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Quasimolecular States Responsible for Quantum-Mechanical Phase Interference in Low-Energy Na$^+$-Ne Inelastic Collisions

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A simple model is presented which affords an unambiguous and quantitative determination of the quasimolecular states responsible for the striking oscillatory structure in the energy dependence of the polarization components of total cross sections for optical emission due to low-energy Na$^+$-Ne collisions. The $^1\Pi$ ($\Omega = \pm 1$) and $^3\Pi$ ($\Omega = \pm 2$) states are identified as the major participants in the quantum-mechanical phase-interference process and not the simple single-electron diabatic states as believed previously.

Measurements of striking oscillatory structure in the energy dependence of total cross sections for optical emission due to low-energy (100 eV to 6 keV) Na$^+$-Ne collisions have been reported previously[1,2] and explained in terms of interfering diabatic molecular-orbital states.[1,2] In this Comment we propose an alternative model which uniquely relates the final Ne($3p$) and Na($3p$) atomic excited states to the specific (NeNa)$^+$ quasimolecular states participating in the quantum-mechanical phase-interference phenomena. Conclusions based on the model do not support the previous interpretations.[1,2]

The optical radiation observed in these experiments arises from the excitation of Ne I and Na I into $3p$ electronic states as a result of direct and charge-exchange collision processes,[3]

$$\mathrm{Na}^+ + \mathrm{Ne} \to \begin{cases} \mathrm{Na}^+ + \mathrm{Ne}^*(3p), \\ \mathrm{Na}^*(3p) + \mathrm{Ne}^+. \end{cases} \tag{1}$$

We have extended the measurements to include the energy dependence of both the perpendicular and the parallel components of the absolute emission cross sections arising from ten Ne I $3s$-$3p$ and two Na I $3s$-$3p$ optical transitions. Examples of the data are given in Fig. 1. In some instances very strong polarization was observed, e.g., Fig. 1(b). Analysis of the results has led to the development of a collision model which accounts quantitatively for the amplitudes of the oscillations in each polarization component of the emission cross sections.

The essential elements of the model are contained in the following three hypotheses:

(1) Oscillations in the energy dependence of the cross sections result from interference between one or more pairs of excited levels which are populated coherently at small internuclear separation ($R \sim R_I$) and then interact at large separation ($R \sim R_0$) as schematically represented in Fig. 2. This dual-coupling mechanism first proposed by Rosenthal and Foley[4] has been estab-

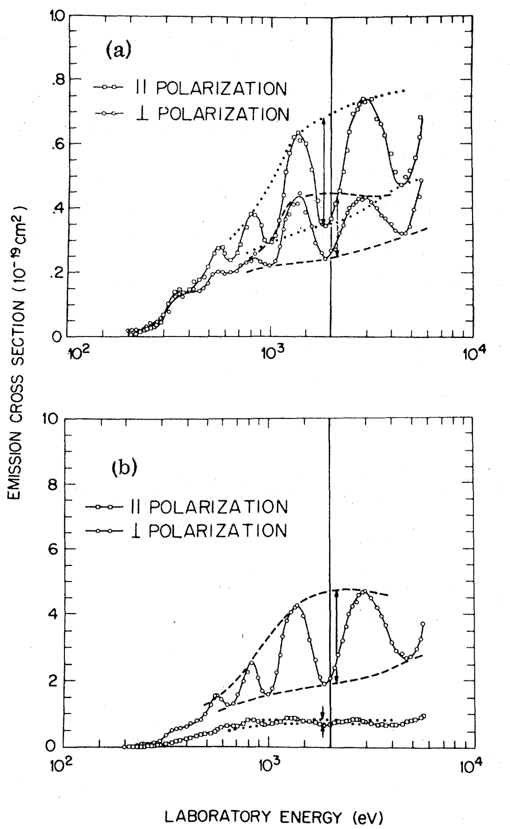

FIG. 1. Absolute emission cross sections, plotted as a function of bombarding energy, for the perpendicular and parallel components of optical radiation emitted at 90° from the beam direction for the (a) Ne $2p_2$ 6030-Å, and (b) Ne $2p_5$ 6266-Å optical lines. These plots show the intensity amplitudes ΔI (dotted and dashed lines define the parallel and perpendicular oscillation amplitudes, respectively) of the regular oscillatory structure. The structure in the cross sections is reproducible to better than 5%, the relative magnitude between each of the two polarization components are uncertain to 15%, and the absolute magnitudes of the total emission cross sections are uncertain to 50%.

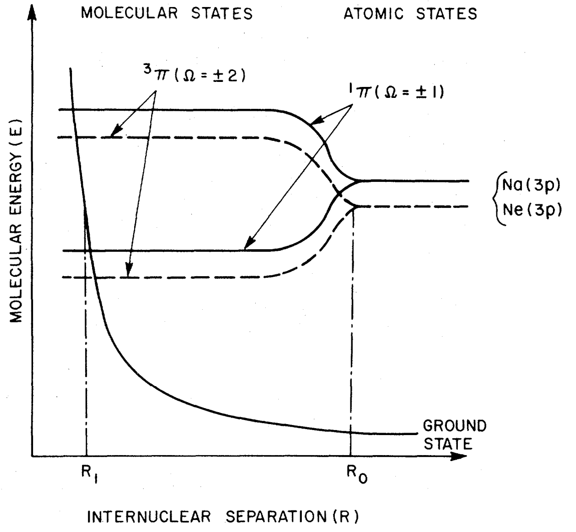

FIG. 2. Schematic illustration of two pairs of coherently excited levels which contribute to the observed quantum-mechanical phase interference.

lished in several related collision processes.[5]

(2) Nonadiabatic interaction at large internuclear separation arises from "quasi-resonant charge exchange" of the type described by Lichten.[6] This is consistent with the observation that oscillations in the Na* radiation are 180° out of phase with those in the Ne* radiation.[1-3]

(3) The distribution of final atomic level populations is a direct reflection of the composition of the precursor molecular electronic states. To state this hypothesis in a quantitative manner, we express the adiabatic electronic wave functions Φ_k of the (NaNe)$^+$ quasimolecule at large internuclear separations $R \gg R_I$ as linear combinations of atomic states:

$$\Phi_k \simeq c_k \sum_{i=1}^{6}\sum_{j=1}^{6} a_{ijk}\xi_i\varphi_j^{\,+} + (1-c_k^{\,2})^{1/2}\sum_{i=1}^{36} b_{ik}\xi_0^{\,+}\varphi_i\,, \tag{2}$$

where $k=1,2,\ldots,72$, and ξ_i, $\xi_0^{\,+}$, φ_i, and $\varphi_j^{\,+}$ are wave functions of atomic states Na($3p$), Na$^+$(^1S), Ne($3p$), and Ne$^+$($^2P_{1/2}$,$^2P_{3/2}$), respectively. The coefficients a_{ijk} and b_{ik} are elements of a unitary transformation relating the spin- and orbital-angular-momentum coupling scheme of the molecular states to that of the isolated atom states. The coefficients c_k describe the relative mixing of the Na$^+$-Ne* and Na*-Ne$^+$ configurations in Φ_k. The rapid variation of c_k with internuclear separation in the outer coupling region, $R \sim R_0$, is responsible for the quasi-resonant charge-exchange mechanism, hypothesis 2.

Hypothesis 3 may now be stated as follows: (a) The relative populations of excited atomic Ne*($3p$) levels arising from a particular (NeNa)$^+$ molecular state Φ_k are proportional to the intermediate-internuclear-separation ($R_I \ll R < R_0$) values of $|b_{ik}|^2$ of Eq. (2), and (b) the relative populations of excited Na*($3p$) are proportional to $\sum_j |a_{ijk}|^2$.

Hypothesis 3, if correct, provides a method for completely characterizing the participating quasimolecular states at intermediate internuclear separations. A molecular state of any given character (i.e., symmetry and angular momentum coupling) will populate a characteristic pattern of final atomic states, determined by the values of a_{ijk} and b_{ik} which can be readily computed.[7] Similarly, it will produce characteristic polarizations. Since we are dealing with predominantly small-angle scattering, at large internuclear separations in the vicinity of the outer coupling region the molecular axis nearly coincides with the laboratory z direction, i.e., the incident beam direction. Therefore by hypothesis 3, the laboratory m_j value of the final atomic state, which governs the polarization of emitted light, is equal to the Ω value of the molecular state from which it was formed.

In the present case, the analysis is complicated by the fact the Ne*(3p) levels are not pure L-S coupling states. Fortunately, the coupling of these levels has been analyzed by Schectman *et al.*[8] By using their results in our angular-momentum-coupling calculations, we have obtained quantitative predictions of the intensities and polarizations of each observed Ne* 3s-3p optical transition that would arise from all 36 molecular (NaNe)$^+$ states correlating with Na$^+$-Ne*(3p). In Table I we compare the measured intensities of the oscillatory parts of the perpendicular and parallel optical polarization components with those predicted to arise from two independent pairs of interfering molecular states, $^1\Pi(\Omega = \pm 1)$ and $^3\Pi(\Omega = \pm 2)$.[9] With the possible exception of the 2p_8 state, agreement is excellent. No other combination of states can satisfactorily reproduce the observed data. Note that the fact that there is no contribution from the $^3\Pi(\Omega = 1)$ state is evidence that at intermediate separations $^1\Pi(\Omega = 1)$ is a pure spin state.

A similar analysis can be applied to explain the nonoscillatory part of the emission cross sections. In the present case it is apparent that a great many (possibly all) of the 36 pairs of excited states make contributions to the incoherent radiation, and no definitive selection of the major contributor can be made.

The $^1\Pi$ and $^3\Pi$ (NaNe)$^+$ states can be constructed either from a $^2\Pi$ core and $^2\sigma$ outer electron or from a $^2\Sigma$ core and $^2\pi$ outer electron. We can distinguish between these alternatives by examining the polarization of the Na* $3p\,^2P_{3/2} - 3s\,^2S_{1/2}$ emission cross sections. In this analysis, we assume that the symmetry of the Na* excited state is determined solely by the outer electron; the distant Ne$^+$ has no effect. With this assumption and hypothesis 3, we predict that the ratio of the parallel and perpendicular polarization components will be either 1.47 or 0.81 depending on whether the outer electron is $^2\sigma$ or $^2\pi$. In contrast, the experimentally observed polarization ratio for the oscillatory part of the radiation from the Na $^2P_{3/2}$ state is 1.00 ± 0.05. We conclude that neither of the molecular-orbital diabatic-state schemes are present in pure form.[10] The $^2\Sigma^+$ core and $^2\pi$ electron and the $^2\Pi$ core and $^2\sigma$ electron configurations mix heavily to form the $^1\Pi$ and $^3\Pi$ molecular states responsible for the oscillations. Consequently, the diabatic (molecular-orbital) picture is not adequate to explain the observed oscillatory structure in the Na(3p) and Ne(3p) emission cross sections in contradiction to the conclusions reached earlier by the present authors[1] and most recently by Andersen, Nielsen, and Olsen.[2]

TABLE I. Experimentally and theoretically derived oscillation intensity amplitudes ΔI.

Atomic state[a]	Polarization	Expt. ΔI (10^{-19} cm^2)[b]	Theory ΔI
2p_1	⊥	0	0
	∥	0	0
2p_2	⊥	2.05	2.21
	∥	4.10	4.42
2p_3	⊥	0	0
	∥	0	0
2p_4	⊥	5.02	4.98
	∥	4.19	3.90
2p_5	⊥	6.22	6.50
	∥	<0.33	0
2p_6	⊥	6.49	6.47
	∥	5.94	5.61
2p_7	⊥	1.33	0.98
	∥	2.24	1.95
2p_8	⊥	2.10	1.60
	∥	1.84	2.52
2p_9	⊥	0.40	0.54
	∥	0.40	0.54
2p_{10}	⊥	0.17	0.09
	∥	0.17	0.08

[a] Expressed in Paschen notation [C. E. Moore, *Atomic Energy Levels,* U. S. National Bureau of Standards Circular No. 467 (U. S. GPO, Washington, D. C., 1949), Vol. 1, p. 76].

[b] Experimental values have been adjusted by use of branching ratios to reflect population cross section rather than emission cross section values.

In summary, using plausible hypotheses we have been able to account quantitatively for the amplitudes and polarization of the oscillatory structure in the emission cross sections resulting from excitation of a $3p$ electron in low-energy Na^+-Ne collisions. As shown in Fig. 2, we have attributed the oscillatory structure to interference of two major pairs of states ($^1\Pi$ and $^3\Pi$) involving eight out of the 72 possible excited molecular states. The quantitative agreement and the simplicity of the picture are strong evidence that our hypotheses are basically correct. This analysis constitutes a new direction in collision spectroscopy, and can provide important information about the detailed mechanisms of low-energy ion-atom collisions.

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[10] If the $^1\Pi$ ($\Omega = \pm 1$) state were constructed from a Σ core and π outer electron, and the $^3\Pi$ ($\Omega = \pm 2$) from a Π core and σ outer electron, then the ratios of Ref. 9 would result in a prediction of $I_\parallel / I_\perp = 0.93$. This does not differ greatly from the observed ratio of 1.0, and must be considered a possibility.

Ringing-Down of the "Wall-Pinned" Mode in ^{3}He-B as a Test of Theories of Spin Relaxation

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The decay in time of the frequency of the so-called "wall-pinned" mode in the nuclear resonance of ^{3}He-B is shown to provide a test of a previously developed theory of spin relaxation and to give a numerical value of a previously unknown parameter of the normal phase.

In a recent Letter,[1] the author and Takagi gave a theory of the damping of the nuclear spin motion in the superfluid A and B phases of liquid ^{3}He, in which the physical mechanism of the damping was assumed to be the conversion, by spin-conserving collisions, of "surplus" Cooper pairs into normal component. The relaxation time for this process, which I will refer to as τ_{LT} or simply τ, was assumed to be only slowly varying with temperature near the transition temperature T_c and to be of the order of the normal-state relaxation time. The predictions of Ref. 1 agree with those of the earlier kinetic-equation approach to the cw resonance problem by Combescot and Ebisawa[2] only if the (different) relaxation time introduced by these authors, τ_{CE}, is *not* of the order of the normal-state relaxation time[2] near T_c but rather diverges[3,4] as $(T_c - T)^{-1/2}$. Very recently, Bhattacharyya, Pethick, and Smith[5] have given an explicit solution of the kinetic equation in the limit $T \to T_c$ and shown that τ_{CE} does indeed diverge in this way: Moreover, they have shown that in this limit τ_{LT} is independent of the phase and numerically equal to $\tau(0)$, the relaxation time of a single quasiparticle at the Fermi surface in the normal phase at T_c. A measurement of the temperature dependence of the NMR relaxation in the superfluid phases would