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PHYSICAL REVIEW A VOLUME 1, NUMBER 2 FEBRUARY 1970

Oscillatory Structure in Total-Charge-Transfer Cross Sections*

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(Received 1 August 1969)

Oscillatory structure has been observed in total symmetric and asymmetric charge-transfer cross-section measurements involving the alkali-metal atoms. Cross sections with oscillations similar to experimental results had been obtained from impact-parameter calculations using a two-state approximation with an interaction potential difference containing a maximum. This paper describes a physical model of charge transfer relating to the oscillatory electron capture probability. The $Li^+ + Li$ calculations of Peek *et al.* are examined and used as an example to relate capture-probability oscillations to those in total cross section. Computed capture probabilities having anomalous oscillations are shown as a function of impact parameter at several velocities. The capture-probability maxima are shown as contours on a plot of impact parameter versus inverse impact velocity. This plot illustrates capture-probability oscillations having a nearly stationary phase over a range of impact parameters, which results in oscillations in the total cross section. Oscillation damping and phase-constant effects are briefly examined to relate experimental results with theory. Near-resonant asymmetric oscillations are also discussed.

1. INTRODUCTION

Measurements of total-charge-transfer cross sections for the alkali-metal atoms revealed the first appearance of regular oscillations in the cross section as a function of the impact velocity.[1,2] Initially, the velocities at most of the oscillation peaks of the asymmetric ion-atom pairs were correlated with transition between excited states. It was assumed that the generation of incident-atom excited states was produced by polarization excitation. In subsequent publications, resonant electron capture has been advanced as an explanation of the oscillations, for both symmetric and asymmetric near-resonance charge transfer with very good results.

The present paper is concerned with an examination of recent theoretical work to determine the relationship between total-charge-transfer oscillations and those observed in electron-capture probability. Using an impact-parameter method, it is sufficient to begin with a potential-difference function containing a maximum at a relatively large internuclear distance to obtain oscillatory structure in the total cross section. By showing the intermediate steps in previous calculations, it is seen how the presence of a potential-difference maximum leads to a stationary phase and to anomalous electron-capture-probability oscillations which also appear in the total cross section.

2. BACKGROUND

It was initially pointed out by Lichten[3] that oscillations in our total cross-section measurements are similar to those observed in angular measurements of resonant electron capture.[4,5]

Smith[6] first showed that oscillations in the total symmetric resonance cross section could be obtained by the impact-parameter method using a two-state approximation and assuming that the difference between the *gerade* and *ungerade* molecular potentials passes through a maximum. He derived an expression, using a stationary phase approximation, for the total cross section which contains a smoothly varying term and an oscillatory term. Semiempirical potentials were constructed to reproduce our measured $Cs^+ + Cs$ cross section with fairly good results.

A formulation similar to that of Smith was applied by Marino[7] to his measurements of all alkali metal ion-cesium atom total-charge-transfer cross sections. The oscillations in Marino's measurements are in general agreement with our measurements for ion-atom combinations and energies in common.

From an *ab initio* calculation of two lowest Li_2^+ states, Peek, Green, Perel, and Michels[8] employed the impact-parameter method to compute a total $Li^+ + Li$ charge-transfer cross section which contains uniform oscillations. The difference between the two potentials as a function of the internuclear distance also contains a maximum (similar to those of Smith and Marino). It is also shown how the approximate formulation of Smith departs from an exact calculation. The results are in general agreement with our preliminary experimental measurements. A more recent measurement is reported by Daley and Perel,[9] and a comparison between theory and the recent measurement is published.[10]

Other total-charge-transfer measurements made in our laboratory, which contains oscillatory structure, have been reported with tabulations of the oscillatory characteristics.[11–13] Still other measurements have been made containing these oscillations and are discussed in Ref. 14. To date, only alkali-metal atom total-charge-transfer cross sections have shown uniform oscillatory structure, with the $Hg^+ + Cs$ cross section[12,15] being the only example in which one of the species is not an alkali-metal atom. Measurements of noble-gas ions and alkali-metal atoms indicate some structure, but do not reveal regular oscillations.[16]

3. MODEL OF ELECTRON-CAPTURE PROCESS

The process of electron capture can be described by a qualitative physical model that considers the classical trajectory for an incident singly charged ion interacting with the atom. The ion trajectory is characterized by a velocity and an impact parameter. As the ion approaches the atom, depicted as an ion core and a single bound electron, the electron binding is modified by the Coulomb field of the ion. The internuclear distance between the two ions, at which this interaction is initiated, is determined by the polarizability of the incident atom and does not appear to depend upon the properties of the incident ion. As the ion approaches closer, the electron orbit extends toward it and makes the first transfer. It is then similarly attracted and transfers back. This process continues with alternate transfers between the two ion cores at a transfer frequency which depends upon the internuclear separation. Since the electron orbit is determined by the two ions, this configuration is better described as a quasimolecular ion with an internuclear separation which varies with time. When the two ion cores separate, the electron can have made several transfers with an odd number of such transfers resulting in electron capture and an even number resulting in elastic scattering. The number of transfers is related to the electron-capture probability, which oscillates between zero and unity, as the velocity and/or the impact parameter is varied.

The electron-capture probability is more rigorously obtained by an impact-parameter method using a two-state approximation. These states, which vary with internuclear distance R, are the potential functions for the interaction between an ion and an atom. Considering the incoming ion as an incident wave being scattered from two potential functions $V_1(R)$ and $V_2(R)$, an interference wave is generated during the collision time. The phase difference η generated in this interaction time t is given by

$$\eta = \tfrac{1}{2}\int_{-\infty}^{\infty} (\Delta V/\hbar)\, dt \ , \tag{1}$$

where $\Delta V(R) = V_1(R) - V_2(R)$. Transforming the time variable to internuclear separation using an impact-parameter method with only small angle scattering due to the collision, the phase difference is given by

$$\eta(\rho, v) = \frac{X}{v} = \frac{1}{\hbar v}\int_{\rho}^{\infty} \frac{\Delta V(R)}{(1-\rho^2/R^2)^{1/2}}\, dR \ , \tag{2}$$

where v is the impact velocity and ρ the impact parameter. The electron capture probability is

$$P(\rho, v) = \sin^2\eta \ . \tag{3}$$

This probability has a value between zero and unity for each value of ρ and v.

This oscillatory probability has been observed for both symmetric and asymmetric electron capture by means of differential measurements. For the case of $He^+ + He$, the potential difference function $\Delta V(R)$ decreases exponentially with R. The capture probability oscillates with uniformly increasing spacing between the oscillations with increasing ρ, as shown in Fig. 1(a), taken from Everhart, Helbig, and Lockwood.[17] At a nearly fixed value of ρ, the oscillations shown in Fig. 1(b), taken from Ziemba and Everhart,[18] are nearly uniformly spaced when plotted as a function of v^{-1}. Note that the measured oscillations have amplitudes less than unity and that the amplitude decreases with increasing v^{-1} (damping).

The total cross section $\sigma(v)$ is found by integrating the probability [Eq. (3)] over all impact parameters at a fixed velocity and is given by

$$\sigma(v) = 2\pi\int_0^{\infty} \rho P(\rho, v)\, d\rho \ . \tag{4}$$

Because of the regularity of the probability oscillations, it was previously found that, by substituting the average value of $P = \frac{1}{2}$ out to an impact parameter where $\eta = 1/\pi$, the same area as the integral can be obtained [see dashed line in Fig. 1(a)]. Thus, the total cross section can be written

$$\sigma_F(v) = \tfrac{1}{2}\pi\rho_F^{\,2}(v) \ , \tag{5}$$

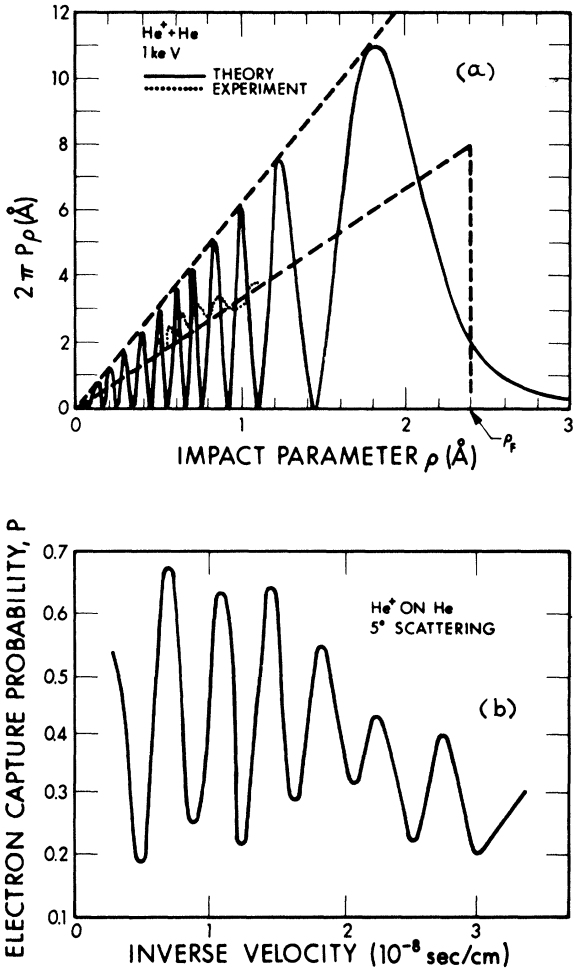

FIG. 1. The $He^+ + He$ electron-capture probability as a function of the impact parameter, (a) and the inverse velocity (b) from Refs. 15 and 16, respectively. In (a), the theoretical probability multiplied by $2\pi\rho$ shows the contribution of each oscillation to total cross section, which is the area of this curve. The total cross section is also given by the dashed triangle bounded by $P = \frac{1}{2}$ out to an impact parameter ρ_F. Note how the spacing between oscillations increases with ρ, which results from the exponential dependence of ΔV upon R. The experimental probability shows similar but highly damped oscillations. In (b), the oscillations are nearly uniformly spaced and show a decreasing amplitude with increasing v^{-1} (damping).

where ρ_F is the Firsov[19] impact parameter determined only from the long-ranged part of the $\Delta V(R)$ curve. This method, however, is insensitive to any structure which may evolve from the shorter ranged part of the interaction.

Smith[6] formulated a $\Delta V(R)$ function containing a maximum which resulted in an oscillatory structure in the total cross section. He developed an approximate expression for the total cross section containing a smoothly varying part, equal to that of Eq. (5), and an oscillatory part. His equation contained a $v^{1/2}$ dependence for the oscillation amplitude and an oscillation phase of $\frac{1}{4}\pi$. Since the experimental results do not strictly conform to these dependencies, this equation is, therefore, written in a more general form:

$$\sigma(v) = \sigma_F(v) - \alpha(v)\cos[\pi(\beta v^{-1} - \delta)] \quad , \tag{6}$$

where $\sigma_F(v)$ is the smoothly varying part of the cross section, $\alpha(v)$ is the amplitude, β is the frequency, and δ is the phase constant of the oscillatory part. Smith's derivation shows the oscillation frequency β to be given by

$$\beta = 2X_0/\pi \quad , \tag{7}$$

and the oscillation amplitude to be given by

$$\alpha(v) = \pi\rho_0(\pi v)^{1/2}\left|\frac{d^2X}{d\rho^2}\right|_0^{-1/2} \quad , \tag{8}$$

where ρ_0 is the critical impact parameter, X_0 is defined by Eq. (2), and $|d^2X/d\rho^2|_0$ is the curvature – all of which are determined at the extremum.

A measurement of a cross section containing oscillations provides direct information on the X function. The long-ranged end of the function is determined from the smoothly varying part of the cross section and the value at the extremum determined from Eq. (7). The critical impact parameter and the extremum curvature cannot be obtained individually because of their product dependence on $\alpha(v)$, seen in Eq. (8), and because the measured amplitudes show a more rapid variation than the theoretical $v^{1/2}$. The measured data cannot be used to determine a unique ΔV function, but can be used for verification. This assumes that large-angle scattering from the ion core is not an important factor in causing oscillations.[20]

4. APPLICATION TO $Li^+ + Li$

In an effort to further understand the source of these oscillations, the $Li^+ + Li$ computations as taken from Peek *et al.*[8] are examined in greater detail. The potential-difference (ΔV) curve as a function of internuclear distance in atomic units[20] is shown in Fig. 2, where $\Delta V = V_u - V_g$ refers to the lowest *ungerade* and *gerade* states of Li_2^+. Below $3a_0$, the curve decreases smoothly to -0.3414 at $\rho = 0$. It is the presence of the maximum which leads to the oscillations and is of particular interest here. From the integral given by Eq. (2), the value of X is determined over an impact-parameter range from $3a_0$ to $16a_0$ and is also shown in Fig. 2. Note the similarity between the ΔV and X

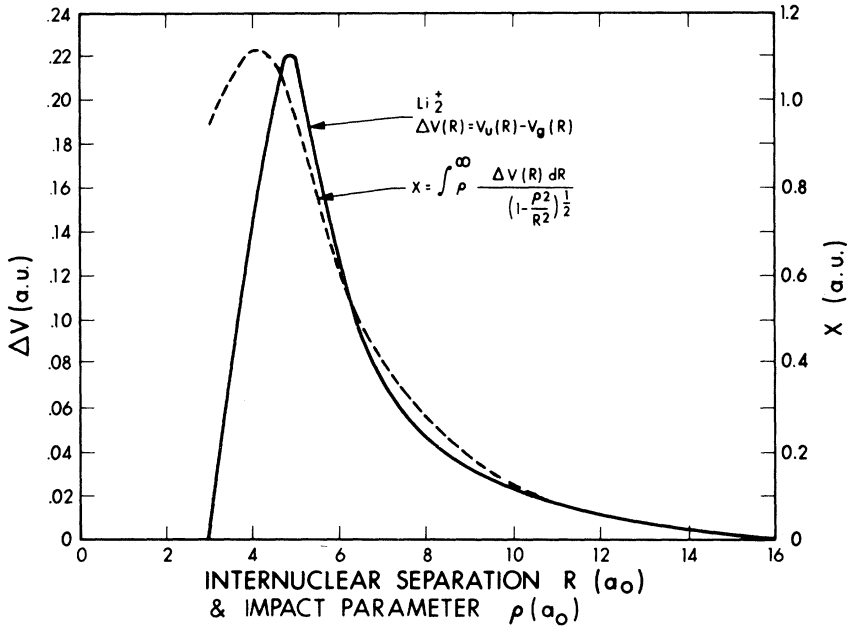

FIG. 2. ΔV versus R in atomic units for Li_2^+ from Ref. 8. A maximum occurs at about $4.9a_0$ with an exponential decrease for increasing R and a near linear decrease for decreasing R. X versus ρ, from Eq. (2), with a similar shape as the ΔV curve but with the extremum at about $4.1a_0$.

curves with the shift of the extremum.

The extremum determines the critical impact parameter where X does not vary greatly, so that the capture probability is nearly constant over a range of impact parameters. The capture probability contains a broad or anomalous oscillation at this critical impact parameter which is not obscured when integrating over all impact parameters to obtain the total cross section. This broad oscillation is seen in Figs. 3 and 4 showing plots of the probability as a function of the impact parameter [Eq. (3)] for different velocities. In these figures, the region below $3a_0$ (not included) should contain regular oscillations which contribute a constant $4.5\pi a_0^2$ toward a cross section at all velocities.

Figures 3(a) and 3(b) show the probability for two different inverse velocities. The oscillation peaks are indexed by odd numbers, which are obtained from Eq. (3) using

$$X(\rho)v^{-1} = n\tfrac{1}{2}\pi, \tag{9}$$

where $X(\rho)$ is shown in Fig. 2, and n is the oscillation index number which as an odd integer produces a probability of unity. From the simple physical model discussed in Sec. 3, n represents the number of electron transfers. Note in Fig. 3(a) that two peaks having the oscillation number of 15 merge into a broad anomalous oscillation with a change in the oscillation-number sequence. These are the main differences between these capture probabilities and those illustrated in Fig. 1(a). Figure 3(b) shows the probability at a velocity in which the total cross section contains an oscillation maximum. The contribution of the anomalous

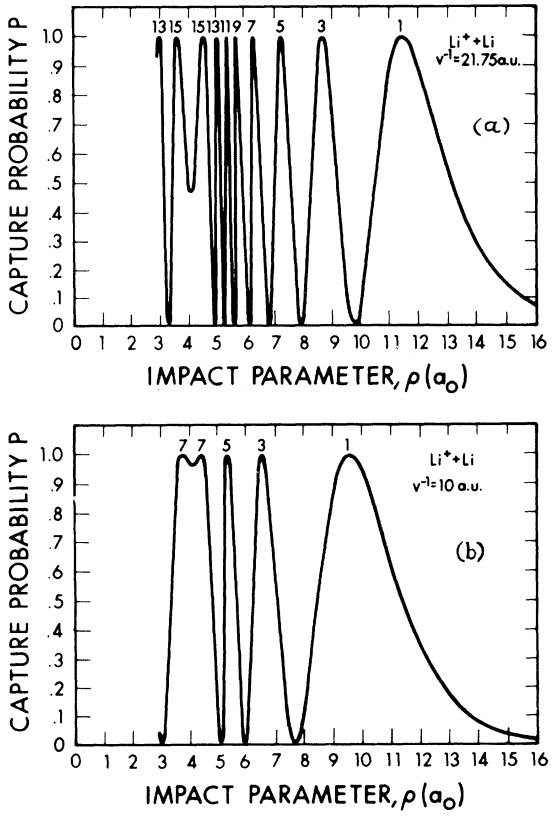

FIG. 3. Computed P versus ρ for $Li^+ + Li$ electron capture at (a) $v^{-1} = 21.75$ a.u. Note the merging of two oscillations, both for $n = 15$, at the critical impact parameter $\rho = 4.1a_0$. In (b), $v^{-1} = 10$ a.u., and the critical oscillation at $n = 7$ contributes an oscillation maximum to the total cross section.

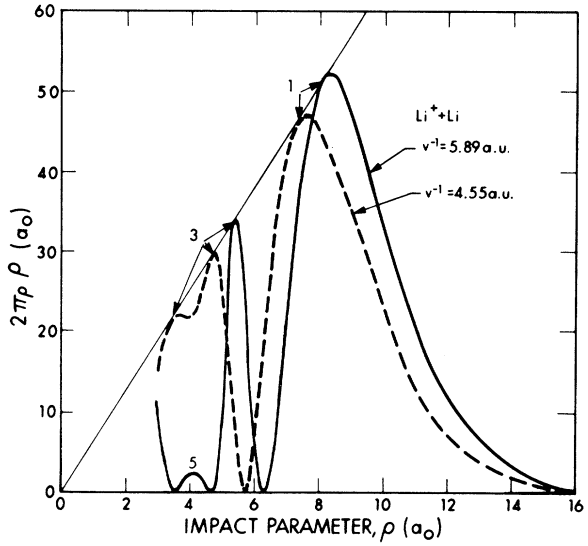

FIG. 4. Computed values of $2\pi\rho P$ versus ρ for $Li^+ + Li$ electron capture. At $v^{-1}=5.89$ a.u., oscillation peaks 1, 3, and 5 appear. At the critical impact-parameter peak, 5 is very small corresponding to a total cross-section minimum. At $v^{-1}=4.55$, only 1 and 3 appear, and 3 is a double peak corresponding to a total cross-section maximum.

oscillation is large enough to be discerned in the total cross section.

Figure 4 shows $2\pi\rho P$ versus ρ for two values of the inverse velocity, where the area under the oscillatory curve is the total cross section. The anomalous oscillation for $v^{-1}=5.89$ a.u. is small corresponding to minimum in the total cross section. Figure 4 also shows the probability at a total cross-section maximum ($v^{-1}=4.5$ a.u.). The increasing width of the critical oscillation with increasing velocity seen sequentially in Figs. 3 and 4 provides the $v^{1/2}$ dependence of the theoretical amplitude. Probability damping results in a steeper variation with velocity.

From an examination of Figs. 3 and 4, it is seen that the peaks above the critical impact parameter shift toward lower impact parameters with decreasing inverse velocity, and they merge to form a broad probability which oscillates with varying velocity. This is seen from a different view in Fig. 5, which shows contours of constant oscillation index numbers on a plot of ρ versus v^{-1}. This plot illustrates how the contours of the oscillation peaks change direction at the critical impact parameter. The oscillatory curve in the upper part of Fig. 5 is the effective impact parameter obtained from $\rho_E=(2\sigma/\pi)^{1/2}$ using the calculated total cross section from Peek *et al.* Note the correspondence between the ρ_E peaks and the critical impact-parameter peaks with a phase shift of about $\frac{1}{4}\pi$. This same type of plot for nonoscillatory total cross-section cases does not have such a change in contour direction. In this latter case, the contours become more and more vertical as they approach $\rho=0$, which can result in very small amplitude oscillations in the total cross section that have not yet been observed experimentally.[21–23]

A direct correspondence exists between Fig. 5 and the plot of the contours of the probability max-

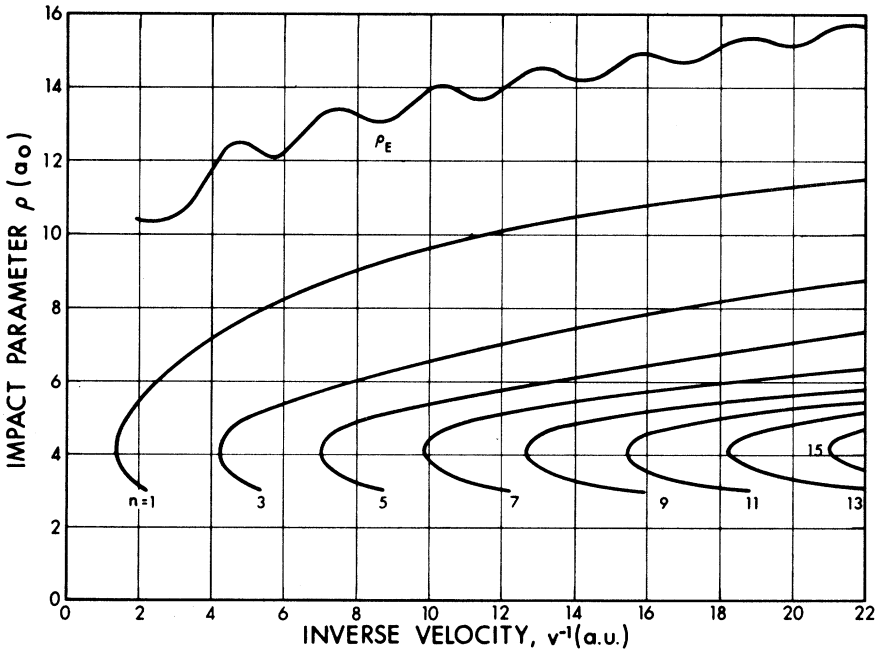

FIG. 5. Contour plot of the electron-capture-probability maxima on ρ versus v^{-1} coordinates. These contours all change in shape at the critical impact parameter. It is this inflection that contributes the oscillations in the total cross section. The oscillatory curve ρ_E is the effective impact parameter at each velocity that generates the total cross section from $\sigma=\frac{1}{2}\pi\rho_E^2$.

ima on energy E versus scattering angle θ coordinates[24,25] because v^{-1} is directly related to E and ρ is related to θ. The latter relationship is more complicated because the two potential curves will produce scattering into two angles which can be very different at larger impact parameters. Nevertheless, one would expect the contours for oscillatory total cross-section cases to slope toward lower energies with increasing angle, in the high-energy region of an E versus θ plot, in contrast with the flat contours for the nonoscillatory cases.

Figure 5 is also a projection of the three-dimension P, ρ, and v^{-1} figure. Intersections of this figure with $v^{-1}=$ const are shown in Figs. 3 and 4. The intersections with $\rho=$ const are similar to that of Fig. 1(b). Because of the weighting factor and the shape of the curves, the total cross-section oscillations have a shift of the phase constant of about $\frac{1}{4}\pi$ with respect to that of the probability oscillation at the critical parameter.[6,7] It was also found that the experimental probability versus v^{-1} for other species has an additional negative phase shift of $\frac{1}{2}\pi$ with respect to the "theoretical" probability.[3,5] If the species having an oscillatory total cross section have a similar phase in the probability, then the net phase term in the total cross sections should be about $\frac{3}{4}\pi$, which is close to the values found in the measurements.[11-14]

Although Eq. (6) is approximate, it is useful to determine the constants to provide some insight into the relation between the cross section and the interaction potentials and to make comparison between results of various impact species. The values of these constants, as obtained from Eq. (6), for the $Li^+ + Li$ calculations are

$$\alpha = 12.5 v^{1/2} \text{ (a.u.)}(\pi a_0^2) \quad ,$$

$$\beta = 0.71 \text{ a.u.} = 1.55\times 10^8 \text{ cm/sec} \quad ,$$

$$\delta = 0.2 \quad .$$

The experimental results show values similar to the calculated ones.[10]

5. DAMPING AND ASYMMETRIC ELECTRON CAPTURE

The discrepancy between the measured variation of oscillation amplitude[7,11,14] and the theoretical dependence[6] [Eq. (8)] is attributed to the exponential decrease of the capture-probability amplitude with decreasing velocity [Fig. 1(b)]. This decrease in the capture probability is described by Lichten[26] as a damping which arises from the effects of close-lying energy levels on the two-state transition. The amplitude varies as $-v_0/v$, where v_0 is a constant characterizing the damping rate. Since damping considerations are not included in the derivation of Eq. (6) or in the computations of Peek *et al.*, it is not surprising that the oscillation amplitudes predicted by the theories do not decrease as rapidly as the experimental results.

Asymmetric charge transfer for most of the alkali-metal atoms is near resonant, and the observed oscillations are very similar to those of the symmetric resonance cases. The primary difference is that the phase constant δ [Eq. (6)] is about $\frac{3}{4}$ for the symmetric cases and $-\frac{3}{4}$ for the asymmetric cases. An important feature of the asymmetric data for conjugate ion-atom combinations $A^+ + B$ and $B^+ + A$ is that values of β are the same, and the cross-section shapes and magnitudes are similar.[1,9,11,13] Thus, β depends upon the characteristics of the quasimolecular ion formed during the collision, which is the same for conjugate combinations. This similarity for conjugate combinations should hold as long as the same two electronic states are involved. When the energy defect for transfer to an excited state for only one of the conjugates is well below that for transfer to the ground state, then the similarity between conjugate combinations no longer exists. In this case the cross section values, the position of the cross section maximum, and the oscillation frequency β should differ greatly between the two cases.[27]

6. CONCLUSIONS

It was previously shown that a maximum in the potential difference between the two lowest states of a quasimolecular ion results in the oscillatory structure in the total-charge-transfer cross section. The oscillatory structure is the result of the electron-capture probability remaining nearly constant over a range of impact parameters. The cross-section oscillation frequency is nearly identical with the capture-probability oscillations at the critical impact parameter with the phase constant somewhat shifted. The oscillation amplitude depends upon the product of the critical impact parameter and the extremum curvature. Thus, neither of these two terms is defined uniquely by a total cross-section measurement. This is further complicated because of electron-capture-probability damping due to coupling to other states.

Despite these complications, calculations were made which compare well with experiments. The relationship between the electron-capture probability and the total-cross-section oscillations can be understood from a contour plot on impact parameter versus the inverse velocity coordinates (Fig. 5).

ACKNOWLEDGMENTS

The author wishes to thank W. Lichten, F. J. Smith, J. M. Peek, T. A. Green, and H. L. Daley for their helpful discussions, and to thank J. M. Mahoney for his assistance in performing computations.

*Work supported in part by the U. S. Army Research Office, Durham.

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