by

$$\alpha(J, M) = \alpha_{sc}(J) + \alpha_t(J)\frac{3M^2 - J(J+1)}{J(2J-1)}, \qquad (2)$$

and the total energy shift in an electric field is

$$W(J, M) = -\tfrac{1}{2}\alpha(J, M)E^2. \qquad (3)$$

The matrix element of z in Eq. (1) can be deduced easily from the oscillator strength of the transitions from 2^3P to 2^3S. The expectation value of the spin-spin interaction can be calculated from the known fine-structure splitting of the 2^3P state, since the spin-orbit and spin-spin contributions have different angular properties. Using this approach, one finds $\alpha_t(^3S) = 3.4\times10^{-3}a_0^3$. Our measurement gives $\alpha_t = (3.41 \pm 0.11)\times10^{-3}a_0^3$. In view of the approximations made in the calculation, this exact agreement is most gratifying.

Work is presently underway in this laboratory to measure the shifts in the metastable states of the other rare gases.

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PHASE-INTERFERENCE EFFECTS IN INELASTIC He^+ + He COLLISIONS*

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In the collision $He^+ + He \rightarrow He^+ + He^*$, excitation at low incident ion energies ($\lesssim$1 keV) proceeds via a pseudocrossing of the elastic $^2\Sigma_g$ diabatic potential with excited-state $^2\Sigma_g$ potentials. In addition, pseudocrossings of inelastic potentials at large internuclear separations mix the amplitudes of the excited-state channels coherently. This many-state mechanism provides qualitative understanding of diverse experimental observations.

In low-energy atom-atom collisions, knowledge of the potential curves of the intermediate molecular system often leads to a qualitative and even semiquantitative understanding of capture and excitation cross sections. Our work indicates that for inelastic processes, such as $He^+ + He \rightarrow He^+ + He^*$, the various inelastic cross sections can only be explained when the potential curves of the corresponding channels are known to rather large internuclear separations. In particular, pseudocrossings among the inelastic adiabatic potential curves occur at large internuclear separations ($\gtrsim$15 a.u.), and such crossings can give rise to coherent mixing of the inelastic probability amplitudes involved.

The excitation of helium atoms by low-energy (50- to 2000-eV, lab) helium ions has been observed and reported,[1] and new data are being reported in the accompanying Letter by Dworetsky and Novick, hereafter referred to as DN. The total inelastic cross sections typically show a sharp threshold lying about 8 eV (c.m.) above the Q value of the reaction. For channels involving excited helium-atom S states, the cross sections exhibit a highly oscillatory energy dependence, but for other channels they are smoother, or even featureless (Fig. 1). The cross sections of the 3^3S and 3^1S states seem to be anticoincident for intermediate energies. When the cross sections are plotted versus v^{-1}, the inverse ion velocity, the peaks are roughly equally spaced. In addition, they show the same features when different helium isotopes are employed for the ion and/or target. When the energy variable is

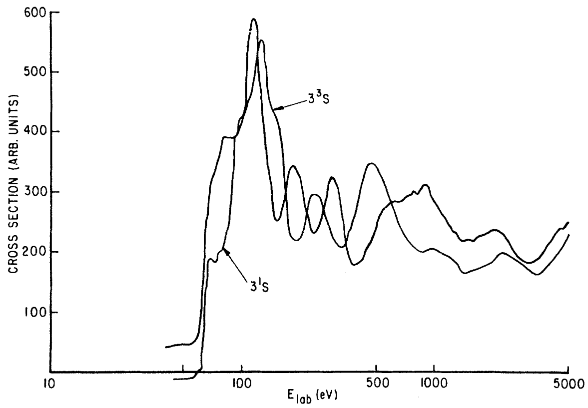

FIG. 1. Excitation functions for the 3^3S and 3^1S helium states.

scaled according to

$$E_{1ab}(M_1 \text{ on } M_2) = \tfrac{1}{4}M_1E_{1ab}(4 \text{ on } 4)+M_1[M_1M_2/(M_1+M_2)-\tfrac{1}{2}]\Delta U \qquad (1)$$

with $\Delta U = 20\text{-}30$ eV, then the experimental data for the various isotope-pairs coincide. (See DN, Fig. 3 and discussion.)

In the system $He^+ + He$, the primary mechanism of populating inelastic states at low ion energies is provided by a pseudocrossing of the $^2\Sigma_g$ potentials of He_2^+ by the elastic, i.e., ground-state, $^2\Sigma_g$ potential. Lichten[2] explains that the $^2\Sigma_g$ ground state can be diabatically represented by $\sigma_g(\sigma_u)^2$, which becomes a state with two excited electrons, Be^+ $1s(2p)^2$, in the united atom limit, while the $^2\Sigma_g$ inelastic states in this limit are only singly excited Be^+. Hence the elastic potential diabatically crosses all inelastic potentials. The $^2\Sigma_u$ elastic potential, on the other hand, shows no such crossings, since this state, $\sigma_u(\sigma_g)^2$, becomes the lowest odd Be^+ state, $(1s)^2 2p$, in the atomic limit. Our calculations agree with those of Michels[3] in claiming that the crossings occur at internuclear separations of 1.2-1.4 a.u. and at energies of 28-33 eV–i.e., a few eV above the excitation energies of He. Landau, Zener, Stueckelberg, and others[4] have shown that at low energies transitions occur only in the region of the crossing. Hence the observation of nonadiabatic processes at low incident ion energies as well as the observed value of the threshold energy are explained by the pseudocrossing of the $^2\Sigma_g$ elastic and inelastic potentials.

It is tempting to try to explain the oscillatory behavior of the cross sections as arising from a phase-interference effect at the crossing of the elastic and inelastic potentials. In a time-dependent formulation, the crossing region is traversed twice: on the way in and on the way out. After the first passage, both elastic and inelastic amplitudes are nonzero and develop a phase difference before being coherently mixed at the second passage through the crossing. The final probability of having made a transition to the inelastic channel is given approximately by the Landau-Zener-Stueckelberg[4] formula

$$P = 4e^{-v_0/v_r}(1-e^{-v_0/v_r})\cos^2(\tfrac{1}{4}+\varphi), \qquad (2)$$

where v_r is the radial velocity at the crossing, and v_0 a characteristic of the crossing,

$$\approx 2\pi\epsilon^2/\hbar \frac{d}{dR}|U_1(R)-U_2(R)|,$$

where the minimum separation of the two curves is 2ϵ. The phase is given approximately by

$$\varphi \approx \int_{r_1}^{R} k_1(r)dr - \int_{r_2}^{R} k_2(r)dr, \qquad (3)$$

where

$$k_i(r) = \left\{\frac{2m}{\hbar^2}\left[E\left(1-\frac{b^2}{r^2}\right)-U_i(r)\right]\right\}^{1/2}, \quad k_i(r_i)=0.$$

The phase φ is a function of the incident energy E and the impact parameter b, or, alternatively, of incident energy and scattering angle. At a given incident energy the probability of excitation $P(b,E)$ should be an oscillatory function of impact parameter up to the maximum impact parameter (at which $v_r = 0$) [Fig. 2(b)]. The interference would thus lead to oscillatory behavior in the differential inelastic cross section. The energy dependence of $\int P(b,E)b\,db$ is not clear offhand, and must be calculated numerically. One finds that this function of E is smooth. Hence, the oscillatory behavior of $P(b,E)$ does not give rise to any marked oscillations in the total inelastic cross section [Fig. 2(c)]. This conclusion is rather independent of the characteristics of the potential curves and is not altered when improved Landau-Zener formulas or numerical solutions are applied to the two-state curve-crossing problem.

In the two-state model, interactions between the inelastic channels are ignored and the amplitude of each inelastic channel is assumed to develop adiabatically after the double passage through the crossing region. The failure of the two-state model to explain the oscillatory features of the cross section leads one to examine the possibility of nonadiabatic behavior. In particular, if there existed a pseudocrossing of two

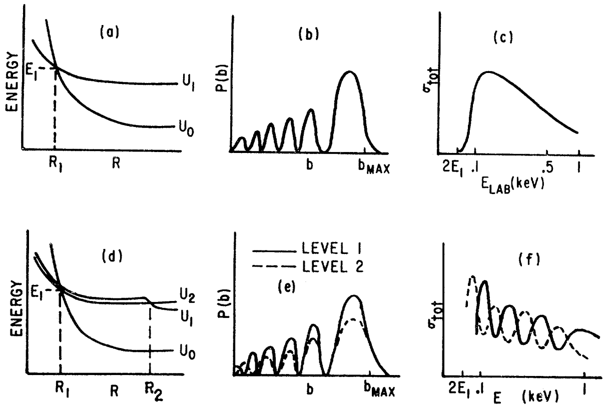

FIG. 2. Diagramatic comparison of the single-crossing region and the two-crossing region models: (a) Two-level crossing scheme. (b) Excitation probability at fixed (typical) energy as a function of impact parameter. (c) Total excitation probability as a function of incident energy. (d) Three-level, two-crossings scheme. (e) The two excitation probabilities at fixed (typical) energy as a function of impact parameter. Note that the levels are sufficiently close that they leave the inner crossing region essentially in phase at most impact parameters. (f) The two total excitation probabilities as a function of incident energy.

inelastic channels at internuclear separation R_2 [Fig. 2(d)] such that the two amplitudes were efficiently mixed, a coherent interference would result in the final populations. The critical phase would be the phase difference between the two inelastic amplitudes at R_2 and would thus be approximately proportional to the time it takes the system to separate from its minimum separation to R_2. This time is essentially independent of impact parameter so that the effect would be observed in the total cross section [Fig. 2(f)]. Moreover, the conservation of probability would predict that the final populations of the two inelastic channels be anticoincident. It becomes clear that a knowledge of the $^2\Sigma_g$ potentials of He_2^+ is essential.

In our calculations 19 LCAO trial functions (linear combinations of atomic orbitals) were constructed, each of which seemed physically reasonable, i.e., had $^2\Sigma_g$ characteristics and at large separations could be interpreted as ion + singlet atom or ion + triplet atom: ground state,

$$\Psi = \hat{G}\,\| |A\alpha Z\rangle |A\beta Z\rangle |B\alpha 2\rangle \|;$$

excited $^2\Sigma_g$ "singlet type,"

$$\Psi = \hat{G}\,\|(|A\alpha i\rangle |A\beta 2\rangle - |A\beta i\rangle |A\alpha 2\rangle) |B\alpha 2\rangle\|;$$

excited $^2\Sigma_g$ "triplet type,"

$$\Psi = \hat{G}\{2\,\| |A\alpha i\rangle |A\alpha 2\rangle |B\beta 2\rangle \| - \|(|A\alpha i\rangle |A\beta 2\rangle + |A\beta i\rangle |A\alpha 2\rangle) |B\alpha 2\rangle\|\};$$

where $\hat{G}$ is the gerade operator, $\|\ \|$ denotes a determinant, and $|Csi\rangle$ is an atomic orbital centered about nucleus C (A or B), with spin component s (α or β) along the internuclear axis, and with quantum numbers and effective-charge parameter denoted by i. In particular, $|A\alpha Z\rangle$ and $|A\alpha 2\rangle$ denote 1s orbitals about nucleus A with $Z_{\rm eff} = Z$ and 2.0, respectively. As a check on the sufficiency of the basis set, the one-electron problem, H_2^+, was solved in this approximation, using $\Psi_i = \hat{G}|A\alpha i\rangle$ as trial function. In both cases the basis was orthonormalized and the electronic Hamiltonian matrix obtained was diagonalized.

Figure 3 shows the results of the calculation for He_2^+. Pseudocrossings are, in fact, evident among various inelastic channels at large internuclear separations (12-40 a.u.). By noting that the features remained when the orbital parameters of the basis were varied, it was shown that these pseudocrossings are not spurious effects due to any insufficiency in the basis set. Moreover, the simpler (one-electron) system H_2^+ is expected to have potential curves similar to He_2^+ at these internuclear separations. Our calculations, as well as the exact solutions of Bates and Reid,[5] show that H_2^+ indeed exhibits the same crossing scheme at large R. It can be shown that according to the Landau-Zener criterion only the crossings labeled 1 and 2 of those shown efficiently mix the inelastic amplitudes at typical

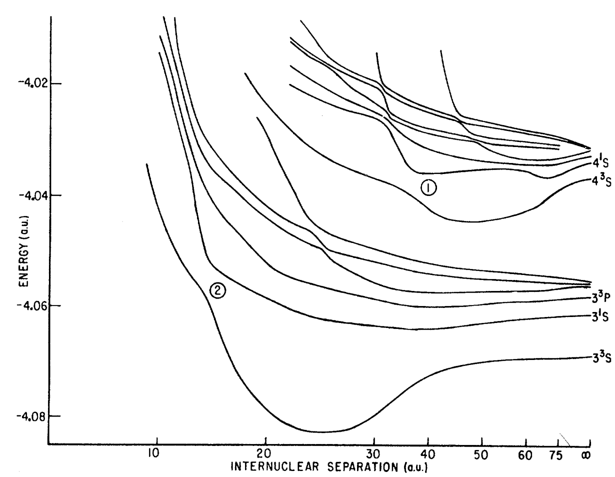

FIG. 3. $n = 3$ and 4 $^2\Sigma_g$ potentials of He_2^+ at large internuclear separations.

energies; i.e., the crossings are such that oscillatory effects can be expected in the $n = 3$ and $n = 4$ ^3S and ^1S populations. The other crossings are diabatic—the opposite of adiabatic but having the same effect, namely, no mixing of amplitudes, and hence smooth cross sections.

The outer pseudocrossings thus seem to explain qualitatively which helium levels exhibit oscillatory energy dependence in the total cross section and which levels do not. In particular the potentials arising from the $n = 2$ He levels exhibit no pseudocrossings which can effectively mix inelastic amplitudes, and thus theoretically the cross sections are determined by the inner cros crossing only. The observation (DN, Fig. 1) of nonoscillatory 2^1P and 2^3P cross sections is in agreement with this prediction. The conservation of probabilities leads one to expect anticoincident cross sections for two states whose potentials cross, and the 3^3S and 3^1S data exhibit such anticoincidence.

The phase difference at R_2 seems also to be of just the right magnitude to explain qualitatively the spacing of the oscillations in the $n = 3$ S states. The separation of the two diabatic inelastic channels, about 0.04 a.u., would lead to a phase 4π at laboratory energies of about 500 eV, and higher phases at lower energies. The spacing of the peaks and dips in the 3^3S and 3^1S experimental cross sections is consistent with an interpretation of the 450-eV 3^3S peak as due to a phase difference of 4π.

Both the spacing of the peaks and the isotope-pair energy scaling law now depend on the relative velocity in the excited rather than elastic channel. In the isotope data, identical features in two isotope pairs are expected when the relative velocities are the same, and the linear scaling law (1) with $\Delta U \simeq 24$ eV merely reflects the fact that the potentials involved lie 20-25 eV above the elastic channel at and around the outer crossings. (See DN, Fig. 3.) It is not clear how the inner-crossing two-state model, with its strong b dependence and assuming no outer crossing, could lead to such a simple linear scaling law.

One concludes that knowledge of the potential curves of He_2^+ to large internuclear separations is essential for an understanding of the mechanism responsible for inelastic processes in low-energy collisions of He^+ with He. To a surprising degree such knowledge is even sufficient for a qualitative understanding of the main features of the cross sections. It seems reasonable to suspect that the same can be said of other low-energy inelastic collision processes.

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