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LETTER TO THE EDITOR

Charge transfer in quasi-one-electron systems at 'high' energy

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Abstract. We have made absolute and relative measurements of differential cross sections for single-electron transfer in collisions between Mg^+ (30–150 keV) and Be^+ (56.25 keV) ions and He atoms. The behaviour of transfer probability as a function of impact parameter can be understood qualitatively from recent molecular orbital calculations of quasi-one-electron systems.

Quasi-one-electron (QOE) collision systems are simple conceptually because they have two closed 'inert' cores and a single outer 'active' electron. Much of the impetus for the study of these systems has been the relative ease with which one can treat the active electron theoretically (Andersen and Nielsen 1982, Nielsen and Dahler 1977). QOE collisions are often considered in two classes: those involving two charged cores (e.g. $Na^+ + Li$ or $Na^+ + H$) and those involving one charged and one neutral core (e.g. $Mg^+ + He$ or $Be^+ + Ne$). In the former case, charge transfer almost always takes place in the QOE context in that the 'active' electron is transferred. In collisions between a charged and an uncharged core however, the charge transfer mechanism usually involves a core electron. Consequently, the collision must be fairly violent for there to be an appreciable transfer probability, i.e. the cores must have significant overlap at the point of closest approach. Such reactions have to be treated theoretically as multi-electron transitions in the molecular orbital electron-promotion model (Fano and Lichten 1965, Barat and Lichten 1972), and the inherent simplicity of the QOE picture is lost.

In recent years, a number of calculations have attempted to deal with the quasimolecular aspects of charged-core–neutral-core QOE collisions (see, e.g., Barat *et al* 1976, Courbin-Gaussorgues *et al* 1983, Knöpfle and Kempter 1983, Kimura and Pascale 1985). While these efforts have added much to our understanding of processes involving the active electron, excitation and transfer of core electrons has received less theoretical attention. Because of their strong dependence on impact parameter, quasimolecular processes are best studied experimentally by cross section measurements which are differential in angle. Following the pioneering measurements of the Aarhus and Orsay groups, however (Brenot *et al* 1975, Barat *et al* 1976, Fayeton 1976, Fayeton *et al* 1976, Olsen and Andersen 1975, Olsen *et al* 1979), little has been done to investigate differential charge transfer cross sections in these systems. This would appear to be useful, in that charge transfer measurements should provide a particularly sensitive test of the quality of MO calculations.

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In recent extensive studies of QOE collisions made in our laboratory, we have determined charge transfer cross sections, differential in angle and summed over neutral states, for the charged-core-neutral-core Mg^+, Be^+-He collisions at collision velocities up to 0.50 au (150 keV Mg^+, 56.25 keV Be^+). These data thus extend the energy range of existing Be^+ charge transfer data by over an order of magnitude. We are unaware of any previous charge transfer data on the $Mg^+ + He$ system.

The data presented in this paper were taken using the ion-energy-loss spectrometer at the University of Missouri-Rolla. Mg^+ and Be^+ ions with a negligible excited-state component (Redd 1986) were accelerated and collimated, and traversed a differentially pumped He target whose density-length product (nl) was known to 3.6%. The beam then passed into an analysing magnet. With the magnet turned off, ions as well as neutrals went directly into a detector consisting of solid-angle-defining slits and an electron multiplier. Relative cross section measurements were made by deflecting the ion beam out of the neutral path, and determining the saturated current-mode detector signal as a function of scattering angle. The angular width of the beam (~100 μrad FWHM) was deconvoluted from the measured angular distributions to yield the final relative cross section values (Park *et al* 1978). All of the data presented were taken in this fashion.

During these runs, the incident ion beam was monitored following deflection by a second detector operating in the pulse-counting mode. Determination of absolute cross sections would thus have required knowledge of both detector efficiencies. Lacking this information, we made measurements of the angular distributions of an undeflected 66.7 keV incident Mg^+ beam (without target gas) and the scattered neutrals using our detector in a pulse-counting mode. The total neutralisation cross section, σ_N, was thus determined using

$$\sigma_N = \varepsilon_0 \int_0^\pi I_0(\theta) \sin\theta \, d\theta \left(\varepsilon_i nl \int_0^\pi I_i(\theta) \sin\theta \, d\theta \right)^{-1} \tag{1}$$

where I_0 and I_i are the angle-dependent counting rates for neutrals and ions, respectively. The detector efficiencies for neutrals and ions, ε_0 and ε_i, are assumed to be equal in this case. Parenthetically, we found the *ratio* of detection efficiencies for ions and neutrals to be the same in both pulse-counting and current modes, which lends credence to this assumption. The angular dependence of the detector signal was completely independent of detector mode. Accurate measurement of σ_N required determination of I_0 at large enough angles to ensure that its contribution to the first integral in (1) was negligible for angles outside the range of measurement. This condition was met at 66.7 keV for measurements at angles up to ~30 mrad in the CM frame. The total cross section thus obtained was $1.76 \pm 0.25 \times 10^{-17}$ cm^2, where the error is the standard deviation of the mean of four runs added in quadrature with the uncertainty in the target thickness. This absolute value was then used to normalise the higher precision relative data obtained earlier at 66.7 keV.

The results of our measurements are shown in figures 1 and 2. A notable feature of these data is the dramatic rise in the cross section for $Mg^+ + He$ at about 1.5 keV deg at 30 and 66.7 keV. It corresponds to similar features in the differential He($n = 2$) excitation and Mg^+(3p) excitation cross sections we have observed (Redd *et al* 1987a, b), and will be discussed below.

In order to further elucidate the relevant charge transfer mechanisms, we have plotted the charge transfer probability, P, as a function of impact parameter, b, in figure 3. This also enables us to compare directly our Be^+ data with the earlier,

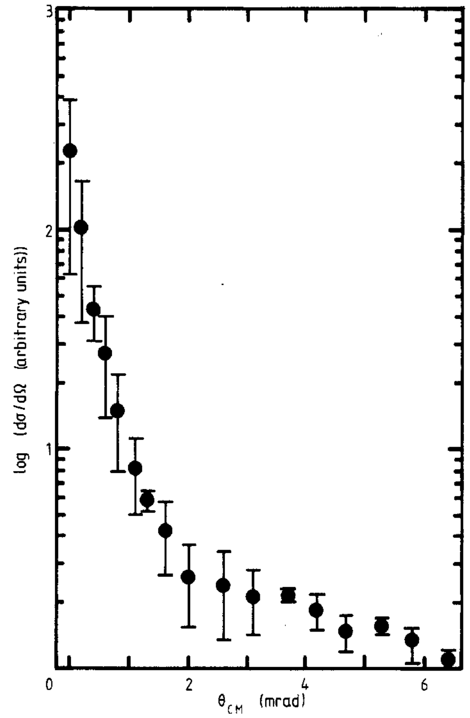

Figure 1. Relative differential charge transfer cross sections for $Be^+ + He$ at a lab energy of 56.25 keV. Error bars represent the standard deviation of the mean of all runs. Scattering angles are given for the centre-of-mass frame.

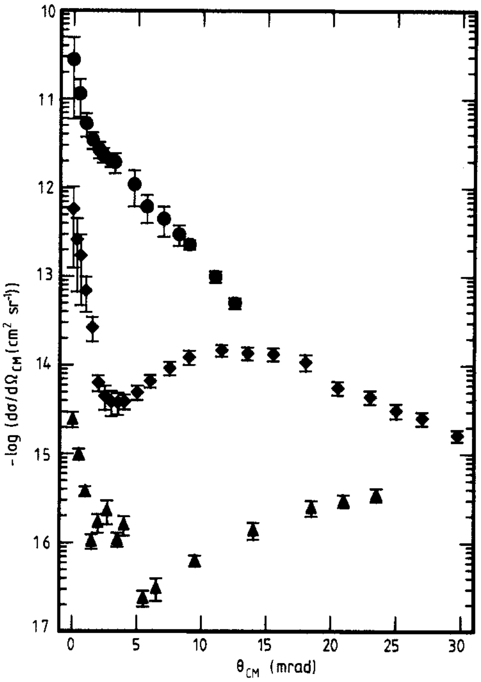

Figure 2. Differential charge transfer cross sections for $Mg^+ + He$ at lab energies of 30 (triangles), 66.7 (squares), and 150 (circles) keV. The scale for the 30 and 150 keV data is arbitrary; the 66.7 keV data are absolute (see text).

low-energy results of Olsen *et al* (1975, 1979). To obtain graphs of P against b, we assumed the usual exponential scattering potential as a function of the internuclear separation, R (Redd 1987b):

$$V(R) = A\,e^{-BR} \tag{2}$$

with strength and range parameters $(A(\mathrm{au}), B(\mathrm{au})) = (19.4, 3.22)$ and $(46.0, 2.88)$ for Be^+ and Mg^+, respectively, given by Sondergaard and Mason (1975).

In transforming the 5 keV data of Olsen *et al*, the scattering angles were so large that the deflection function had to be integrated numerically to yield a b-θ relationship, in contrast to the usual practice of making a small-angle impulse approximation (Redd 1986, Redd *et al* 1987b). In this regard, we note the rather small values of b obtained for the 5 keV data. The combined He(1s)-Be(1s) and He(1s)-Mg(2s) radii are 0.87 and 1.14 au respectively (Slater 1960). While the results of figure 3 thus indicate significant core interpenetration in all cases, the 5 keV Be data have such low b that the model assumption of a simple exponential potential is called into question. Nonetheless, the results serve as a useful qualitative guide.

The simplest conclusion to draw from the $P(b)$ plots is that charge transfer begins when the cores penetrate. The Mg^+-He complex is physically larger than the Be^+-He one, and thus the $P(b)$ curve for $Be^+ + He$ is shifted to smaller impact parameters.

The molecular diagrams of the collision complexes are shown in figure 4. Charge transfer in low-energy $Be^+ + He$ collisions must occur via either the Σ-Σ crossing at

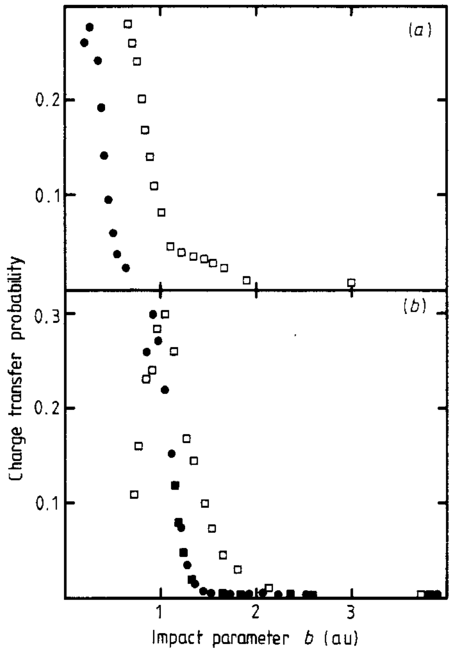

Figure 3. Charge transfer probability against impact parameter. Transformations of the smoothed results of figures 1 and 2 are shown. (*a*) The relative 56.25 keV (□) Be^+ data have been normalised to have the same maximum value as the absolute 5 keV (●) results of Olsen *et al* (1979). (*b*) The 150 (□) and 30 (■) keV relative Mg^+ data have been normalised to the absolute 66.7 keV (●) results at 0.96 and 1.1 au respectively.

about $R = 0.4$ au (calculation of Sidis; Fayeton 1976), or the Σ-Π rotational coupling in the united-atom limit. There are no firm theoretical calculations indicating the relative importance of the two. The pronounced energy dependence of the Be^+-He differential cross sections (compare, e.g., figures 1(*a*) and (*b*) of Olsen *et al* 1979) can be interpreted as being due to varying relative importance of the two couplings as the collision velocity is increased (Francois *et al* 1972). On the other hand, when our data and the data of Olsen *et al* (1979) are plotted as the reduced cross section $\rho(=[d\sigma/d\Omega]\theta \sin \theta)$ against $E^{3/2}\theta$ (Park *et al* 1975), their energy dependence is largely removed, suggesting the dominance of the united-atom rotational coupling over the energy range from 1.5 to 56.25 keV. A definitive experimental test of the relative importance of the two mechanisms will require state-selective detection of the neutrals.

The $Mg^+ + He$ data can be understood qualitatively by considering the calculations of Courbin-Gaussorgues *et al* (1983, 1985) for the isoelectronic Na–He system. They found strong coupling between the promoted He(1s) 3dσ orbital and the Rydberg levels of Na and He at about $R = 1.1$ au, as indicated in figure 4. The effects of these couplings are seen clearly in our complementary data for Mg^+ (3s→3p) excitation (Redd *et al* 1987b) and He $(n=1 \rightarrow n=2)$ core excitation (Redd *et al* 1987a) in $Mg^+ + He$ collisions. The dramatic enhancement of charge transfer in, e.g., figure 2 at 66.7 keV for $\theta(\textsc{cm}) > 5$ mrad (and also He excitation—see figures 3 and 4 of Redd *et al* 1987a), corresponds to the onset of transitions from the helium core via the 3dσ orbital into Mg^+ and He Rydberg levels, and can also be seen as a 'draining' of flux from the simple excitation channel in figure 1 of Redd *et al* (1987b). It is interesting

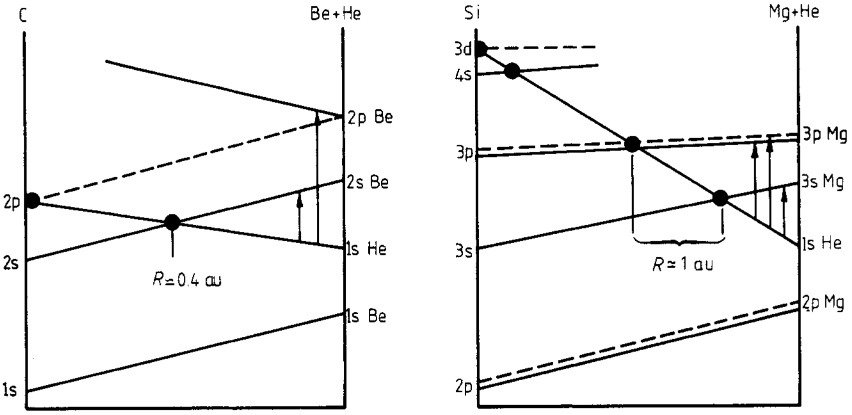

Figure 4. Schematic diabatic MO diagram for the respective quasimolecules formed during the collisions. Full lines represent Σ states; broken lines represent Π states. Relevant curve crossings for $Be^+ + He$ collisions, indicated by dots, are the $2p\sigma$–$2p\pi$ rotational coupling at $R = 0$, and the radial $2p\sigma$–$2s\sigma$ crossing, calculated by Sidis (Fayeton 1976) to occur at ~0.4 au. Several 'direct' radial couplings are indicated by vertical arrows. In the $Mg^+ + He$ case, the strongly promoted He(1s) $3d\sigma$ orbital crosses those leading to Mg^+ and He Rydberg levels at ~1.1 au (Courbin-Gaussorgues *et al* 1983). Possible direct transitions are also indicated.

to note that the deviation from the AO 'direct' theory (Nielsen and Dahler 1985) for excitation at large angle in the 66.7 keV data is of comparable value to the charge transfer enhancement seen in figure 2, indicating that the neutralisation and simple excitation channels play a comparable role for $b \leq 1$ au. The picture developed by Courbin-Gaussorgues *et al* is of course consistent with our $P(b)$ results, which are virtually identical to the $P(b)$ data of Redd *et al* (1987a) and Tuan *et al* (1980, as quoted in Courbin-Gaussorgues and Sidis (1985)) for He core excitation. In an attempt to learn more about the coupling dynamics in the Mg^+ collisions, we plotted our normalised data in both the ρ against $E\theta$ and ρ against $E^{3/2}\theta$ formats. Neither plot produced a convincing universal energy curve.

In both Mg^+ and Be^+ collisions, appreciable charge transfer occurs at the highest energies for impact parameters larger than the combined radii of the colliding inner shells. (This is also seen as an enhancement of the reduced cross section at the lowest values of $E^{3/2}\theta$ for the 56.25 keV Be data.) We attribute this to the importance, at the highest energies, of 'direct' excitation of core electrons to MO corresponding to charge transfer, as indicated in figure 4. Although the distinction is somewhat artificial, direct excitation in this context refers simply to a radial or rotational coupling at large impact parameter where there are no diabatic MO curve crossings. As in the case of valence electron excitation, direct core electron excitation resulting in charge transfer will occur most readily at energies higher than those where 'molecular' excitation is dominant (Andersen and Nielsen 1982). In the Be^+ case, the enhancement is almost certainly due to radial coupling; high-velocity enhancements of the $R = 0$ Σ–Π rotational coupling would still yield reduced cross sections which lie on the 'universal' ρ against $E^{3/2}\theta$ curve. Again, determination of the neutrals' final state would provide definitive information about the relative importance of the various channels.

In conclusion, these data provide us with a more complete picture of violent collisions within the QOE framework, and should serve as a sensitive test of calculations employing molecular basis sets for these collisions. In particular, the broad energy range over which data now exist yield further insight into the relative importance of various dynamical couplings in these violent collisions.

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