Brief Reports

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Low-lying negative-ion states of calcium

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Studies of electron transmission through Ca vapor reveal two prominent resonances in the range 0–4 eV. The energies and widths of these temporary anion states suggest that they may be assigned to the strongly mixed $(4s^2 3d)^2D$ and $(4s4p^2)^2D$ states of Ca^-. This interpretation is supported by *ab initio* configuration-interaction calculations and is consistent with previously unassigned structure observed in the photodetachment cross section.

The recent evidence found by Pegg *et al.*[1] for a stable negative ion of calcium and the theoretical support for this anion by Fischer *et al.*[2] have motivated us to present in more detail our earlier low-energy electron-scattering data.[3] Our results bear on the ordering of the unfilled atomic orbitals in the calcium negative ion and provide, in the temporary negative-ion states, an unusual illustration of strong configuration interaction between a shape and a core-excited resonance. The present studies, furthermore, provide insight into the structure appearing in photodetachment measurements on Ca^-.

Our experimental study examined the sharp structure in the total scattering cross section of Ca using the electron-transmission method of Sanche and Schulz.[4] The apparatus has been described in detail elsewhere,[5] and we note only a few relevant points here. A magnetically collimated electron beam from a trochoidal monochromator[6] was passed through a heated cell containing the metal vapor supplied from an independently heated oven. An electrode following the cell was biased to discriminate against electrons having lost axial velocity by collisions in the cell, and the unscattered, or transmitted, current passed through to a collector. To accentuate the sharp structures, the electron energy in the cell was modulated with a small sinusoidal voltage, and the derivative of the transmitted current was measured with a synchronous detector.

The apparatus described above has worked well in a number of the alkali-metal and group-IIb metal vapors. In calcium, however, we were able to take data only for a short period before the electrode insulators shorted out and the apparatus had to be completely dismantled and cleaned. Although it was not possible to determine the energy scale by admixture of a gas with known resonances, a calibration was carried out by reference to the energy at which the onset of current through the cell occurs. For this reason and because of the instability of the surface potentials during the runs, the sharp structures can be located conservatively only to within ±0.15 eV.

Figure 1(a) shows the derivative of electron current transmitted through calcium vapor as a function of electron energy from 0 to 4 eV. The locations of all the excited states of neutral calcium in this range are also indicated. The experimental curve is dominated by two features 1-1′, a relatively broad resonance centered at 1.1±0.15 eV, with a minimum to maximum separation of 0.5±0.1 eV, and a sharp resonance 2-2′, which lies at 2.8±0.15 eV, well above the lowest excited $(4s4p)^3P$ states of neutral calcium near 1.89 eV. The measured width of the latter resonance, as indicated by the minimum to maximum separation, is approximately 80 meV. This is somewhat broader than the anticipated full width at half maximum (FWHM) of the electron distribution of the apparatus, which is typically 50 meV or less.

In previous studies[5] of shape resonances formed by addition of p electrons to the ground states of alkali metals and group-IIb elements, the minimum to maximum separations of such resonances were found to be roughly equal to the resonance energies. In contrast, the feature

at 1.1 eV is comparatively narrow. Primarily for this reason, we attributed[3] the 1.1-eV structure to a shape resonance of configuration $(4s^2 3d)^2 D$. Earlier calculations by Amusia and Cherepkov[7] had located this ^2D state at 1.67 eV and a $(4s^2 4p)^2 P$ shape resonance at 0.13 eV. Based on a comparison with our measured value and the absence of any sharp structure in our spectrum below 1.1 eV, we suggested[3] that the $(4s^2 4p)^2 P$ negative ion state might well be stable, as subsequently verified by Pegg *et al.*[1]

We turn now to a discussion of the core-excited resonances in Ca. Electron-transmission spectra[8] in Mg, Zn, Cd, and Hg are all characterized by one or more pronounced resonances appearing at the thresholds of the $(nsnp)^3 P$ excited-state multiplet. The lowest-lying

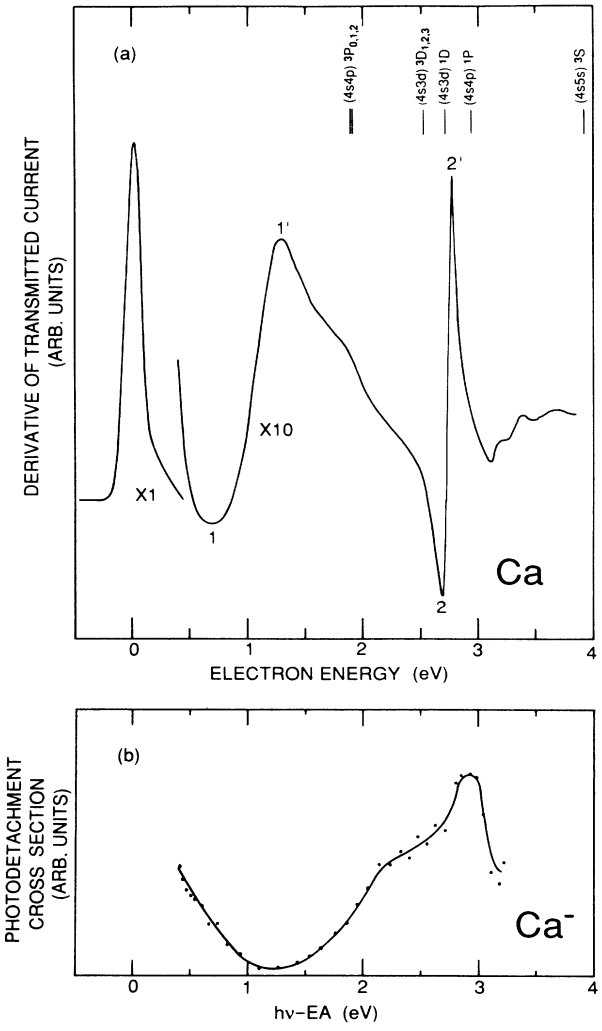

FIG. 1. (a) Derivative of transmitted electron current through a cell containing Ca vapor as a function of electron energy. The vertical lines indicate the energies of the neutral excited states of Ca. (b) Photodetachment cross section of Ca^- as measured by Heinicke *et al.* (Ref. 15). The photon energy scale has been shifted by the small electron affinity (EA) of Ca to permit resonance structures in (a) and (b) to appear at the same energy in both curves.

configuration to which these features can be assigned is undoubtedly $nsnp^2$, which supports states having ^4P, ^2P, ^2D, and ^2S symmetries. Of these atoms, only the resonances in Hg have been extensively studied,[9] where it is found that only the ^4P and ^2D resonances appear prominently in the total cross section or in the excitation functions near threshold for the ^3P neutral excited states. In the lighter elements Mg and Zn, as well as Ca, where spin-orbit effects may be neglected, we expect therefore that the $(nsnp^2)^2 D$ resonance will be the largest feature and that it should lie near the $(nsnp)^3 P$ threshold. The locations of the other resonances of this configuration will not alter our argument. In contrast to Mg and Zn, however, the Ca spectrum displays near the $(4s4p)^3 P$ threshold only a weak, rather broad structure lying on the high-energy side of the 1.1-eV resonance. The largest resonance, feature 2-2', lies approximately 0.8 eV higher still.

The most prominent difference between the neutral states of Ca and those of the metals above is in the substantially lower energy of the $(4s4p)^3 P$ state compared to the corresponding states in Mg, Zn, Cd, and Hg. Thus the $(4s4p^2)^2 D$ resonance associated with this state might be expected to lie close to the $(4s^2 3d)^2 D$ shape resonance. We suggest, therefore, that the observed difference in energies between resonance 1-1' and 2-2' reflect a considerable contribution from configuration interaction. In this regard, we note that 1-1' and 2-2' are almost equally spaced by 0.8 eV on either side of the $(4s4p)^3 P$ state. Such positions might be expected if the hypothetically noninteracting resonances were virtually degenerate close to the $(4s4p)^3 P$ threshold and were then mixed by configuration interaction in roughly equal amounts.

Our preliminary calculations on these states of Ca^- support the foregoing interpretation. The method is essentially Fano's treatment[10] of the configuration interaction between a quasibound state and the continuum, adapted to atomic resonances.[11] A primitive basis of Slater orbitals was constructed, starting with the "Hartree-Fock" basis for Ca given by Clementi and Roetti[12] and adding $5s$, $4p$, and $3d$ orbitals optimized to enhance the representation of the quasibound states. Hartree-Fock orbitals obtained from optimizing both ^1S and ^1D states of Ca were combined in $n+1$ electron functions for Ca^-, and the quasibound states were represented as linear combinations of these for 16 different configurations. The energies and widths (Γ) of the two lowest ^2D resonances were then obtained from the interaction with the continuum in the normal way. The *ab initio* theoretical values for the energies are 0.8 and 3.2 eV, to be compared with the experimental energies of 1.1 ± 0.15 and 2.8 ± 0.15 eV, respectively. The energy of the $(4s4p)^3 P$ state for the core-excited resonance is found to be 1.61 eV using the same basis, whereas its experimental value is 1.89 eV. Thus the calculated value is well separated from either of the resonances, although not so close to the middle as shown in the experiment.

The differences between the theoretical and experimental energies are within the limitations of our calculations. More correlation in the calculation of the ground-state $(4s)^2$ energy would make the calculated excitation ener-

gies of the lower resonance and the $(4s4p)^3P$ state closer to experiment. In addition, more correlation in the Ca^- states should lower the calculated position of the upper resonance more than that of the lower. These changes should all bring theory closer into line with experiment.

The calculated widths of the two resonances are found to be 1.1 and 0.080 eV for the lower and upper features, respectively. The latter width includes approximately 0.050 eV from decay to the ^1S and 0.030 eV from decay to the ^3P target states. Care must be taken in the comparison of the widths to the experimental results. The upper resonance is likely to be well described by a Breit-Wigner, or single-level, profile. For the case in which the resonance profile is symmetric, the minimum to maximum separation in the derivative signal corresponds to $\Gamma/\sqrt{3}$. Assuming that the resonance profile is symmetric with a measured minimum to maximum separation in the derivative signal of 0.080 eV and, further, that the instrument function is represented by a Gaussian with a full width at half maximum of 0.050 eV, the unfolded resonance width (Γ) is 0.098 eV, in good agreement with the theoretical prediction of 0.080 eV.

The profile of the lower resonance is not well described by a single-level formula, so we have computed the actual derivative of the cross section and found the separation of the extrema to be 0.46 eV, which is in excellent agreement with the experimental value of 0.5 ± 0.1 eV.

In several calculations using different numbers of CI functions, the relative fraction of the core-excited:shape character in the lower resonance is found to be nearly 50:50. Thus, it is inappropriate to characterize either resonance as "shape" or "core-excited." The signs of the coefficients in the CI wave functions are such that the width of the lower state arises from a positive combination of the width functions of the two states, and the small width of the upper one is the result of considerable cancellation between the two width functions. This explains nicely the quite different magnitudes of the two lifetimes and the unexpected result of the upper resonance being half shape in character but with such a small width.

Our conclusions bear directly on a study of the photodetachment cross section of Ca^- carried out by Heinicke *et al.*[13] and shown in Fig. 1(b). At the time of these measurements the state of the Ca^- produced in the ion source was unknown. It was assumed to be metastable, since the ground state was believed to be unstable. Thus the structure in the photodetachment curve could not be uniquely interpreted.

Optical transitions from $Ca^-(4s^24p)^2P$ into the two ^2D resonances observed in our studies are dipole allowed and should occur at photon energies of 1.1 and 2.8 eV plus the small binding energy (the Ca electron affinity) of 0.043 eV.[1] The upper resonance in the electron-scattering measurements agrees very well with the upper peak in the photodetachment curve, which lies near 2.9 eV. A more precise comparison is not possible since the photon resolution was not specified by Heinicke *et al.*

There is no evidence, however, for the lower resonance in the photodetachment data, indeed, the cross section appears to be close to a minimum at the resonance energy. In light of the interpretation above, this may seem puzzling since we suggest that the two resonances are nearly 50-50 mixtures of the same two configurations. Detailed calculations show, however, that the transition dipole matrix elements for the lower resonance are considerably smaller than those for the upper. This occurs because of a cancellation in the case of the lower resonance. The moments were calculated from wave functions in which we augmented further the Slater-type-orbital basis described above. We obtained moments in the ratio of 12.4 (upper divided by lower), which implies that optical absorption into the upper resonance is some 150 times more intense than into the lower. Our understanding of the electron-scattering process in terms of a strong mixing between the two ^2D configurations is thus supported by a consistent interpretation of the photodetachment results.

One further detail of the photodetachment spectrum may also be interpreted. The shoulder near 2.2 eV lies just above the $(4s4p)^3P$ states and is likely due to the opening of detachment into this channel.

Finally, we note that Romanyuk *et al.*,[14] in an unusual variation of the trapped electron technique, observed resonances in the total scattering cross section of Ca at 0.7 ± 0.1 and 1.7 ± 0.1 eV which were attributed erroneously to p and d shape resonances, respectively. The discrepancy in the resonance energies with respect to those found here under less than ideal experimental conditions warrants further work with improved energy calibration. Electron-transmission studies would be best carried out in a crossed-beam geometry[15] rather than the static cell arrangement used here. Further theoretical studies are also needed to refine the agreement with experiment and examine the observed, rather subtle, interaction between calculated energies and resonance widths.

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