Electron binding motifs in the (CS$_2$)$_n^-$ ($n>4$) cluster anions

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Photoelectron imaging spectroscopy of (CS$_2$)$_n^-$, $n>4,$ reveals a new state with an electron binding energy smaller than that of any of the corresponding CS$_2^-$ and C$_2$S$_4^-$ states known to date. With support from ab initio calculations, two long-lived, metastable binding motifs with small electron binding energies are discussed for these clusters. The first is a solvent network permeating state, where the excess electron is delocalized over a number of linear CS$_2$ molecules. The second is an excited $^2B_1$ state of the core CS$_2^-$ anion stabilized at a slightly bent geometry by the solvation interactions. Based on the observed solvation-induced shifts in binding energy, the second motif is favored. © 2008 American Institute of Physics. [DOI: 10.1063/1.3046481]

I. INTRODUCTION

Excess electron states are of considerable interest to chemists. For example, a great deal of attention has been devoted to the hydrated-electron clusters, (H$_2$O)$_n^-$—a classic model for delocalized electron binding interactions.1–7 While a single water molecule does not bind an excess electron, a variety of interior, surface, and “network permeating” states have been proposed for (H$_2$O)$_n^-$ 8 Excess electron binding in these states relies on the collective interactions of a network of H$_2$O molecules with the diffuse electron, as well as correlation effects.

In contrast, quite different electron binding motifs are usually found in clusters of molecules that are individually capable of supporting stable or metastable anionic states. Prominent examples are the (CS$_2$)$_n^-$, (CO$_2$)$_n^-$, and other similar cluster anions.9–11 Depending on the conditions and cluster size, the excess electron in these clusters is bound to either one or two constituent molecules, corresponding, for example, to the CS$_2^-$/(CS$_2$)$_{n-1}$ or (CS$_2$)$_2^-$/(CS$_2$)$_{n-2}$ cluster structures.

In view of these vastly different binding motifs, are solvent-based, broadly delocalized electronic states (similar to the hydrated-electron states) also possible in (CS$_2$)$_n^-$ and similar cluster anions with strongly bound ground states? Such metastable states could play important roles in the formation and photochemistry of the clusters, even though normally they would be masked by the more energetically favorable structures characterized by the well-defined anionic cores. As an additional possibility, the excited states of the core anions themselves may also be important, particularly if they can be stabilized sufficiently by solvation and result in new metastable cluster states.

We report the observation of a new metastable state of the (CS$_2$)$_n^-$ ($n>4$) cluster anions with an electron binding energy (eBE) smaller than that of any of the corresponding (CS$_2$)$_n^-$ states known to date. In the previous studies of this cluster series, the coexistence of the CS$_2^-$ · CS$_2^-$ ion-molecule complex and several covalently bound isomers of C$_2$S$_4^-$ was examined (see, for example, Refs. 9 and 12–14 and the references therein). The population of the covalent dimer-anion core structures was shown to decrease with increasing cluster size due to the more favorable solvent interactions with CS$_2^-$ compared to C$_2$S$_4^-$ 15 Each of the past studies identified the photodetachment of solvated CS$_2^-$ in the ground electronic state as the lowest-energy detachment transition in (CS$_2$)$_n^-$. The new, lower-energy transition reported here suggests a previously unobserved electron binding motif for (CS$_2$)$_n^-$, $n>4$, involving either a delocalized solvent-based state or an excited state of the core anion stabilized by solvation.

II. EXPERIMENTAL APPARATUS

The experiments are carried out using a time-of-flight ion mass spectrometer equipped with a photoelectron imaging assembly.16 The (CS$_2$)$_n^-$ cluster anions are formed by secondary electron attachment to neutral clusters after crossing the supersonic expansion of a CS$_2$/Ar gas mixture (40 psi backing pressure, operated at a 50 Hz repetition rate) with a 1 keV continuous electron beam. Several tens of microseconds following their formation, the mass-selected cluster anions are irradiated with pulsed, linearly polarized laser light. The detached electrons are accelerated in the direction perpendicular to the ion and laser beams using a velocity-map17 imaging18,19 arrangement.

The photoelectron images are accumulated over 25 000–50 000 experimental cycles using the frequency doubled and tripled output of a neodymium doped yttrium aluminum garnet laser (532 and 355 nm, with the corresponding pulse energies of about 30 and 10 mJ, respectively). The photoelectron spectra are obtained from the images following the Abel-inversion analysis with Reisler’s BASEX program.20

III. RESULTS

The photoelectron spectra for (CS$_2$)$_n^-$, $n=4$–8 and $n=8$–12, acquired at 532 and 355 nm, respectively, are shown in Fig. 1. The higher-energy photons are used for larger clusters to compensate for the solvent-induced shift of the pho-
todetachment transitions. A more detailed example of raw data is shown in Fig. 2, which displays an expanded version of the 532 nm (CS$_2$)$_n^-$ spectrum alongside the image from which it was obtained. To emphasize the relative intensities of the photoelectron bands revealed in the data, Fig. 2 also displays the photoelectron speed distribution (i.e., the e-velocity spectrum) obtained from the same image.

The relative intensities of the bands in Figs. 1 and 2 may vary depending on the ion source conditions, but the band appearance and positions are reproducible between different experimental runs. The band labeled $I$, present in all the spectra shown, corresponds to the well-characterized $X^1A_1 (1^2\Sigma^+_-) \rightarrow X^2A_1$ photodetachment transition in CS$_2^-$, shifted by solvation with $(n-1)$ neutral CS$_2$ molecules. This band is the lowest-eBE transition known (to date) for (CS$_2$)$_n^-$. The bands peaking near zero electron kinetic energy (eBE $= 3.5$ eV) in the 355 nm spectra are due to the covalent dimer-anion (C$_2$S$_4^-$) cluster-core structures. In this report, we focus on the previously uncharacterized transition labeled $S$ (for solvent based or solvent stabilized), observed for $n > 4$. Band $S$ appears at smaller (by $>0.5$ eV) binding energies compared to band $I$. Similar to $I$, band $S$ shifts to progressively higher eBEs as the cluster size increases.

FIG. 1. Photoelectron spectra of the (CS$_2$)$_n^-$ cluster anions. Left: $n=4–8$ at 532 nm; right: $n=8–12$ at 355 nm. All bands labeled $I$ correspond to the $X^1A_1 (1^2\Sigma^+_-) \rightarrow X^2A_1$ transition in the CS$_2^-$ cluster core, shifted by solvation by $(n-1)$ neutral CS$_2$ molecules. Band $S$ (for solvent based or solvent stabilized) corresponds to a previously uncharacterized transition.

FIG. 2. (Color online) An expanded example of raw data for (CS$_2$)$_8^-$ at 532 nm. Top: The raw photoelectron image and the corresponding eBE spectrum (also shown in Fig. 1 for 532 nm, $n=8$). The laser polarization direction is vertical in the image plane, as indicated by the double arrow. The (nearly) linear and bent core-anion (CS$_2^-$) structures believed responsible for the observed spectral bands are also shown. Bottom: The photoelectron velocity spectrum (i.e., the speed distribution). The speed as shown increases from right to left, with the units corresponding to the charge coupled device camera pixels.

IV. DISCUSSION

Plausible assignments for band $S$ will be considered shortly, after ruling out several other possibilities for its origin. First, this band cannot be attributed to a direct two-photon detachment transition because for any given $n$ the band appears at the same eBE in both the 532 and 355 nm spectra. Second, the band is not due to the photodetachment of photofragments. Such mechanism would also correspond to a two-photon process, and yet the images acquired at different laser fluences were consistently found to be unchanged overall. Specifically, all data in Fig. 1 were acquired with slightly collimated laser beams of $\sim 5$ mm diameter at the ion interaction region. These conditions correspond to moderate laser fluences of $<10^8$ W/cm$^2$, which fall at the lower end of the typical laser fluences employed in our experiments. Fragment photodetachment within the same laser pulse is not expected to have an observable contribution in this regime.

Third, vibrational hot bands are also ruled out as the origin of band $S$. In the (CS$_2$)$_n^-$, $n=5–12$ clusters, the band appears as a reasonably well-defined transition at eBEs more than half an eV lower than the $X^1A_1 (1^2\Sigma^+_-) \rightarrow X^2A_1$ transition in CS$_2^-$ (band $I$). The energy difference is even more significant relative to any transition involving the covalent dimer-anion cluster core, C$_2$S$_4^-$. Shifts of this magnitude are well in excess of not only the frequency of any vibrational mode in the cluster but also the solvent binding energy of CS$_2$ to the charged cluster. Hence, although band $S$ obviously originates from excited cluster states, these states lie too high in energy to be attributed to vibrational excitation in the parent cluster anions. Although, in principle, band $S$ can still be described as a “hot band,” it is actually too “hot” to be viewed as such in the conventional sense—its origin must include an electronically excited state and/or metastable isomers of the parent anion.
Having ruled out these possibilities, we now summarize the necessary background knowledge concerning the electronic structure of negative ions of carbon disulfide, on which we will base our account for the appearance of band $S$. Specifically, we will suggest new electron binding motifs for (CS$_2$)$_n^-$, $n > 4$, that differ qualitatively from the smaller-size clusters. This assignment relies on the known properties of CS$_2^−$.

At its equilibrium corresponding to the $X^2A_1$ electronic state, the CS$_2^−$ anion is bent at $\angle$SCS $\approx 144^\circ$. However, the formation of metastable CS$_2^−$ ions at (near) linear geometry is also possible, as demonstrated in the Rydberg electron transfer experiments by Dunning and co-workers.26,27 They observed two forms of metastable (long-lived) CS$_2^−$, characterized by differing electron binding strengths. For the first form, external fields of $<$3 kV/cm sufficed for the detachment of the excess electron, while the second form required $>$10 kV/cm for the field-induced detachment to occur. The timescale for conversion of these metastable anions to stable CS$_2^-$ was $\sim$2 ms. Ab initio calculations by Gutsev et al.24 indicated that at its linear geometry the lowest electronic state of CS$_2^-$ is stable toward autodetachment by $\sim$16 meV. Accordingly, Dunning and co-workers attributed the formation of the two types of metastable CS$_2^-$ with different field-detachment characteristics to a near-linear structure with different amounts of bending vibrational excitation. Radiative decay to lower vibrational levels was suggested as the stabilization mechanism.26,27

In their abovementioned calculations, Gutsev et al.24 considered only the ground electronic states of CS$_2^−$ and CS$_2$. To complete the picture, we performed relaxed potential energy scans as functions of the bending angle in CS$_2$ and CS$_2^−$, including the first excited electronic state of the anion. The calculations were carried out at the MP2/6-311 +G(3df) level for geometry optimizations and CCSD(T)/aug-cc-pVTZ for single-point energy determinations using GAUSSIAN 03 software package (Ref. 28) on the University of Arizona super computer. At each fixed SCS angle, the C−S distances were optimized subject to the C$_2v$ symmetry constraint, followed by the CCSD(T) energy calculation. The results are plotted in Fig. 3.

The $X^2A_1$ and $^2B_1$ states of CS$_2^-$ form a well-known Renner–Teller pair. At the linear geometry the two states are degenerate, corresponding to the $^2\Pi_u$ resonance. The potential energy curves in Fig. 3 indicate that both anionic states lie adiabatically below the $X^2A_1$ neutral state. In electron capture by CS$_2$, the anion can initially be formed in either the $X^2A_1$ or $^2B_1$ electronic state. Since the potential energy gradient for the $^2B_1$ state is directed toward the linearity, this state’s population will eventually be funneled to $X^2A_1$ through the Renner–Teller coupling.

With this in mind, we now put forth two possibilities to account for band $S$ in the photoelectron spectra of (CS$_2$)$_n^−$. The first is based on CS$_2$’s ability to bind an electron adiabatically at a linear geometry. With several CS$_2$ molecules present, an excess electron entering a (CS$_2$)$_n$ cluster may be trapped in the network of linear CS$_2$ molecules before a stable (bent) CS$_2^−$ anion is formed. Considering the difference in electron affinities of H$_2$O and CS$_2$, network permeating states predicted by Sommerfeld and Jordan8 for (H$_2$O)$_n^−$ seem even more plausible for (CS$_2$)$_n^−$. Such states would be based not so much on electrostatic interactions but electron correlation effects, resulting in relatively small electron binding energies. However, the photoelectron band positions corresponding to such states should depend rather weakly on the cluster size, contrary to the experimental observations in Fig. 1.

Another possible assignment for the origin of band $S$ is the contribution of the metastable $^2B_1$ state of the CS$_2^−$ cluster core. According to the results in Fig. 3, this state lies lower in energy than the neutral ground state, even in isolated CS$_2^−$, and it may be stabilized additionally by solvation—to a progressively greater extent as the cluster size increases. Although in isolated CS$_2^−$ the $^2B_1$ state minimum is at a linear geometry, the metastable equilibrium shifts toward slightly bent structures under asymmetric solvation, similar to CO$_2^−$ in water clusters.28 The bending is expected to weaken the Renner–Teller coupling and may slow the population transfer from the $^2B_1$ to the $X^2A_1$ state. The slight bond length elongation from 1.56 Å in neutral CS$_2$ to 1.60 Å in CS$_2^−$ ($^2B_1$) (as estimated from ab initio calculations) may further impede electron detachment or delocalization between several CS$_2$ moieties.

Therefore, in the (CS$_2$)$_n^−$ clusters the CS$_2^−$ core anion may exist in the metastable $^2B_1$ state, giving rise to band $S$ in the photoelectron spectra. While the eBE in isolated CS$_2^−$ in the $^2B_1(^2\Pi_u)$ state is small (see Fig. 3), the locations of band $S$ in the photoelectron spectra (Figs. 1 and 2) are consistent with the additional solvation stabilization energy due to the $(n−1)$ neutral CS$_2$ molecules in the [(CS$_2^−$($^2B_1$)) (CS$_2$)$_{n−1}$] clusters. Hence, this assignment for the origin of band $S$ is consistent with both its relatively low binding energy and the magnitude of the solvation-induced shift.

V. SUMMARY

The photoelectron spectra of (CS$_2$)$_n^−$, $n = 4–12$, reveal a new transition for $n > 4$ at electron binding energies smaller than any of the corresponding (CS$_2$)$_n^−$ bands described to date. Two distinct electron binding motifs are discussed in relation to the new band. The first is a delocalized solvent-
based state, analogous to that for the hydrated electron. In this state, electron transfer among several CS$_2$ moieties may take place before CS$_2^-$ relaxes to its equilibrium geometry. The second motif invokes a solvated, slightly bent CS$_2$ cluster core, trapped in the metastable $^2B_1$ state that lies adiabatically lower in energy compared to the ground state of neutral CS$_2$. The solvation-induced shift of band $S$, evident in Fig. 1, suggests that the second motif, involving a solvation-stabilized, metastable CS$_2^-$ cluster core, is the most plausible explanation for the newly observed transition.

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