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OSCILLATIONS IN THE TOTAL CROSS SECTION FOR RESONANT CHARGE TRANSFER IN Li-Li^+ COLLISIONS*

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A simplified two-state theory is used to predict the total cross section for resonant charge transfer in Li-Li^+ collisions. This cross section exhibits oscillations for collision energies below 10 keV and is in qualitative agreement with preliminary experimental measurements.

Oscillations in the total cross section for charge transfer in collisions between various alkali-metal atom-ion combinations have been observed by Perel and co-workers[1] and by Marino.[2] Smith[3] has shown that a two-state theory of the resonant capture process predicts oscillations similar to those observed experimentally provided the energy difference between the two states included in the theory goes through an extremum. Smith[3] had considerable success in reproducing the experimental results for Cs-Cs^+ collisions by optimizing assumed forms for the required potential curves. In this note, we predict the total Li-Li^+ resonant charge-transfer cross section using a two-state expansion within the framework of the impact-parameter method. The energy differences between the lowest $^2\Sigma_g{}^+$ and $^2\Sigma_u{}^+$ potential energy curves of $Li_2{}^+$ are required for a completely theoretical prediction of the cross section. Certain calculations for $Li_2{}^+$ are available,[4,5] but they are not considered to be adequate for this analysis, and we present the results of a new determination of the required energy differences.[6] The energy differences from both Ref. 4 and the present calculation exhibit extrema, and the resulting total cross sections for resonant charge transfer have oscillations of the type predicted by Smith for the Cs-Cs^+ system. The cross section based on our determination of the energy differences is in good qualitative agreement with published data[7] and preliminary experimental measurements.

A two-state expansion of a resonant process, in the impact-parameter method and neglecting momentum transfer, gives the total cross section as

$$Q = 2\pi \int_0^\infty \rho d\rho \sin^2[\chi(\rho)/V], \tag{1}$$

where

$$\chi(\rho) = \tfrac{1}{2}\int_{-\infty}^{\infty} \Delta E(R) dz. \tag{2}$$

The energy difference between the two states included in the expansion, $\Delta E(R)$, is defined as

$$\Delta E(R) = E(^2\Sigma_u^+) - E(^2\Sigma_g^+), \quad (3)$$

where $E(^2\Sigma_u^+)$ and $E(^2\Sigma_g^+)$ are the lowest electronic states of Li_2^+ having the indicated term symbols and R is the internuclear separation. All quantities are in atomic units. The integral in Eq. (2) is evaluated for straight-line trajectories along the z axis with a distance of closest approach for the Li nuclei of ρ; V is the relative collision velocity.

Our calculated values[6] for $\Delta E(R)$ are shown in Table I. The continuous curve for $\Delta E(R)$ required for the evaluation of the integral in Eq. (2) was constructed in the following manner. The $\Delta E(R)$ curve was drawn between $R = 3a_0$ and the experimental value[8] at $R = 0$ in a qualitative way. However, calculations show the cross section to be insensitive to the assumed form for this part of the $\Delta E(R)$ curve for the collision energies of interest. The calculated data between $R = 3a_0$ and $R = 11a_0$ were interpolated with a cubic spline function. For $R > 11a_0$, the formula $\Delta E(R) = \exp(-\frac{1}{2}R)(0.160\,55R + 1.659\,61)$ was used. This is the form[9] of ΔE for an electron in the field of two protons correlating to a proton plus a hydrogen atom with $n = 2$ at large R. The numerical coefficients were chosen to make the formula coincide with our calculated values at $R = 9a_0$ and $R = 11a_0$. It is expected that this formula should be qualitatively correct for Li_2^+. More important, Q of Eq. (1) may change in magnitude but its oscillatory behavior will not be influenced by the form of $\Delta E(R)$ for large R. This point was tested numerically for several variations of the formula for $\Delta E(R)$.[10] From the results of these calculations, we infer that the oscillatory nature of Q is completely determined by the calculated data given for $\Delta E(R)$ in Table I.

Table I. The energy difference $\Delta E(R)$ [see Eq. (3)] for Li_2^+ tabulated as a function of R. All quantities are in atomic units.

R	$\Delta E(R)$
0.0	−0.3414[a]
3.0	0.005
4.0	0.151
4.5	0.200
5.0	0.220
5.5	0.165
6.0	0.121
6.5	0.094
7.0	0.070
7.5	0.056
8.0	0.047
9.0	0.032
10.0	0.022
11.0	0.014

[a]See Ref. 8.

The total resonant charge-transfer cross section for Li-Li^+ collisions is shown in Fig. 1 as the upper solid curve. For the purpose of comparing an analytical approximation[2,3] with the oscillatory part of the cross section, $Q - Q_F$ is also shown as the lower curve in Fig. 1 where Q_F is the Firsov cross section.[11] We have also determined Q from values of $\Delta E(R)$ obtained from the calculation by Pfeiffer and Ellison.[4] Their $\Delta E(R)$ curve exhibits an extremum at $R \approx 6.5a_0$, has a magnitude at the extremum roughly one-third that found in the present calculation, has a much lower curvature near the extremum, and exhibits a much larger energy separation for long-range interactions than does our data. The use of their predicted $\Delta E(R)$ curve leads to a cross section which oscillates with about twice the amplitude at half the frequency and has about twice the overall magnitude of the results shown in Fig. 1. The calculation of James[5] is for the $^2\Sigma_g^+$ state at a single value of the internuclear separation and is of little value in this analysis.

Experimental data for the collision process

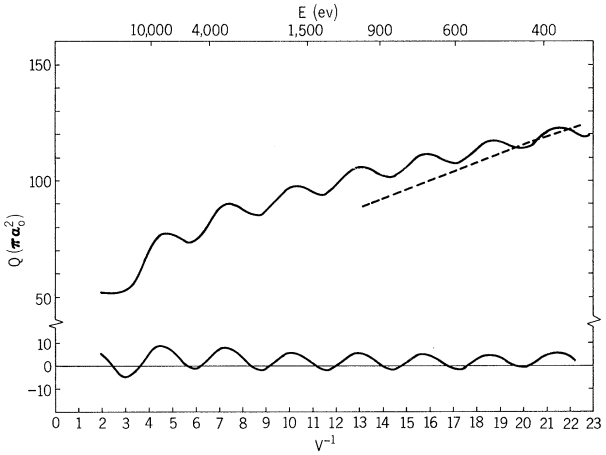

FIG. 1. The total cross section Q, in units of πa_0^2, is shown by the upper solid curve as a function of the reciprocal of the collision velocity V which is in atomic units. The top scale is the corresponding collision energy for a Li^+ ion colliding with a stationary Li atom. Experimental data from Ref. 7 are shown by the dashed curve. The lower solid curve is $Q - Q_F$ where Q_F is the Firsov cross section.

have been published by Lorentz et al. for collision energies up to 1 keV. These data are shown as the dashed curve in Fig. 1. The overall magnitudes[10] and trends with energy are in good agreement. The experimental data from Ref. 7 do not show the oscillations expected on the basis of this theory. However, we have preliminary experimental measurements of relative values of this total cross section which do exhibit oscillations with a frequency and amplitude close to that shown by the theoretical results of Fig. 1. A more detailed comparison of experiment and theory will be presented[12] when the experimental studies are completed. From the discussion presented in the previous paragraph, however, it follows that the cross section based on the $\Delta E(R)$ from Ref. 4 is not in good agreement with experiment.

In conclusion, we observe that the upper solid curve in Fig. 1 represents a completely theoretical prediction of the Li-Li^+ resonant charge-transfer cross section. Potential curves exhibiting the shape in $\Delta E(R)$ conjectured by Smith[3] do indeed exist for this system, and as he demonstrated, oscillations are found in the total cross section. Our calculation of $\Delta E(R)$ produces a magnitude[10] for the total cross section that is in qualitative agreement with experimental results.[7] We anticipate that the oscillatory character of the total cross section will also be essentially correct; however, the final decision on the point must await completion of the experiment.[12] Despite our claim of good agreement with experiment, it should be kept in mind that the theory used in this calculation may not include all the important physical phenomena taking place in these collisions. For example, there are other low-lying electronic states of Li_2^+ that may couple strongly to the states used in the present two-state formulation. Further analysis of this scattering problem is therefore somewhat dependent on our progress in understanding the molecular structure of Li_2^+.

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[8]The $^2\Sigma_u^+$ state of Li_2^+ correlates to the ground ^2P_u state of C^+ in the united atom limit and the $^2\Sigma_g^+$ state of Li_2^+ correlates to a mixture of states, the lowest doublet being $(1s^2 2s\, 2p^2)^2D_g$. Hence, according to Eq. (3) $\Delta E(R=0)$ is less than zero and is, to the accuracy necessary for this calculation, equal to -0.341 a.u. See, for example, C. E. Moore, Ultraviolet Multiplet Table, National Bureau of Standards Circular No. 488 (U. S. Government Printing Office, Washington, D. C., 1950), Sec. 1, p. 9.

[9]I. V. Kamorov and S. Yu. Slavyanov, Zh. Eksperim. i Teor. Fiz. 52, 1368 (1967) [translation: Soviet Phys. -JETP 25, 910 (1967)].

[10]It is a relatively simple matter to explore the effect of different choices for the large-R behavior of $\Delta E(R)$ on the overall magnitude of Q, provided the formula is not greatly different from the one used in this calculation. Defining the cross section for a different choice of $\Delta E(R)$ as Q', it was found that $Q' = Q - Q_F + Q_F'$ represents a rather accurate approximation to numerical calculations of Q'. The Firsov cross sections Q_F and Q_F' can be easily found by analytical evaluation of Eq. (2).

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