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Electron-impact excitation cross sections for transitions in atomic copper

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We report results of the first *ab initio*, close-coupling calculations of the electron-impact excitation of atomic copper in the 0.1–8.0-eV range. Integrated, inelastic cross sections are given for the low-lying $^2P^o$ and $^2D^e$ excited states, which are important to the kinetics of the copper vapor laser. The calculated cross sections exhibit a rich resonance structure due to Cu^- states, which have not been previously known.

The excited states of atomic copper relevant to the copper vapor laser[1] (CVL) are populated primarily by collisions with electrons. The ground $(3d^{10}4s)^2S^e$ state is collisionally excited preferentially to the $(3d^{10}4p)^2P^o$ states, where a population inversion is created with respect to the lower, metastable $(3d^94s^2)^2D^e$ states. The $^2P^o$-$^2D^e$ transitions are the sources of the observed laser lines. Recent interest in more powerful CVL's has prompted detailed kinetic calculations to optimize laser geometries, input voltages, and electron temperatures and densities.[2] These modeling studies require as input the various electron collisional cross sections. The excitation cross sections have neither been calculated from first principles nor measured within the energy range typical of the CVL environment where the electron temperature is usually less than 5 eV.[2] Rather, the required low-energy data have been obtained by either simple theoretical estimates[3,4] or extrapolation from the 6–100-eV region, where reliable close-coupling calculations have been performed[5] and experimental results[6] are available. Trajmar, Williams, and Srivastava[6] have measured (between 6 and 100 eV) the relative magnitudes of the inelastic differential cross sections, which, subsequently, have been put on an absolute scale in several contradictory ways.[4,6,7] In spite of all this work, no reliable electron-impact excitation cross sections of atomic copper exist for $E<6$ eV. In addition, it is known[8] that Cu^- supports one bound state, $(3d^{10}4s^2)^1S^e$, which lies 1.23 eV below the ground state of neutral copper. Thus it is expected that negative ion resonances will strongly contribute to the collisional cross sections for electron energies relevant to CVL experiments and modeling.

In this Rapid Communication we report results of *ab initio* calculations of the electron-impact excitation cross sections of atomic copper in the 0.1 to 8-eV range. It is found that the cross sections do exhibit a rich resonance structure, and that, in fact, some transitions [e.g., the $^2S^e$-$(3d^94s^2)^2D^e$] are dominated in the energy range of interest by resonances which have heretofore not been known.

We have calculated the cross sections within the framework of R-matrix theory,[9,10] using the Belfast package of the (nonrelativistic) R-matrix codes.[11] The computational advantage of this approach, being based on a basis set expansion, is that one can calculate the cross sections at as many energies as is required (~ 100 energy points in our case) for about the same cost as that for one energy. This is obviously important when the cross sections exhibit a large amount of structure as a function of electron energy, the determination of which requires a fine energy grid.

No matter which technique is used, the requirements for calculating accurate scattering data are twofold; first, accurate target wave functions and second, a reasonable description of the scattering event. We took as our target wave functions those developed in the recent work of Msezane and Henry.[5] Four states were used to describe the target; a five-configuration $^2S^e$ ground state, a single-configuration $(3d^{10}4p)^2P^o$ excited state, and two $[(3d^94s^2)$ and $(3d^{10}4d)]^2D^e$ states, each consisting of three configurations. The atomic orbitals had been adjusted to give the best possible level splittings, as well as an accurate oscillator strength for the $^2S^e$-$^2P^o$ transition. This latter requirement is important because, in the high-energy limit, the cross section for an electric-dipole-allowed transition is proportional to the oscillator strength. For the $^2S^e$-$^2P^o$ transition, the calculated oscillator strength[5] is 0.644 in both the length and velocity form, compared to the experimental value[12] of 0.65. For the $^2P^o$-$(3d^{10}4d)^2D^e$ transition, we have calculated the oscillator strength to be 1.33 in the length form and 0.58 in the velocity form as compared to 0.83 determined experimentally.[12] This transition constitutes an important loss mechanism of the population of the $^2P^o$ upper laser levels.

In the Belfast implementation of the R-matrix method,[9–11] the total scattering wave function describing the electron-target system is expanded in the inner region ($r \le r_0$, where r_0 is the radius of the R-matrix boundary) in terms of antisymmetrized products of the N-electron target wave functions and one-electron R-matrix basis states. In the present calculations, we took $r_0=19.9a_0$, and used 25 basis states for each angular momentum of the scattering electron. In addition, the $(N+1)$ electron total wave function also contains so-called "correlation terms," which are antisymmetrized products of the bound atomic orbitals appearing in the target wave functions. These terms provide an approximate description of the bound state(s) and quasibound resonances of Cu^-. In the present work, the correlation terms were constructed by taking the $1s$, $2s$, $3s$, $2p$, and $3p$ atomic orbitals fully occupied and allowing the following possible occupation numbers for the other orbitals: $3d$:9-10, $4s$:0-2, $4p$:0-2, $4d$:0-2, $4f$:0-1. As usual, the many-electron basis states were constructed to correspond to definite values of the total angular momenta (S and L) and parity (P).

The total cross sections are obtained from the converged sums of partial cross sections calculated for the possible SLP cases. For each L, both even and odd parity and singlet and triplet partial waves were calculated. For all energies considered ($E \leq 8$ eV), the maximum total angular momentum required was $L=9$, even for the slowly convergent optically allowed transitions. It is to be noted that both the R-matrix method employed in the present work and the method used by Msezane and Henry[5] involve the close-coupling approximation. With identical target states and terms retained in the close-coupling expansions, the two calculations should give identical results. In practice, Msezane and Henry[5] restricted the number of correlation terms. Nevertheless, we find good agreement between the two calculations when all the channels are open. For example, at 6 eV, the elastic cross section of the ground state is calculated to be within 10% of the previously published value, whereas the inelastic cross sections for the ground state are all in agreement to better than 1%.

Electron scattering methods that employ basis set expansions often suffer from the appearance of spurious, nonphysical resonances in the calculated cross sections. We have found no pseudoresonances in the present work for $E \leq 8$ eV. All features in the cross sections were examined and properly identified by careful inspection of the many-electron scattering wave functions.

The present calculations yield many results characteristic of inelastic scattering problems. In Fig. 1 we show the total and some of the partial cross sections for elastic scattering by the $^2S^e$ ground state. The $^1S^e$ partial cross section [Fig. 1(a)] remains finite at zero energy where its magnitude $\sim 49\pi a_0^2$ is determined, to some extent, by the existence of the bound state of Cu^-. In the present work, we obtained 1.246 eV for the electron affinity of the neutral Cu, as compared to the measured value[8] of 1.226 eV. Figure 1(b) clearly shows that the total elastic cross section is dominated by the $^3P^o$ symmetry, which exhibits a large peak near 0.3 eV. An analysis of the wave function around this energy identifies this as a $(3d^{10}4s4p)^3P^o$ shape resonance of Cu^-. An analogous, but much weaker resonance occurs in the $^1P^o$ channel around 0.5 eV [feature "a" of Fig. 1(a)]. Two other broad resonances $(3d^94s^24p)^1P^o$ and $^3P^o$ account for the shoulder at ~ 2.3 eV [e.g., feature "b" of Fig. 1(a)]. Last, a cusp [feature "c" of Fig. 1(a)] appears in the $^1P^o$ partial cross section at the calculated threshold, 3.55 eV, for the $(3d^{10}4p)^2P^o$ state. (For comparison, the experimental threshold[13] is 3.81 eV.) A cusp can appear at a threshold when the scattered electron has zero angular momentum, i.e., when it is an "s-wave" electron,[14] as in the present case.

The $^1D^e$ partial elastic cross section of the ground state, shown in Fig. 1(a), also exhibits a variety of features, the most pronounced occurring at 3.5 eV, just below the $(3d^{10}4p)^2P^o$ threshold. Again, analysis of the wave function near this energy identifies this peak (feature "e") as being due to a $(3d^{10}4p^2)^1D^e$ Feshbach resonance, which has not been observed or calculated previously. Just above this resonance, where the $^2S^e$-$^2P^o$ channel becomes open, the $^1D^e$ partial cross section shows a dip (feature "f") which is due to flux conservation. According to the present calculations, the $^1D^e$ Feshbach resonance is quite broad (~ 0.4 eV) and its high-energy tail extends above the $(3d^{10}4p)^2P^o$ threshold. Because the $(3d^94p^2)$ quasibound state couples strongly to both the $3d^{10}4skd$ and

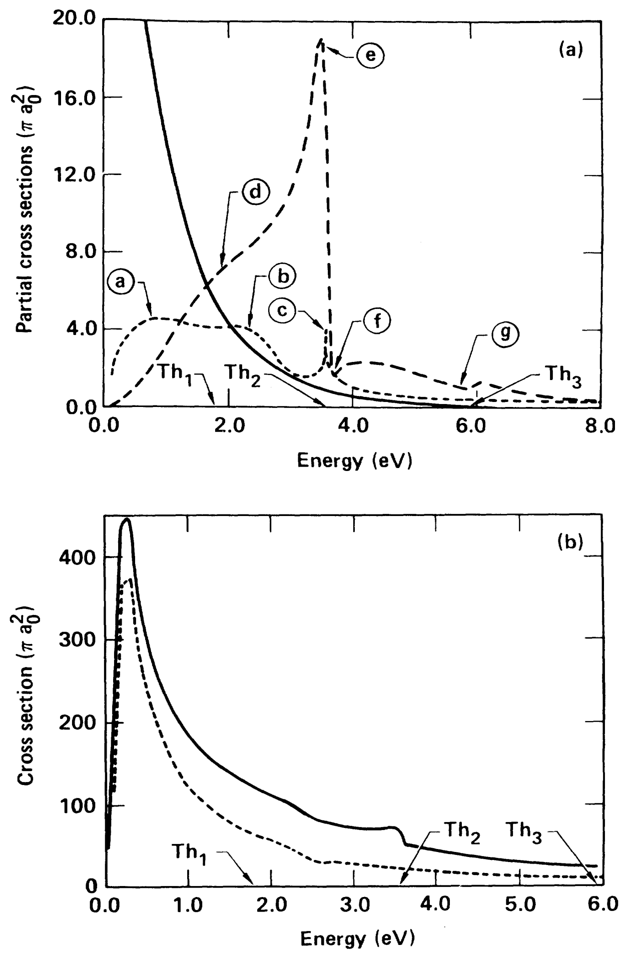

FIG. 1. Total and partial cross sections for elastic scattering of electrons from the $^2S^e$ ground state of Cu. (a) Partial cross sections: $^1S^e$ (——); $^1P^o$ (---); $^1D^e$ (– – –). The letters label the Cu^- resonances and other structures discussed in the text. (b) Total (——) and $^3P^o$ partial (---) cross sections. Th_1, Th_2, and Th_3 indicate the calculated thresholds for the $(3d^94s^2)^2D^e$, $(3d^{10}4p)^2P^o$, and $(3d^{10}4d)^2D^e$ states, respectively.

$3d^{10}4pkp$ continuua, it also contributes to the $^2S^e$-$^2P^\circ$ inelastic cross section. As this cross section rises from threshold, flux is taken from the elastic channel, and a minimum occurs.[15] Last, Fig. 1(a) shows two other features in $^1D^e$ symmetry. The first is a broad $(3d^{10}4s4d)$ shape resonance which appears as a shoulder near 2 eV (feature "d"). The second is a cusp (feature "g") at the $(3d^{10}4d)^2D^e$ threshold (calculated to be at 5.93 eV as compared to the measured[13] value of 6.19 eV).

As mentioned before, the electron temperature in the CVL is usually below 5 eV, and the relevant momentum-transfer cross section is dominated by elastic collisions. Consequently, the aforementioned low-energy features which are prominent in the elastic cross section of the ground state, in particular the $(3d^{10}4s4p)^3P^\circ$ shape resonance, will also be important for the correct determination of momentum transfer and, hence, electron transport in the CVL discharges.[16]

The total cross section for the transition $(3d^{10}4s)^2S^e$-$(3d^94s^2)^2D^e$ is illustrated in Fig. 2. The most striking feature of this cross section is the large peak at 2.5 eV which is composed primarily of the contributions from two-shape resonances: $(3d^94s^24p)^{1,3}P^\circ$. This result is of particular importance to the CVL kinetics because of the large effect it can have on the deexcitation process $^2D^e \rightarrow {}^2S^e$ which depletes the population in the $^2D^e$ metastable state. Indeed, it has been known for some time that the $^2D^e$ state depletes much faster[16] than kinetic calculations predict. Figure 2 clearly shows that near 2.5 eV the previously used $^2S^e$-$^2D^e$ cross section is smaller than the present result by an order of magnitude. We emphasize that, up to now, values for this inelastic cross section at energies below 6 eV have been estimated[2,16] by extrapolating the known cross sections at higher energies,[5,7] using the Wigner threshold law—a procedure which altogether misses the large resonance structure near 2.5 eV.

The remaining process of interest is the excitation of the

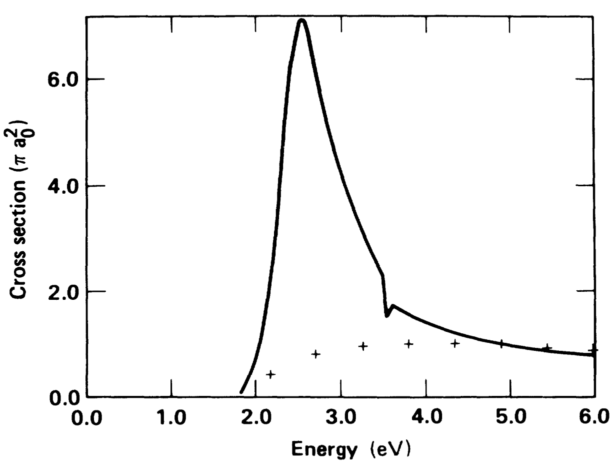

FIG. 2. Total electron-impact excitation cross section for the $(3d^{10}4s)^2S^e$-$(3d^94s^2)^2D^e$ transition in Cu. Present results (——) and previous estimates (+ + +). The dip at 3.55 eV is due to a cusp in the $^3P^\circ$ partial cross section at the $(3d^{10}4p)^2P^\circ$ threshold.

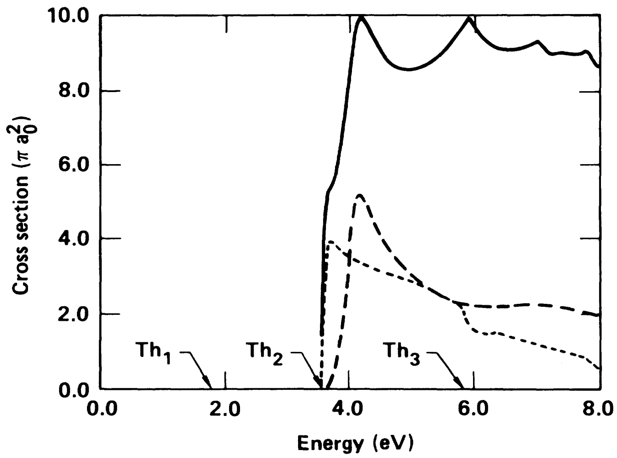

FIG. 3. Total and some partial cross sections for the excitation of the $^2S^e$ ground state of Cu to $(3d^{10}4p)^2P^\circ$: total (——), $^1D^e$(---), $^3F^\circ$ (– – –). The arrows indicate the inelastic thresholds as in Fig. 1.

$^2S^e$ to the $^2P^\circ$ state which is responsible for the population inversion in the CVL. Figure 3 shows the total, as well as the $^1D^e$ and $^3F^\circ$ partial inelastic cross sections for this transition. The shoulder in the total cross section just above threshold is due, as we mentioned before, to the manifestation of the $(3d^{10}4p^2)^1D^e$ Feshbach resonance in this channel. The peak near 4.2 eV is due to yet another shape resonance, namely, $(3d^{10}4p4d)^3F^\circ$. Though these details are interesting, the overall shape and magnitude of the total cross section is not greatly affected by the resonances, presumably due to the long-range nature of the interaction for this dipole-allowed $4s-4p$ transition.

In conclusion, we have calculated the cross sections for electron-impact excitation of atomic copper, and found an abundance of resonance structure. Previous kinetic calculations have evidently underestimated the magnitude of the important $(3d^{10}4s)^2S^e$-$(3d^94s^2)^2D^e$ cross section near threshold by an order of magnitude. The current calculation is based on a four-state close-coupling description of the collision dynamics with reasonably accurate target states. A more detailed description of the Cu atom will undoubtedly lead to additional resonance features, improved target states, and presumably more accurate cross sections. For example, the use of more elaborate configuration interaction wave functions, which properly account for the intershell correlation between the $4l$ valence and $3d$ core electrons, leads to significantly improved $^2P^\circ$-$^2D^e$ oscillator strengths,[17] especially for the $3d^{10}4p$-$3d^94s^2$ laser transitions. Given the importance of the precise positions and widths of some of the resonances to the low-energy behavior of the electron-scattering cross sections, and, hence, to the CVL's kinetics, a more extensive description (e.g., including some low-lying quartet states) of the Cu atom is desirable. Such calculations are in progress[17] and results will be forthcoming in a later publication. In addition, it would be useful to have direct experimental verification of the largest resonances identified in our calculations.

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