

Quantum-Mechanical Phase-Interference Effects in Low-Energy He⁺-Ne and Ne⁺-He Inelastic Collisions

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Total relative emission cross sections for the production of He I, Ne I, and Ne II radiation have been measured as a function of energy in low-energy He⁺-Ne and Ne⁺-He collisions. These are the first ion-atom excitation measurements of atomic states populated through two different incoming pseudomolecular-potential curve channels. The oscillatory structure in the He⁺-Ne data can be explained in terms of phase-interference effects between potential curves at pseudocrossings occurring at large internuclear distances.

We have observed radiation and measured total relative emission cross sections associated with the excitation of He, Ne, and Ne⁺ in low-energy (10 eV to 5 keV) He⁺-Ne and Ne⁺-He collisions. These are the first ion-atom collisional-excitation measurements of given atomic states populated through two different incoming pseudomolecular channels (i.e., He⁺-Ne and Ne⁺-He). Our results show that only the He⁺-Ne excitation cross sections exhibit marked oscillatory structure. When the same excited atomic states are populated in Ne⁺-He collisions, only a gradual increase with energy in the cross section is observed, without a pronounced oscillatory structure. Our analysis of the structure observed in the He⁺-Ne cross sections provides strong evidence for the hypothesis that these oscillations are associated with quantum-mechanical phase development. This development is postulated to occur between an inner (1 to 2 a.u.) incoming-state/excited-state pseudocrossing of the He⁺-Ne molecular potential-energy curves and an outer (15 to 40 a.u.) pseudocrossing between two excited-state curves.

The apparatus used for these measurements included an electron-bombardment ion source,¹ electrostatic lenses, and a collision chamber. The radiation from the interaction region was measured with a McPherson 0.3-m, *f*/5 monochromator and an S-20 phototube. The ion-beam intensity varied as a function of energy from 1×10^{-7} A at 10 eV to 1×10^{-5} A at 5 keV. The spread in ion-beam energy was measured to be less than 1 eV over a wide range of energies. Single-photon-counting techniques were employed to facilitate sensitive radiation detection.

Figure 1 shows excitation functions for some He I, Ne I, and Ne II excited states obtained in both He⁺-Ne and Ne⁺-He collisions. In all cases, the locations of the excitation thresholds occur above the location required by simple energy-

conservation considerations. These results are consistent with the hypothesis that excitation occurs by means of an inner (1 to 2 a.u.) pseudocrossing between the incoming-state and excited-state curves of the associated molecular complex. In general, such a pseudocrossing occurs above the energy of the final state. Thus, additional energy is required to populate the excited state. This interpretation is given considerable support from molecular calculations performed by Michels² and by Coffey, Lorents, and Smith,³ as well as from previous experimental results with various collision combinations.⁴

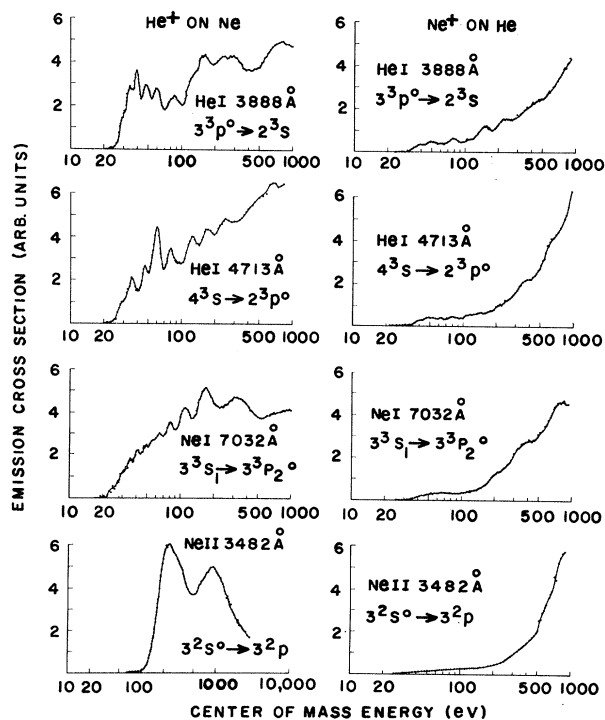


FIG. 1. Relative total emission cross sections of prominent optical lines in He⁺-Ne and Ne⁺-He collisions. Each graph is plotted independently in arbitrary units. The structure in the cross sections is reproducible to better than 2%.

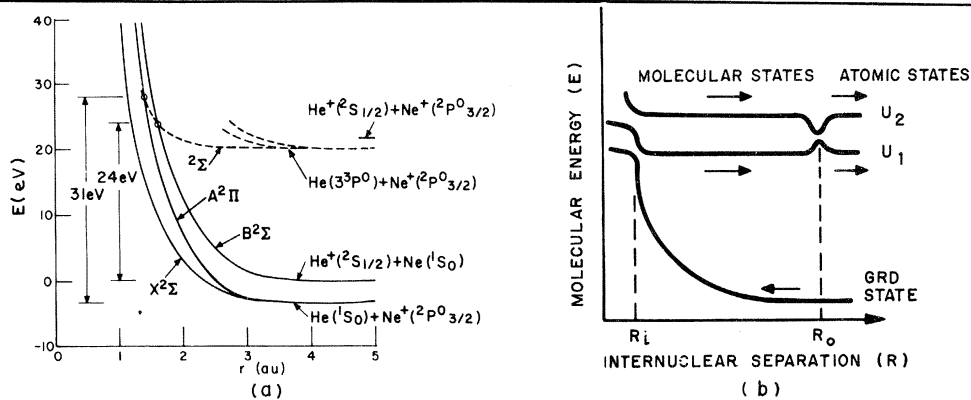


FIG. 2. Potential-energy curves appropriate to the collision process. (a) Molecular-potential energy curves for $(\text{HeNe})^+$ calculated by Michels (Ref. 2) and Coffey, Lorents, and Smith (Ref. 3). (b) Schematic illustration of the dual crossing model.

While the calculations of the $(\text{HeNe})^+$ system^{2,3} [Fig. 2(a), solid lines] do not specify any of the incoming-state/excited-state crossings, our measurements enable us to propose a plausible pseudocrossing scheme. The dotted lines in Fig. 2(a) represent the possible location of the $\text{He}(3^3P^0) + \text{Ne}^+(2P_{3/2}^0)$ excited states. For the purpose of this discussion, we consider the excitation of the $\text{He}(3^3P^0)$ state in both He^+ -Ne and Ne^+ -He collisions. Since the particular incoming-state potential curve which populates the $\text{He}(3^3P^0)$ level is determined by the collision combination under study, we expect that the excitation threshold may be different in the two collision cases. With the measured threshold information, we may establish the location in energy of the interaction which populates the $\text{He}(3^3P^0)$ state in each collision process. For the He^+ -Ne case, the threshold occurs 24 eV above the initial energy of the He^+ -Ne ground state. For the Ne^+ -He case, the threshold is 31 eV above the initial energy of the Ne^+ -He ground state. Since the initial energies of the He^+ -Ne and Ne^+ -He systems differ by 3 eV, we conclude that the two regions of interaction are separated by 4 eV.

A distinct feature of the 3888-Å $\text{He I}(3^3P^0-2^3S)$ line, as well as all other observed lines arising from Ne^+ -He collisions, is the lack of a sharp threshold. The gradual increase of the Ne^+ -He cross sections with bombarding energy suggests that a well-defined pseudocrossing does not occur. Rather, transitions may take place as a result of the potential curves gradually approaching degeneracy with decreasing internuclear separation.⁵ On the other hand, the sharp onsets which appear in the He^+ -Ne cross sections indicate that in this case the region of interaction between the ground- and excited-state curves

occurs at a definite pseudocrossing.

Rosenthal and Foley have shown that inner pseudocrossings alone cannot account for structure in He^+ -He excitation cross sections.⁶ To explain such oscillatory structure, they have hypothesized the existence of pseudocrossings that occur at large internuclear distances in the $(\text{HeHe})^+$ pseudomolecular complex. The oscillatory structure⁷ which we have observed in He^+ -Ne cross sections may be explained by a similar energy-dependent phase-development process that occurs between the near and outer pseudocrossings. Assuming the existence of near and outer pseudocrossings in the $(\text{HeNe})^+$ molecular collision complex, we have analyzed our data in a new way to show the development of phase between the two crossing regions.

Figure 2(b) shows schematically the case of two pseudocrossings. The two inelastic channels, U_1 and U_2 , are populated from the incoming ground-state channel U_0 . At R_0 another transition, which does not involve the ground state, takes place—this time between U_1 and U_2 . The phase difference developed in the interval $R_i < r < R_0$ may be written approximately as

$$\Delta\varphi = \frac{1}{\hbar} \int_{R_i}^{R_0} \left(\frac{P_1^2}{2m} - \frac{P_2^2}{2m} \right) dt, \quad (1)$$

where

$$P_1^2/2m = E(1 - b^2/r^2) - U, \quad (2)$$

with b the impact parameter and E the total energy in the center-of-mass system.

In the interval of interest $b^2/r^2 \ll 1$, and $\Delta U = U_1 - U_2$ is considered to be independent of time. The final expression for the phase can then be

written approximately as

$$\Delta\varphi = (1/\hbar) \Delta U \Delta R / v + \Delta\varphi_0,$$

where $\Delta R = R_0 - R_i$, $v^2 = (2/m)(E - U)$, and $\Delta\varphi_0$ is the initial phase difference. Since the cross section is proportional to $\cos^2(\frac{1}{2}\Delta\varphi)$, it will exhibit maxima whenever the following condition is satisfied:

$$\Delta\varphi = 2\pi n \cong (1/\hbar) \Delta U \Delta R / v + \Delta\varphi_0.$$

Thus, if the measured cross sections are plotted as a function of $1/v$, the peaks should be equally spaced. An integer n may then be assigned to each peak and the intercept of the plot of n vs $1/v$ will give the initial phase difference to an additive integral multiple of 2π . The slope of the line will give the product $\Delta U \Delta R$ which will constitute a check on molecular potential-curve calculations as they become available.

Figure 3 shows the He^+ -Ne collision cross sections plotted versus $1/v$. In each case the peaks in the cross sections are regularly spaced. In the case of the 7032-Å Ne I line, there are eight equally spaced peaks, and a least-squares fit shows an intercept of 0.01 ± 0.06 indicating 0 initial phase difference. The analysis of the initial phase difference assumes that the initial phase corresponds to the phase at infinite velocity. The quantity $\Delta U \Delta R$ is determined to be 1.24×10^{-7} eV cm. If ΔU is assumed to be 1 eV, a reasonable energy difference between excited atomic states, ΔR becomes 25 a.u. which is generally consistent with the internuclear distances found by Rosenthal and Foley in the $(\text{HeHe})^+$ molecular complex.⁶ The two peaks in the 3482-Å Ne II data are analyzed to behave similarly with an intercept of 0.08 ± 0.09 , again indicating an initial phase of 0. $\Delta U \Delta R$ is found to be 0.88

$\times 10^{-7}$ eV cm. The analysis of the He I lines, 3888 and 4713 Å, proceeds similarly. In the 3888-Å case, the lower energy peaks can be matched to a line whose Y intercept is 0.58 ± 0.14 denoting an initial phase of π rather than 0. Evaluating the slope gives a value for $\Delta U \Delta R$ of 0.9 ± 10^{-7} eV cm. Additional high-energy peaks also appear which cannot be incorporated into any scheme at present. The He I 4713-Å cross sections provide an additional complication in that although the peaks are regularly spaced in $1/v$, the locations are not all equally spaced but are separated by integral multiple spacings. The reason for this anomalous behavior is not clear at present. The Y intercept for 4713 Å is 0.82 ± 0.23 corresponding to 0 initial phase difference. Here $\Delta U \Delta R$ is 2.0×10^{-7} eV cm.

The data presented herein give evidence of the existence of both an inner pseudocrossing, where the excited states are populated, and outer pseudocrossings at which the developed phases of the various states are compared and the interference occurs. The fact that structure occurs only in the case of the He^+ -Ne collision and not the Ne^+ -He case, even though outer crossings occur in the potential curves of the $(\text{HeNe})^+$ molecular complex common to both collision processes, can be readily explained on the basis of this picture. The lack of structure as well as the slow gradual rise can be accounted for if no well-defined inner pseudocrossing is assumed to occur between the incoming states ($^2\Pi$ and $^2\Sigma$) and the excited molecular states. Consequently, no well-defined initial phase can be established.

It is hoped that by this study and future studies of these collision processes we will be able to make definite statements as to both the nature and the relative strengths of the Σ - Σ , Π - Π , and

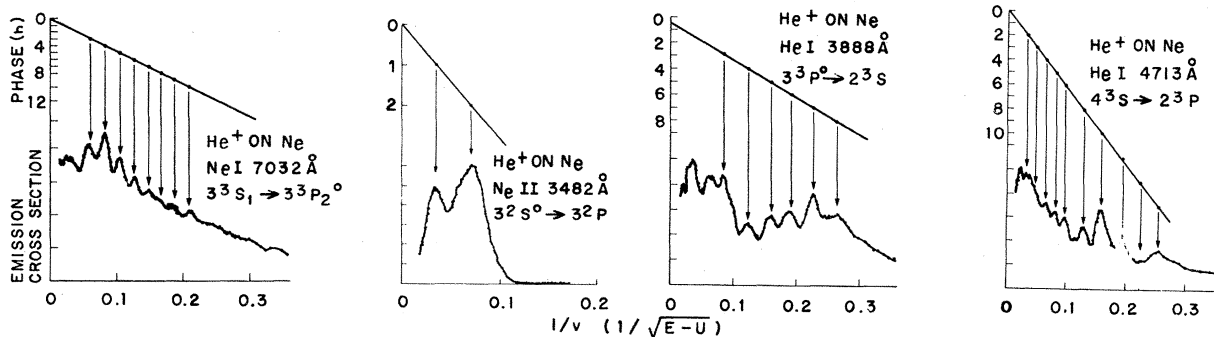


FIG. 3. Relative total-emission cross sections plotted as a function of $1/v$. The v is proportional to $(E-U)^{1/2}$ with E the center-of-mass energy and U the average excited-state energy above the ground state. The straight line at the top of each plot is a linear least-squares fit of the phase integers n versus the locations in $1/v$ of maxima in the cross sections.

Σ -II interactions. Not only have our data provided substantial evidence for the essential correctness of the dual pseudocrossing molecular picture, but we have also provided basic parameters and conclusions about the molecular levels participating in the collision process which constitute important experimental facts for future calculations dealing with collision spectroscopy.

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⁷Structure in He^+ -Ne emission cross sections at higher energies (>300 eV) has also been observed by L. W. Muller and F. J. deHeer (to be published).

Asymptotic Time Behavior of Correlation Functions

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The asymptotic time behavior of the velocity autocorrelation function and of the kinetic parts of the correlation functions for the shear viscosity and the heat conductivity is derived. The results are expressed in terms of the transport coefficients and the specific heats and are valid for all densities.

In a recent publication Alder and Wainwright¹ reported on molecular dynamics calculations of the velocity autocorrelation function for a two- and three-dimensional system of hard spheres. The asymptotic decay was observed to be of the form $t^{-d/2}$ (where d is the dimensionality of the system). They also proposed a hydrodynamical explanation of their observations on the basis of a numerical solution of the Navier-Stokes equations. It is the purpose of this Letter to show that the asymptotic time behavior of such correlation functions can be established precisely in terms of the transport coefficients and equilibrium thermodynamic quantities.

As a typical example consider the normalized velocity autocorrelation function

$$C_D(t) = \langle v_{1x}(0)v_{1x}(t) \rangle / \langle v_{1x}^2(0) \rangle, \quad (1)$$

where $\vec{v}_1(t)$ is the velocity of particle 1 at time t . The average $\langle \rangle$ refers to an equilibrium ensemble and the thermodynamic limit is always taken as the final step. The numerator of (1) can be written as

$$\langle v_{1x}(0)v_{1x}(t) \rangle = \int d^3v_0 v_{0x} \int d^3r_0 \int d^3r \langle v_{1x}(t) \delta(\vec{r}_1(t) - \vec{r}) \delta(\vec{v}_1(0) - \vec{v}_0) P(\vec{r}_1(0) - \vec{r}_0) \rangle, \quad (2)$$

where $P(\vec{r})$ is a function which integrates to unity. The form of $P(\vec{r})$ is in principle arbitrary, and we shall choose it to be slowly varying (on a macroscopic scale). The insertion $\delta(\vec{v}_1(0) - \vec{v}_0) P(\vec{r}_1(0) - \vec{r}_0)$ in the average selects out of the equilibrium ensemble those initial configurations in which the velocity of particle 1 is precisely determined as \vec{v}_0 , while its position is given only by the extended probability