Oscillations Due to Two-Electron Exchange during He-Ne Collisions

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(Received 4 February 2000)

$\mathrm{Ne}^-(1s^22s^22p^53s^2)$ and $\mathrm{He}^-(1s2s^2)$ autodetachment peaks in electron spectra arising from He-Ne collisions at energies ranging from 350 eV to 6 keV have been measured. The areas of these two peaks are found to oscillate approximately in antiphase, with a constant wavelength, on a $(\mathrm{velocity})^{-1}$ scale. It is shown that this behavior can be explained by the "quasiresonance" situation for the separating particles in the channels Ne^--He^+ and He^--Ne^+. This explanation implies that the oscillations can be understood as being due to the simultaneous "hopping" of two electrons.

PACS numbers: 34.10.+x, 34.50.Fa, 34.70.+e

If a particle is bound by two neighboring identical potential wells with a finite barrier in between, its eigenfunctions are "gerade" or "ungerade" superpositions of the wave functions describing its state on the different sites. The ammonia molecule is a well known "textbook" realization of this situation for the case of an atom [1(a)]. Formation of the molecule at a well defined time point with the N atom on one of the sites leads to a periodic change of the population of the two sites with the well known inversion frequency of ammonia. For the case of a single electron an equivalent situation arises during symmetrical ion-atom collisions, with the only difference that the "hopping frequency" of the electron changes as the potential barrier between the atoms changes during the collision. Depending on the relation between hopping frequency and collision time, a certain number of "hops" can occur. In this sense, maxima in oscillatory capture cross sections may be ascribed to, respectively, 1, 3, 5, etc. hops during the collision. A well known example is the oscillations in the differential capture cross section for $\mathrm{H}^+ + \mathrm{H}$ collisions at keV collision energies [1(b)]. Recent studies have shown that the concept of one-electron hopping may be used more generally: Oscillations in total cross sections for quasiresonant charge exchange between ions and Rydberg atoms [2], as well as for inelastic $\mathrm{He}^{2+} + \mathrm{H}$ collisions [3,4] could be explained in this way.

For hopping oscillations to become visible in total cross sections, the range of impact parameters relevant for the observed process needs to be sufficiently narrow to define sufficiently accurately the number of hops. Rosenthal and Foley [5] found that, for inelastic collisions, this condition is fulfilled if excitation occurs at small impact parameters into two molecular states which couple again at large distances. An example is oscillations in the total cross section for $\mathrm{Ne}^*(3p)$ and $\mathrm{Na}^*(3p)$ formations observed in $\mathrm{Na}^+ + \mathrm{Ne}$ collisions [6]. In this case, excitation of a strongly bound $2p$-electron requires a small impact parameter, while the interaction of the observed channels, $[\mathrm{Ne}^*(3p) + \mathrm{Na}^+]$ and $[\mathrm{Na}^*(3p)\text{-}\mathrm{Ne}^+]$, respectively, is strong at large distances, because of an asymptotic quasiresonance and because of the fact that the involved $3p$ orbital is rather large. The observed oscillations of the populations of the two quasiresonant channels are found to be in antiphase and to have a constant frequency on a $(v_c)^{-1}$ scale (v_c: collision velocity).

The standard two-state quantum mechanical description of the "two site" situation outlined above [1(c)] is not explicitly restricted to one-particle states. In principle, therefore, (quasi)resonant *two-electron* charge exchange might be possible. If it occurs, it would be observable as oscillations interpretable in terms of "*simultaneous two-electron hopping.*" We report here such oscillations for the first time. They arise in the total cross section for formation of the negative ions $\mathrm{Ne}^{**-}(2p^53s^2)$ and $\mathrm{He}^{**-}(1s2s^2)$ in collisions of He with Ne. The two excited channels $(\mathrm{Ne}^{-**} + \mathrm{He}^+)$ and $(\mathrm{He}^{-**} + \mathrm{Ne}^+)$ are asymptotically quasiresonant, with energies of (40.795 eV) and (40.930 eV) [7]. Both channels are observed in our experiment, and the population of the two channels is found to oscillate in antiphase and with a constant frequency on a $(v_c)^{-1}$ scale.

The negative ions decay by autodetachment yielding electron peaks at 16.2 eV and 19.3 eV for Ne^- and He^-, respectively. We measure the area under these peaks as a signal proportional to the formation probability of the ions. Since the peaks are superimposed on a continuous electron spectrum [8], the area can be obtained without systematic uncertainties.

The measurements are carried out under single collision conditions in a magnetically shielded tank at high vacuum, in an energy range from 350 eV to 6 keV. The experimental procedure followed is rather standard. Briefly, He^+ ions are produced in a hollow cathode ion source, accelerated to the desired energy, mass selected by 60° magnetic deflection, and finally partially neutralized by resonant charge transfer. After passing an electric field region in which the remaining ions are removed, the beam of neutral He atoms is collimated by a diaphragm down to an angle of divergence of 0.2° and crossed with an effusive thermal Ne beam, which is also collimated and has a density low enough to guarantee single collision conditions. Because of the low divergence angle of 0.2°, a possible metastable state component in the neutral He beam is negligible.

0031-9007/00/85(13)/2713(4)$15.00

Electrons formed in the collision volume are detected in a direction perpendicular to the He beam by a hemispherical electrostatic analyzer. The analyzer utilizes microchannel plates with position sensitive detection at the exit, allowing one to analyze simultaneously an energy band of a width of 20% of the transmitted energy at a resolution of 3%. This energy band contains the two negative ion peaks. At each collision energy the area under the peaks is normalized by the He-beam intensity and by the target density. In Fig. 1 we show a plot of this intensity on the $(v_c)^{-1}$ scale.

We observe clear oscillations of the intensity with the collision energy. These oscillations are approximately in antiphase for the two negative ions, and, in part of the energy region, 100% modulated. Further, the "wavelength" of the oscillations is approximately constant on the $(v_c)^{-1}$ scale. As outlined in the introduction, this strongly suggests the simultaneous exchange of two electrons whose sum of the binding energies on the two different ions, He^+ and Ne^+, is accidentally almost equal. The oscillatory dashed curves also shown in Fig. 1 are calculated intensities obtained from a theoretical model based on the assumption of such a "quasiresonance."

In the model we consider only the two channels asymptotically connected to the observed negative ion states. According to the electron promotion mechanism [9,10], these two channels are populated "on the way out" at rather large distances, but in a narrow distance region, where the channels belonging to double excitation of $\mathrm{Ne}^{**}(\dots 2p^4 3131')$ couple to the considered ion pair states. This coupling can occur either directly or indirectly via channels belonging to simultaneous single excitation of both collision partners.

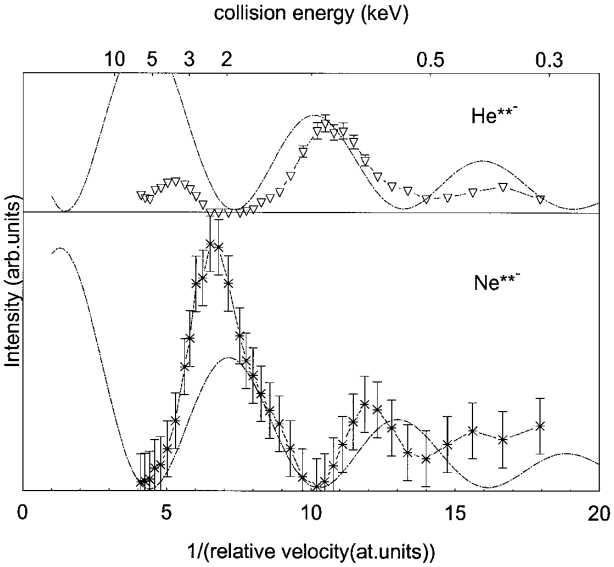

FIG. 1. Plot of the areas of the He^{**-} peak and the Ne^{**-} peak (linear scale) vs the reciprocal relative collision velocity. The dashed oscillatory curves are calculated (see text). The statistical error is smaller than the point markers. The estimated possible systematic error stemming from beam calibration is indicated by error bars.

The initial population distance is a parameter in the model. What is actually calculated are the final asymptotic population probabilities for the observed channels that result from certain initial population amplitudes on the way out. To carry out this calculation, we use the potential curves given in Fig. 2. The diagram shows a pair of *adiabatic* molecular potentials that separate with decreasing distance due to an increasing electronic coupling strength, and the pair of corresponding *diabatic* states which arise when the electronic coupling is omitted. The diabatic energies ε_1 and ε_2, and the corresponding electronic wave functions, we assume to be independent of the distance (R). For a two-state system modeled in this way, the desired expressions can be derived without knowledge of the wave functions, using standard quantum mechanics [see, e.g., [1(c)]]. By transforming the R dependence of the electronic system into a time dependence via the introduction of a radial collision velocity dR/dt, we derive the following set of differential equations for the probability amplitudes $(a_{1,2})$ of the adiabatic states:

$$da_1/dt = -a_2 \times f_1 \times \exp\left\{(i/\hbar) \int_\tau (E_1 - E_2)\, dt\right\},$$

$$da_2/dt = -a_1 \times f_2 \times \exp\left\{-(i/\hbar) \int_\tau (E_1 - E_2)\, dt\right\}.$$

Here the adiabatic energies are given by $E_{1,2} = \pm[W^2 + (\Delta/2)^2]^{1/2}$, with $\Delta = \varepsilon_1 - \varepsilon_2$. (W) is the electronic coupling matrix element, and the factors $f_{1,2}$ are given by

$$f_1 = (d\delta_1/dt) \times \{\sin(\delta_1)\cos(\delta_2) - \cos(\delta_1)\sin(\delta_2)\},$$

$$f_2 = (d\delta_2/dt) \times \{\sin(\delta_2)\cos(\delta_1) - \cos(\delta_2)\sin(\delta_1)\}.$$

In these relations, we have introduced so called "mixing angles" defined as

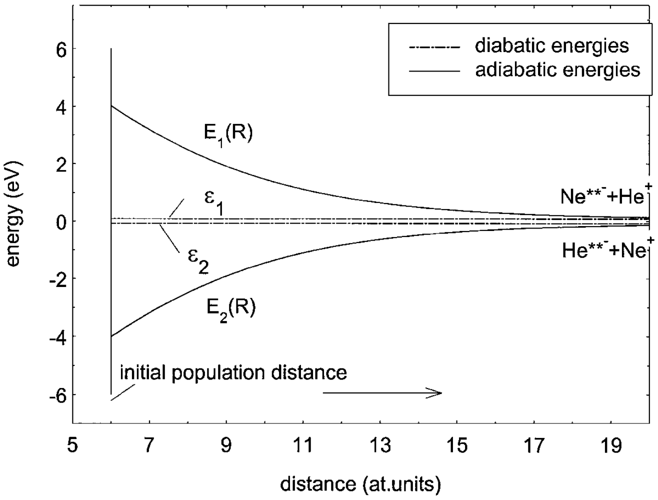

FIG. 2. The potential curve diagram representing the two-state model used to analyze the oscillations. The adiabatic energies $E_{1,2}$ are calculated using the coupling matrix element determined by fitting the experimental data.

$$\delta_1 = \arctan\{W/(E_1 - \varepsilon_1)\}, \quad \text{and}$$
$$\delta_2 = \arctan\{W/(E_2 - \varepsilon_1)\}.$$

If the functional form of the coupling matrix element $W(R)$ is known, the derivatives of the mixing angles $(d\delta_{1,2}/dt)$ become simple analytic expressions that can be obtained from their definition given above, and the coupled differential equations allow one to calculate numerically the population probabilities $|a_{1,2}(t = \infty)|^2$ from the initial population amplitudes at time point $a_{1,2}(t = \tau)$ for a given radial velocity $v_{\text{rad}} = v_c[1 - (b/R)^2]^{1/2}$ (v_c: asymptotic collision velocity; b: impact parameter).

For the case of one-electron exchange, the coupling matrix element has been found to be given in good approximation by the function [11]

$$W(R) = A \times R \times \exp(-\beta R),$$

with the constants A and β being determined by the asymptotic binding energies of the one electron involved. We use the same general form of the coupling matrix element. In order to adapt it to the present case, where two electrons are exchanged, we replace the one-electron binding energy by the sum of the binding energies of the two electrons involved, $E_b = E_b^1 + E_b^2$, and introduce a factor of 2 in the preexponential factor because of the exchange degeneracy of the final state of the two-electron capture process. The resulting function is

$$W(R) = \alpha^3 \times R \times \exp\{-0.86\alpha R\},$$
$$\text{with } \alpha = [2E_b]^{1/2}.$$

The factor (0.86) appears also in the original expression of Olson *et al.* [11] and is a result of the fit of the general function to experimental data available on one-electron exchange systems.

The final population probabilities are dependent only on the integral over $W(R)$, which depends (i) on the starting distance $[R(\tau)]$ and (ii) on the function itself. Since the function itself is expected to be different for two-electron exchange, we choose an estimated fixed initial population distance of $R(\tau) = 6$ a.u. (atomic units) and allow the constant $k = 0.86$ to take on a different value.

The actual numerical calculations are carried out by solving the differential equations in R space for a given impact parameter, and integrating over impact parameters from zero up to a certain $b_{\max}$. As outlined above, except for the ratio of the initial population amplitudes $[a_{1,2}(\tau)]$, the only free parameter that can be adapted is the factor (k) appearing in the exponent of the coupling matrix element. In principle, there could be a relative phase between the initial population amplitudes; however, it turns out that such an initial relative phase does not influence the final probabilities $|a_{1,2}(\infty)|^2$. We therefore choose the initial amplitudes to be real. A clue as to the ratio of their real values is the fact that the modulation of the measured oscillations is 100% in the main region of collision energies. Such a 100% modulation of the final probabilities can be obtained in the calculations only if $[a_1(\tau)]^2 = [a_2(\tau)]^2 = (1/2)$. We therefore use these initial conditions in the calculations. Based on the promotion mechanism [9,10], which requires overlap of the He$(1s)$ orbital with the Ne$(2p)$ orbitals, we may assume that $b_{\max} < 2$ a.u. The precise value is uncritical up to a value of ca. 3 a.u. where the calculated modulation of the probabilities starts to become significantly less than 100% in the subtended velocity region. We use $b_{\max} = 2$ as the limit for the integration over impact parameters. The best agreement with the experiment is obtained for the value $k = 0.62$. The coupling matrix element describing double electron exchange thus becomes, with $\alpha = 0.63$,

$$W(R) = 0.25 \times R \times \exp(-0.39 \times R) \text{ (a.u.)}.$$

This is actually the matrix element used to construct the adiabatic energy lines in Fig. 2. For the agreement achieved, the precise value of the estimated integration limit $R(\tau)$ is unimportant, because the final population probabilities depend only on the integral over $W(R)$: A different $R(\tau)$ would result in a different value of (k).

Within our interpretation, the experimental curves in Fig. 1 result from a common excitation cross section curve multiplied by the oscillating probabilities. We see immediately that this is an idealization, but we show later that the data are consistent with this interpretation. To facilitate a first direct comparison of calculated and measured oscillations, we plot in Fig. 1 the calculated probabilities multiplied by a smooth function to simulate a common cross section. We notice that the oscillations are rather well reproduced. This is already strong evidence for the validity of the model and, hence, for the two-electron hopping hypothesis. While distortions of the observed oscillations can have several reasons not relevant in the present context, their exact antiphase character is important. Here the data as presented in Fig. 1 seemingly do not qualify with sufficient accuracy. However, if we tentatively "reconstruct" the experimental relative population probabilities, which we obtain from the curves of Fig. 1 by first "correcting" the He curve and then dividing each curve by the sum of the curves, we find that the data are indeed consistent with exact antiphase behavior. This is shown in Fig. 3, where also the calculated probabilities are given. The "correction function" we used for the He curve increases rather steeply towards low $(v_c)^{-1}$ and has the form $C/[(v_c)^{-1} - D]$, with ($C = 20$ and $D = 3.5$). It is chosen to compensate for possible extra loss from the observed He channel, which is suggested by the experimental data. There is no special reason for the functional form chosen, except that, by multiplying the He signal with this function, the overall velocity dependence of the resulting He signal resembles the one of the Ne signal. By calculating the probabilities using this corrected He signal, we obtain the curves shown in Fig. 3. The important antiphase criterion

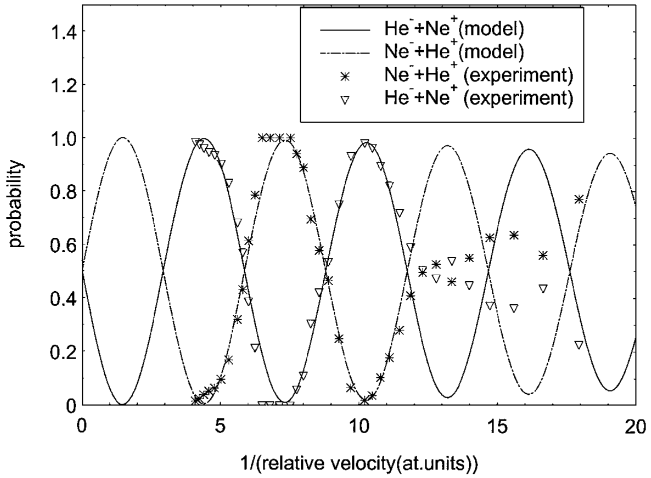

FIG. 3. Comparison of population probabilities extracted from the experimental data of Fig. 1, with the probabilities following from the theoretical model.

is now fulfilled and the quality of agreement between calculations and experiment has considerably been improved. This shows that the experimental data are consistent with the physical interpretation on which the calculations are based.

The theoretical description allows one to follow the probabilities for population of the diabatic states during a collision, i.e., of the states (Ne^{**-}-He^{+}) and (He^{**-}-Ne^{+}), which transform into each other by the transition of two electrons. As an example we show in Fig. 4 these probabilities for a collision velocity of 0.14 a.u., where the Ne^{-} signal has approximately its maximum. We notice that the two electrons change places several times during the collision. With decreasing velocity the number of hops increases. At the lower velocities the oscillations in the experimental curves probably disappear because the large number of hops is not sufficiently well defined.

In summary we reported the observation of oscillations in the total cross section for the formation of Ne^{-} and He^{-} in keV He + Ne collisions. A two-state model description based on the assumption that the oscillations are due to the "quasiresonance" situation for the channels $He^{-} + Ne^{+}$ and $Ne^{-} + He^{+}$ is found to describe the oscillations satisfactorily. This description implies the coupling due to two-electron exchange, which, in a diabatic picture, may be ascribed to *simultaneous two-electron hopping* between the collision partners during the collision. To our knowledge this is the first demonstration of the phenomenon.

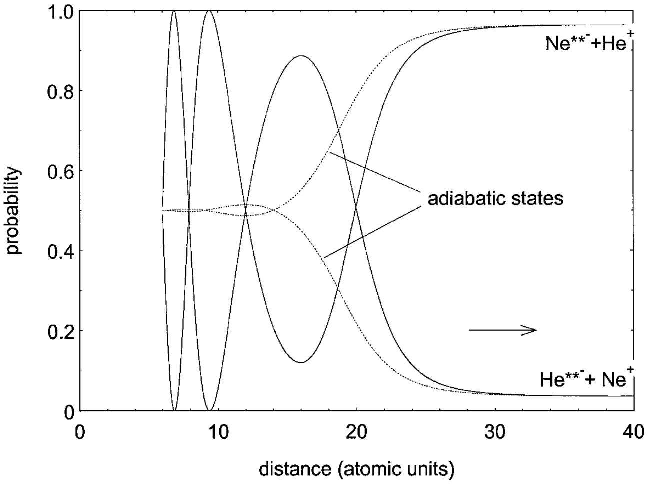

FIG. 4. The population probabilities for the adiabatic and diabatic states as a function of distance at a fixed collision velocity of 0.14 a.u. 100% population of one of the diabatic states implies that both electrons are attached to one of the collision partners. The oscillations of the diabatic state populations therefore imply "hopping" of two electrons.

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