New Oscillatory Structure in Electron Energy Spectra from Autoionizing Quasimolecules: Subthermal Collisions of $He(2^3S)$ Atoms with $He(2^1S,2^3S)$ Atoms

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We report the first study of the energy spectra of electrons from autoionizing quasimolecules formed at very low collision energies ($\bar{E}_{rel}=1.6$ meV). The electron spectra due to ionizing $He(2^3S)$-$He(2^3S)$ and $He(2^1S)$-$He(2^3S)$ collisions in a single atomic beam show significant structure, which is explained on the basis of accurate new *ab initio* potentials for the relevant excited states. Fast oscillations due to the interference of incoming and outgoing waves of the heavy-particle motion are observed in both the experimental $He(2^3S)$-$He(2^3S)$ spectrum and the corresponding quantum mechanical calculations.

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Airy-type interference structure associated with two coalescent points of stationary phase is a well-known phenomenon.[1-10] In atomic collision physics, we mention as three examples the presence of rainbows in differential scattering cross sections[5]; the observation of satellites in the far-wing line broadening of spectral lines[6]; and the now well-documented[3,4,7-10] Airy-type peak structure in the energy distribution of electrons ejected from autoionizing quasimolecules, for which the distance-dependent difference potential $V^*(R)-V^+(R)$ exhibits a clear extremum at a particular distance R_M. For electron energies E around $E_M=V^*(R_M)-V^+(R_M)$ and an average over a sufficiently large number of partial waves of the heavy-particle motion, the electron energy spectrum is well described by the square of an Airy function[3,4,7] because of the contributions from the two points of stationary phase (i.e., equal electron energy E) around the coalescence point $E=E_M$. For a single partial wave (or a narrow band of angular momenta) one expects,[3] superimposed on the Airy-type peak structure, higher-frequency oscillations. These are associated with the interference of incoming and outgoing heavy-particle waves and reflect rapid variations of the transition-matrix element with electron energy. To our knowledge, these fast oscillations have not been observed experimentally to date. We mention that similar rapid oscillations superimposed on Airy-type structure have been discussed for spectra of optical bound-free transitions; see, e.g., Mies and Julienne.[11] We also note that incoming-outgoing interference structure has been reported for quasimolecular x-ray spectra emitted in impact-parameter–selected collisions of 10-MeV Cl^{16+} with Ar.[12]

Quantum mechanical calculations of the electron spectrum for model systems with a clear minimum in the difference potential show[13] that the modulation depth of the fast oscillations is close to 100% for systems with opacities $O\ll 1$, but may be small for systems with $O\rightarrow 1$. In any case, the number of contributing partial waves has to be sufficiently small to prevent the oscillations from being smeared out.[13]

We have recently started a series of experiments aimed at the investigation of autoionizing quasimolecules at very low collision energies and a correspondingly restricted range of orbital angular momenta. The idea is to use a single atomic beam containing two different species A^* and B with similar velocity distributions of rather narrow range and to detect electrons due to ionizing collisions of A^* and B from a certain reaction volume with high efficiency and sufficient electron energy resolution. In this paper, we report electron spectra $P(E)$ for the two reactions

$$He(2^3S)+He(2^3S)\xrightarrow{k_1}He+He^++e^-, \quad (1)$$

$$He(2^1S)+He(2^3S)\xrightarrow{k_2}He+He^++e^-, \quad (2)$$

which have large rate constants ($k_1\approx 2\times 10^{-9}$ cm^3/s,[14,15] $k_2/k_1\approx 2.5$,[15] at $T=300$ K) and are important in helium discharges. We have measured $P(E)$ for reactions (1) and (2), both with crossed $He(2^1S,2^3S)$ beams and with a single mixed $He(2^1S,2^3S)$ beam. Here, we concentrate on the latter results which are of particular interest because the average collision energy is very low ($\bar{E}_{rel}=1.6$ meV) and the number of contributing partial waves is correspondingly small (e.g., $J_{max}=17$ for $E_{rel}=1.6$ meV). The results obtained with crossed beams ($\bar{E}_{rel}=63$ meV) and a comparison with previous attempts[15,16] to measure $P(E)$ for reactions (1) and (2) will be given elsewhere.[13]

In our experiment, we energy analyze electrons due to ionizing collisions occurring within a single, well-

collimated (1:80), mixed metastable $He(2^1S,2^3S)$ beam. The atomic beam originates from a differentially pumped discharge source and contains $He(2^1S)$ and $He(2^3S)$ atoms in a ratio of about 1:9. The average metastable velocity $\bar{v}_{He}$ is 1750 m/s and the velocity width $\Delta v/\bar{v}_{He}$ around 31%.[10] The $He(2^3S)$ density in the reaction region is about 4×10^7 cm^{-3}. The atomic beam does not contain any *fast* He atoms which could produce signals in the electron energy range of interest.[4]

For the comparison of measured electron spectra with calculated cross sections, we have derived from the known velocity flux distribution of the metastable atoms an effective distribution of relative collision energies $f(E_{rel})$ such that the electron energy distribution $P(E)$, averaged over collision energy E_{rel}, is given by

$$P(E)=\int P(E;E_{rel})f(E_{rel})dE_{rel}.$$

The distribution $f(E_{rel})$ peaks at $E_{rel}=0$ and decreases monotonically with rising E_{rel}. The average collision energy amounts to $\bar{E}_{rel}=1.6$ meV.

For the energy analysis of the electrons we use a cylindrical mirror spectrometer with 2π acceptance at the magic angle (54.7°) with respect to its axis, which is normal to the direction of the metastable atom beam. A constant pass energy of 12 eV with a resolution of 60 meV (FWHM) was used. The dependence of the spectrometer transmission on the electron energy is negligible in the range of interest; with the transmission optimized for electron energies around 15 eV the overall detection efficiency is close to 1%. The energy scale is calibrated accurately (±4 meV) by comparison with the well-known spectra for $He(2^1S,2^3S)+Xe$,[17] simultaneously measured by use of a weak, effusive xenon target beam. The Xe spectra were also used to determine the relative flux of $He(2^1S)$ and $He(2^3S)$ atoms, as explained elsewhere in detail.[10]

Figure 1 shows the spectrum of detected electrons in the range 17.9–13.3 eV, as accumulated over 270 h (1700 s/channel, channel width 8 meV). Above the background intensity (dashed line), which is (according to tests with different residual pressures) mainly due to electrons ejected from surfaces upon impact of scattered metastables, one clearly observes structured spectra for reactions (1) and (2) which cover the ranges 15.2–14.2 and 16.1–15.1 eV, respectively; a weak intensity due to $He(2^1S)$-$He(2^1S)$ ionizing collisions (range 16.8–16.1 eV) is also visible. One observes that for both (1) and (2) associative ionization (i.e., formation of stable He_2^+ ions), which corresponds to electron energies $E\geq E_0+E_{rel}$, is a minor channel. From the spectral areas for process (1) and (2) and the known $He(2^3S)$, $He(2^1S)$ composition of the metastable beam, we obtain for the ratio of the respective ionization cross sections $q_1/q_2\approx0.4$; this result is mainly due to the fact that the $He(2^3S)+He(2^3S)$ $^5\Sigma_g^+$ quasimolecule cannot autoionize (see below).

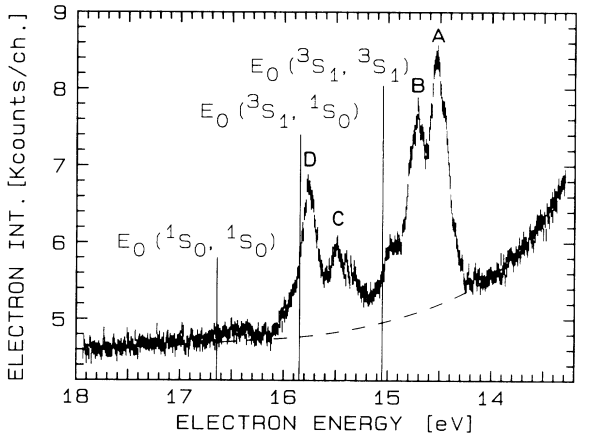

FIG. 1. Energy spectrum of electrons due to ionizing collisions between pairs of metastable $He(2^1S,2^3S)$ atoms within a single atomic beam ($\bar{E}_{rel}=1.6$ meV). The vertical lines indicate the nominal electron energies E_0, given by the sum of the two excitation energies minus the ionization energy of ground-state He atoms.

The interpretation of the electron spectra is rather involved because several excited-state potentials and two ionic potentials play a role. The latter are accurately known,[18] and real parts $V^*(R)$ of the local complex potential $V_c(R)=V^*(R)-\frac{1}{2}i\Gamma(R)$ for the three symmetries ($^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_g^+$) of the $He(2^3S)+He(2^3S)$ system, calculated with an *ab initio* method, have been reported by Garrison, Miller, and Schaefer[19] together with an estimated (average) autoionization width

$$\Gamma(R)=\Gamma_0\exp[-0.921R/a_0] \quad (3)$$

with $\Gamma_0=0.3$ a.u. $=8.163$ eV.

Autoionization is spin forbidden for the $^5\Sigma_g^+$ entrance channel and can be neglected, as proved by Hill *et al.*[20] Therefore, four autoionization amplitudes contribute to reaction (1):

$$1\,^3\Sigma_u^+\rightarrow{}^2\Sigma_u^++e^-, \quad (4a)$$

$$1\,^3\Sigma_u^+\rightarrow{}^2\Sigma_g^++e^-, \quad (4b)$$

$$1\,^1\Sigma_g^+\rightarrow{}^2\Sigma_u^++e^-, \quad (4c)$$

$$1\,^1\Sigma_g^+\rightarrow{}^2\Sigma_g^++e^-. \quad (4d)$$

Reaction (2) has two entrance channels with $^3\Sigma_g^+$ and $^3\Sigma_u^+$ symmetry; again, four ionization amplitudes are expected to contribute, but so far no detailed information is available on the entrance channels or widths.

With use of advanced *ab initio* methods to calculate the real part of molecular resonance states,[21] we obtain a set of reliable potential curves for $He(2^1S,2^3S)+He(2^3S)$, including effects due to the rather close-lying higher states such as those correlating to $He(2^3P)+He(2^3S)$. These potentials $V^*(R)$ are shown in Fig. 2 together with the ionic potentials.[18] For $He(2^3S)$

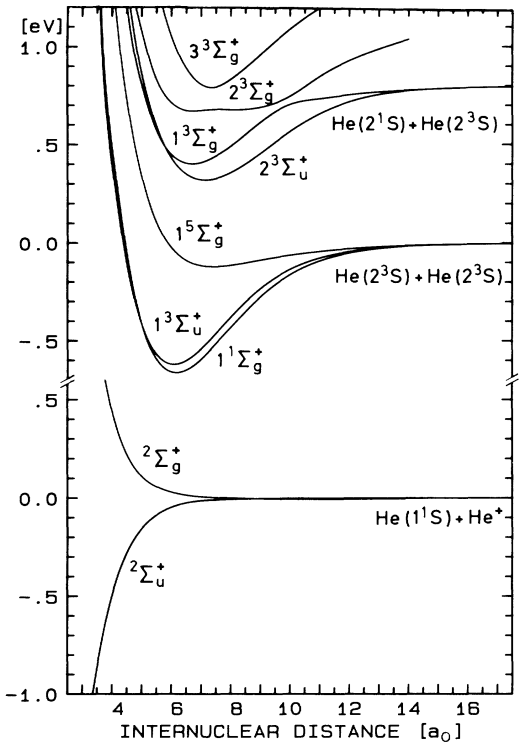

FIG. 2. Potential energy curves relevant for collisions of $He(2^1S,2^3S)$ atoms with $He(2^3S)$ atoms; see text.

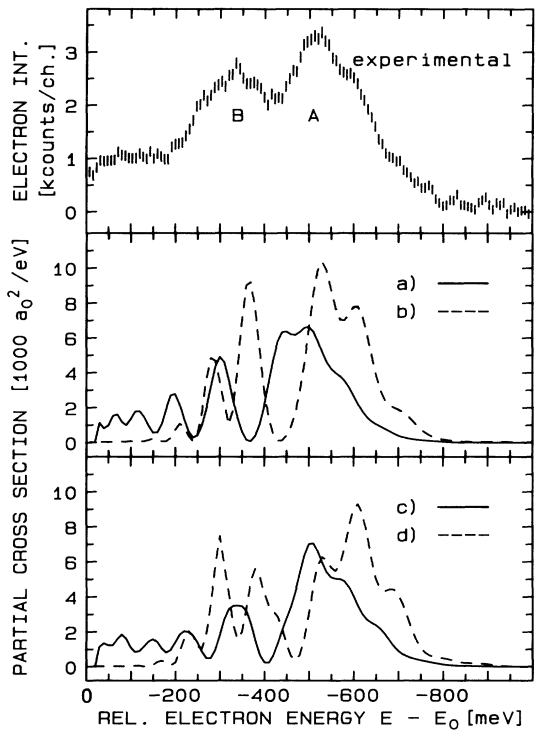

FIG. 3. Comparison of the experimental Penning electron energy spectrum for $He(2^3S)+He(2^3S)$ collisions with quantum mechanically calculated individual spectra for the processes (4a)–(4d).

$+He(2^3S)$, the present potentials are more attractive than those of Garrison *et al.*,[19] and the order of $^1\Sigma_g^+$ and $^3\Sigma_u^+$ is interchanged with the $^1\Sigma_g^+$ state being the lowest. For $He(2^1S)+He(2^3S)$, one observes an interesting avoided crossing near $9.8a_0$ between $^3\Sigma_g^+$ curves originating from different limits.

Inspection of the difference potentials and semiclassical[4] model calculations of the electron spectra[13] based on the potentials shown in Fig. 2 indicate that the peaks marked as A–D in Fig. 1 have the following origins: Peak A is the main Airy peak due to the combined action of the four transition amplitudes for reaction (1), peak B is the first of the supernumerary Airy peaks,[3,4,8–10] peak C is associated with transitions from the $2^3\Sigma_u^+$ state, and peak D corresponds to autoionization from the $2^3\Sigma_g^+$ state, to which the $He(2^1S)+He(2^3S)$ system switches diabatically from the $1^3\Sigma_g^+$ state (Landau-Zener estimate for the transition probability $\gtrsim 60\%$). The good agreement of the experimental and semiclassically calculated[13] energy positions of the peaks A–D, and in particular the position and narrow width of peak D, strongly support our judgement that the excited-state potentials in Fig. 2 are quantitatively correct.

Closer inspection of peak A reveals partially resolved oscillatory behavior, which we attribute to the rapid incoming-outgoing interference structure mentioned above; in Fig. 3 (upper part) the relevant part of the $He(2^3S)$-$He(2^3S)$ electron spectrum (background subtracted) is displayed again on a broader relative energy scale. The results of quantum mechanical calculations of separate electron spectra due to each of the four autoionization amplitudes Eqs. (4), averaged over the collision energy distribution, are shown in Fig. 3 (lower part) for comparison; the respective potentials shown in Fig. 2 were used and the width function $\Gamma(R)$ given in Eq. (3) was employed in all the calculations. For better comparison of the spectral shapes, we have ignored the differential statistical weights of the $1^1\Sigma_g^+$ and $1^3\Sigma_u^+$ entrance channels. Rich structure is observed in all the calculated spectra and the fast oscillations are especially clear in the two spectra associated with the $^2\Sigma_g^+$ ionic state. The phase of the oscillatory structure observed experimentally in the low-energy side of peak A is seen to be in good agreement with that of the theoretical oscillations. Note that the calculated spectra have not been convoluted with the experimental resolution (60 meV FWHM) in order to show their original structure. If one adds the resolution-convoluted spectra (4a)–(4d) according to the statistical weights of the two entrance channels, one obtains good agreement in the peak positions and structure with the experiment, but peak B comes out too small relative to peak A. A complete calculation of the electron spectrum requires, however, the

knowledge of the individual widths for the processes (4a)–(4d). Corresponding computations are in progress.

We note that calculations with a reduced width (simply realized by lowering Γ_0 by a factor of 2, whereby the total cross sections are decreased by only about 25%) showed oscillations with a significantly deeper modulation depth, and peak B is raised relative to peak A.[13] This dependence promises to be useful as a probe of the autoionization width. In any case, the presence of fast oscillations is bound to a sufficiently restricted number of contributing orbital angular momenta, as achieved in the present experiment by use of very low collision energies. As an alternative way for a selection of a narrow band of partial waves, which can be applied also at higher collision energies, we mention coincidence detection of electrons with ions scattered into a suitably chosen solid angle.

In the future, we hope to be able to reduce the collision energy further by decreasing the average metastable velocity and the width of the velocity distribution. For more detailed studies of fast oscillations in electron spectra from autoionizing quasimolecules it is desirable to investigate such cases at low collision energies for which autoionization occurs from a single entrance channel to a single exit channel. Work on the systems $He(2^3S)+Li,Na(^2\Sigma)$ is underway, both experimentally and theoretically.

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