l_1+2l_2}n_1^3n_2^3}\,\frac{(2l_1+1)(2l_2+1)}{5+l_1+l_2} \times (l_1+\tfrac{1}{2})!^{-2}(l_2+\tfrac{1}{2})!^{-2}\,. \qquad (11)$$

Because of the large values of n_1 and n_2 we have also approximated $(n+l)!/(n-l-1)!$ by n^{2l+1}. As mentioned earlier, this derivation applies to charge exchange. A similar but somewhat messier derivation can be carried out for collisional excitation as well, and it arrives at the same n and l dependence.

Besides the well established n^{-3} dependence[8] of the cross section, Eq. (11) shows that the populations of high l states decrease relatively at high energy by factors of v^{-2l} in agreement with Oppenheimer's[16] findings. Combined with the increase of the other l terms at low l this produces a maximum in the l dependence which varies with collision energy. For a magnesium projectile it is easy to verify that with the electron initially in an s state ($l_1=0$) the cross-section maximum will be located as shown in Fig. 4.

The Brinkman-Kramers approximation thus predicts that the cross section has a maximum which moves to states of lower angular momentum for progressively higher collision energies. This trend has been observed experimentally in, e.g., H^+–, He^+–inert-gas collisions at high keV energies.[11–13] In contrast, our data (Fig. 1) do not show such a shift in the position of the maximum, although Fig. 4 clearly predicts maxima in the range j–f for our magnesium collisions at 40–150 keV; instead they all peak at the d level. Apparently, our projectile velocities are too small to justify the use of the Brinkman-Kramers approximation, and the expectation stated in the beginning of this section that the coupling to high-lying Rydberg states be small is unwarranted. In view of the intuitively obvious character of this expectation its failure is an important result of this paper.

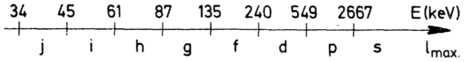

FIG. 4. Maximum in the charge-exchange cross section vs orbital angular momentum quantum number for magnesium collisions is predicted by the Brinkman-Kramers approximation to appear at the indicated l values for the different projectile energy intervals shown.

D. Velocity matching

Blaney and Berry[2] found trends similar to ours in their study of the Li^+-H_2 collision leading to Li I levels, and they explained their findings in terms of velocity matching. Electrons in orbitals of high angular momentum are found, on the average, at larger distances from the nucleus. Therefore, their average velocities are smaller, and consequently, that collision energy at which the maximum value for the charge transfer probability occurs will decrease with increasing l. Unfortunately, this can only explain why the excitation versus l has a maximum, not why the location of that maximum is independent of n and the collision energy (in our energy regime). According to this conjecture the l value connected with the target excitation must decrease with increasing energy *and* with increasing n to maintain correspondence between the electronic and nuclear velocities.

Velocity matching phenomena are certainly known to occur in total charge-exchange cross sections.[20] However, if this were the explanation of the general features of Fig. 1, a larger resemblance should exist between the data of Figs. 1 and 3 since the excitation distribution is then primarily related to the electron structure of the projectile. Also, our beam-foil data ought to follow the trends shown in Fig. 1, since beam-foil excitation is believed to happen as electron pickup from the back of the foil,[21] and this is clearly not the case (see Fig. 2). Taking these things into account, it seems to us that the systematics of our data cannot be explained merely in terms of velocity matching.

IV. CONCLUSION

The experimental findings presented here seem to rule out several models for the excitation mechanism, leaving only a quasimolecular interpretation. This conclusion is in full agreement with our previous investigation[8] of the n dependence of total cross sections in which we also found quasimolecular effects to be important for projectile velocities $\lesssim 1$ a.u. Similarly, the explanation[14] of oscillatory structure in total Rydberg level excitation cross sections versus projectile energy in the same energy range rests solely on the formation of a quasimolecule. The conclusion is unfortunate in that it leaves us without simple ways of calculating the excitation and charge-transfer cross sections in this energy range.

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