

LETTERS TO THE EDITOR

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COMMUNICATIONS

Anion photoelectron spectroscopy of iodine-carbon dioxide clusters

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Anion photoelectron spectroscopy has proved to be a powerful method for the study of molecular clusters because it combines mass-selectivity and reasonable spectral resolution. Anion photoelectron spectra have been reported for elemental and molecular clusters of the type A_n^- , in which the additional electron is delocalized over the entire anion cluster,¹⁻⁶ and for mixed clusters of the type $X^-(M)_n$, in which a distinct X^- chromophore interacts with a "solvating" species, M .^{7,8} The $X^-(M)_n$ photoelectron spectra obtained thus far have exhibited the same vibrational and electronic features seen in the bare X^- spectrum, although these features are typically shifted and broadened in the cluster anion spectra due to the X^-/M interaction. In this Communication, we present photoelectron spectra of the anion clusters $I^-(CO_2)_n$, $n=1-13$, that are qualitatively different from the I^- spectrum in that they show pronounced progressions in vibrational modes of the solvating CO_2 molecules. These arise from perturbations to the solvent molecules by the I^- core. While Markovich *et al.*^{8(a)} have obtained photoelectron spectra for $I^-(CO_2)_n$, $n=1-7$, they did not observe any vibrational structure due to the lower resolution in their experiment. Our results represent a new level of detail in the study of "solute-solvent" interactions in clusters.

The experimental apparatus, described in detail elsewhere,⁹ employs a pulsed molecular beam (2% HI/ CO_2) propagating at a right angle to a 1 keV electron beam to generate vibrationally and rotationally relaxed anion clusters of the form $I^-(CO_2)_n$. The anions are injected into a Wiley-McLaren type time-of-flight mass spectrometer; a typical mass spectrum is shown in Fig. 1. Anion clusters of the desired mass are photodetached with a properly timed light pulse from a Nd:YAG laser. The fourth (266 nm; 4.66 eV) and fifth (213 nm; 5.82 eV) harmonics of the Nd:YAG were used for these experiments. Energy analysis of the photoelectrons is performed by time-of-flight over a one meter field-free flight tube using microchannel plate detection. The instrumental resolution of the apparatus is 11 meV at 0.65 eV and varies as a function of $(eKE)^{3/2}$ ($eKE \equiv$ electron kinetic energy).

Photoelectron spectra of I^- , $I^-(CO_2)$, and $I^-(CO_2)_2$ taken at $h\nu=4.66$ eV are presented in Fig. 2. Figure 3 shows the photoelectron spectra of $I^-(CO_2)_n$, $n=1-13$, taken with $h\nu=5.82$ eV. The 5.82 eV spectra of $I^-(CO_2)$ and $I^-(CO_2)_2$, compared with the 4.66 eV spectra, demonstrate the dependence of the instrumental resolution on the eKE. The I^- spectrum consists of two peaks corre-

sponding to the $^2P_{3/2}$ ground state and the $^2P_{1/2}$ excited state of the iodine atom; the spin-orbit splitting is 0.943 eV. The $I^-(CO_2)_n$ spectra, in contrast, consist of two groups of peaks. The two bands in each spectrum, separated by approximately the I atom spin-orbit splitting, represent transitions to different electronic states of the neutral cluster which, to first order, can be labeled $I(^2P_{3/2}) \cdot (CO_2)_n$ and $I(^2P_{1/2}) \cdot (CO_2)_n$. The peaks in the $I(^2P_{3/2}) \cdot (CO_2)_n$ band, when they can be resolved at all, are noticeably broader than those in the $I(^2P_{1/2}) \cdot (CO_2)_n$ band at lower eKE. This is partly, but not totally (see below), due to the poorer resolution of the band at higher eKE. The intensities of peaks at very low eKE (<0.3 eV) are reduced due to the cutoff function of the electron detector.⁹

The cluster anion spectra show two important trends relative to the bare I^- spectrum. First, the spectral peaks are located at progressively lower eKE's as the number of CO_2 molecules is increased. This "solvent shift," seen in other $X^-(M)_n$ photoelectron spectra,^{7,8} arises from the stronger attraction of CO_2 to I^- than to an I atom. The cluster size dependence of the solvent shift is shown in Fig. 4.

The more novel characteristic of these spectra is the vibrational progression in each of the bands. The average progression spacing¹⁰ in the $I^-(CO_2)_n$ spectra, 665 ± 90 cm^{-1} (82 meV), is essentially identical to the CO_2 bending

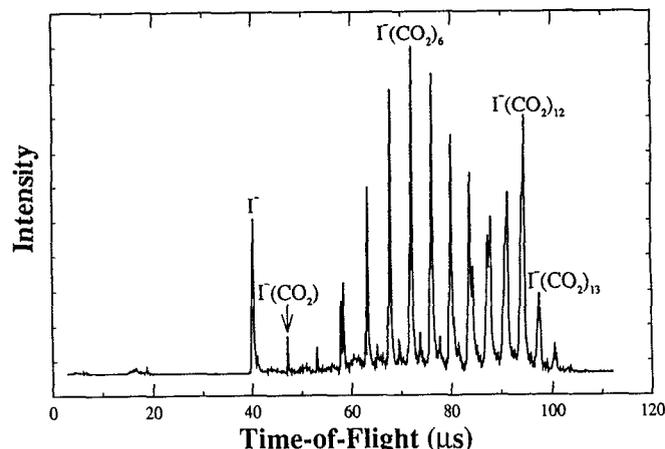


FIG. 1. Time-of-flight mass spectrum obtained after optimization of $I^-(CO_2)_{13}$ signal. Peaks with $n > 3$ are split because of presence of clusters of the type $I^-(HI)_m(CO_2)_{(n-3m)}$.

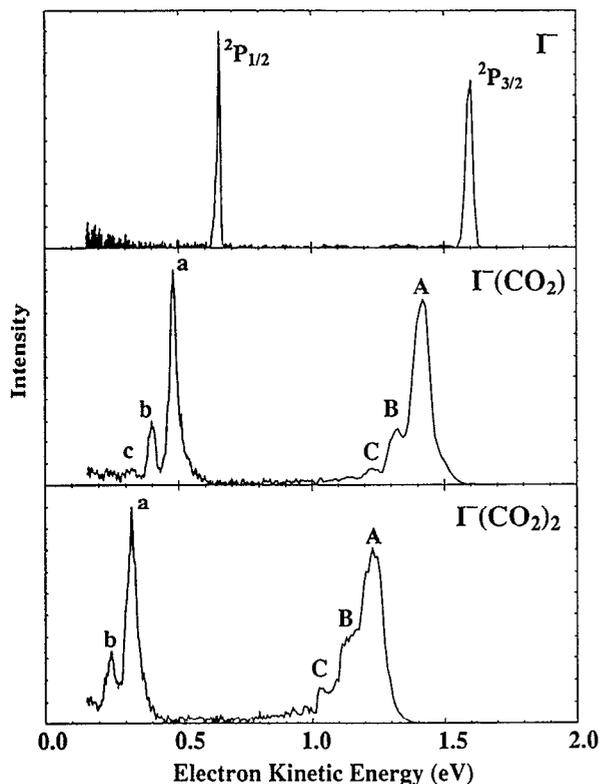


FIG. 2. Photoelectron spectra of I^- , $I^-(CO_2)$, and $I^-(CO_2)_2$ using a 4.66 eV photodetachment energy. The intensity of peak b in the bottom spectrum is artificially low due to the detector cutoff at low eKE.

frequency ($\nu_2 = 667 \text{ cm}^{-1}$).¹¹ This progression becomes more extended in the $I(^2P_{1/2}) \cdot (CO_2)_n$ bands with increasing n up to $n=9$, and the overall shape of the $I(^2P_{3/2}) \cdot (CO_2)_n$ bands indicate a similar trend. Photodetachment of $I^-(CO_2)_n$ apparently results in bending excitation of the CO_2 molecules in the neutral cluster, implying a different OCO angle in the anion and neutral clusters. Since the weak van der Waals interactions in the neutral cluster are unlikely to perturb the CO_2 bond angle, the more likely source of the bend progressions is a distortion of the solvating CO_2 molecules in the anion cluster by the I^- chromophore.

The electrostatic charge-quadrupole interaction present in the $I^-(CO_2)$ anion leads to the formation of a T-shaped, C_{2v} cluster. However, our spectrum implies that the CO_2 is bent in the anion, indicating that long-range electrostatic forces do not fully describe the bonding in the cluster. Since the π_u LUMO of CO_2 is stabilized if the molecule is bent ($\angle OCO = 134^\circ$ and 122° for CO_2^- and the $CO_2 \tilde{A}^1B_2$ excited state, respectively^{12,13}), any charge transfer from the I^- to this LUMO will tend to bend the CO_2 in the anion. The spectrum therefore strongly suggests that some charge delocalization occurs in the anion. We can estimate $\angle OCO$ with a one-dimensional Franck-Condon simulation of the vibrational progression, in which we treat the active mode in the photoelectron spectrum as the CO_2 bending vibration. The best result, shown in the top spectrum in Fig. 3, was obtained with $\angle OCO = 175^\circ$ in

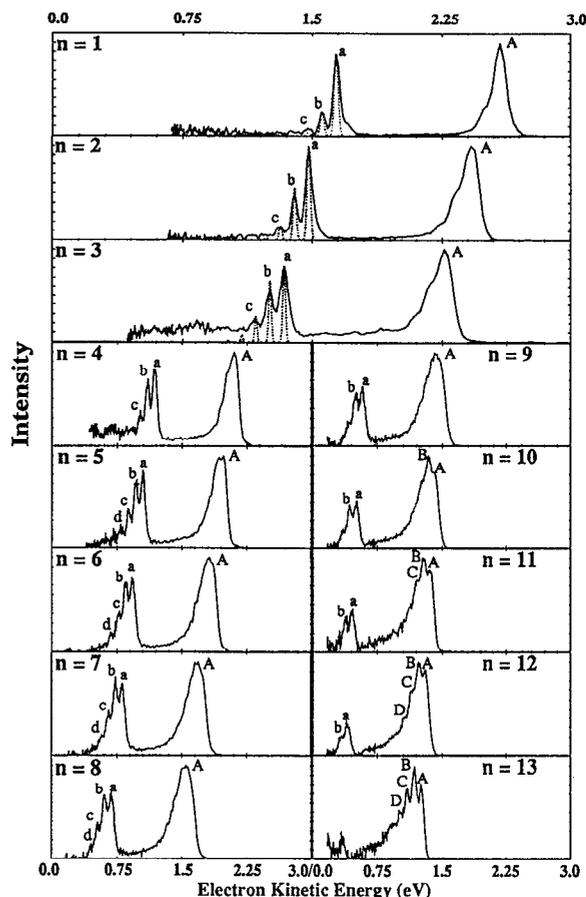


FIG. 3. Photoelectron spectra of $I^-(CO_2)_n$, $n < 13$, using a 5.83 eV photodetachment energy (solid) and simulations (dashed) for $I^-(CO_2)_n$, $n = 1-3$. The simulations assume $\angle OCO = 175^\circ$ and 180° for all anion and neutral clusters, respectively.

the anion. One also might expect the C-I bond length to change upon photodetachment, leading to a progression in the I- CO_2 van der Waals stretch, and we do observe this at higher resolution.¹⁴

Analysis of the larger clusters first requires consideration of their rudimentary structural characteristics. Do the clusters consist of an $I^-(CO_2)$ chromophore sur-

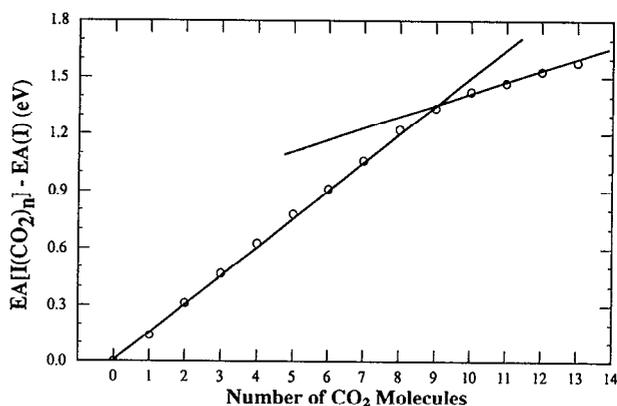


FIG. 4. Plot of $EA[I(CO_2)_n] - EA(I)$ vs the number of CO_2 molecules in the cluster. Note the change in slope at $n=9$.

rounded by more weakly interacting CO₂ molecules, or is the I⁻ anion interacting equally strongly with all the CO₂ molecules in the cluster? The approximately equal energy stabilization (≈ 0.15 – 0.20 eV) by each CO₂ molecule up to I⁻(CO₂)₉ (shown in Fig. 4) supports the idea that in the I⁻(CO₂)–I⁻(CO₂)₉ clusters, the n CO₂ molecules occupy approximately equivalent sites. Structures of this type have been predicted in *ab initio* calculations on Cl⁻(CO₂) _{$n < 4$} clusters.¹⁵ This picture, if correct, must provide a consistent explanation for the observed extension of the CO₂ bend progressions in the photoelectron spectra as the cluster size increases.

As an initial approximation, consider the photodetachment of an I⁻(CO₂) _{n} cluster in which all OCO angles and bond strengths (i.e., force constants) are the same as that of I⁻(CO₂). Photodetachment should excite the collective CO₂ bending mode in the neutral cluster in which all the CO₂ molecules vibrate in phase with each other. The extent of the bend progression in the photoelectron spectrum is determined by $\Delta Q_n^{\text{CO}_2}$, the displacement in the normal coordinate for this in-phase bend, upon photodetachment. For the same change of OCO angle in I⁻(CO₂) _{n} and I⁻(CO₂), one can show that for properly normalized normal coordinates,¹⁶ $\Delta Q_n^{\text{CO}_2}$ is enhanced relative to $\Delta Q_1^{\text{CO}_2}$ by

$$\Delta Q_n^{\text{CO}_2} \approx \sqrt{n} \Delta Q_1^{\text{CO}_2}. \quad (1)$$

Therefore, if the OCO bond angle is independent of n , then Eq. (1) predicts a longer vibrational progression as n increases.

The photoelectron spectra of I⁻(CO₂) _{n} can be simulated using a one-dimensional Franck–Condon analysis with the change in normal coordinate given by Eq. (1). The simulations assuming $\angle \text{OCO} = 175^\circ$ for I⁻(CO₂)₂ and I⁻(CO₂)₃, shown in Fig. 3, indeed reproduce the trend of more extended progressions as n increases. However, the simulation for I⁻(CO₂)₂ slightly overestimates the intensity of peak b in the experimental spectrum (the transition to the $\nu = 1$ bend level in the I(²P_{1/2}) band). The deviation is somewhat larger for I⁻(CO₂)₃. This suggests that we can explain the spectra (for $n < 9$) if we assume that in each cluster, the CO₂ molecules are equivalent with the same OCO bond angle, but that this angle approaches 180° as the size of the cluster increases. This is a reasonable result; one expects the average charge shared by the I⁻ anion with each CO₂ molecule to decrease with increasing n , producing less distortion in each CO₂ molecule.

Another interesting feature in Fig. 3 is the reemergence of vibrational structure in the I(²P_{3/2}) band for $n > 10$. This structure becomes progressively more pronounced up to $n = 13$, the largest cluster studied, for which the peak widths of the I(²P_{3/2}) band are about 70 meV. While the resolution of the apparatus does improve at lower eKE's, this is not sufficient to explain the absence of resolved peaks in the $n = 9$ spectrum and their emergence in the $n > 10$ spectra. The resolution at the eKE of the I(²P_{3/2}) band improves only slightly, from 30 meV for I⁻(CO₂)₉ to 25 meV for I⁻(CO₂)₁₃, and both of these values are considerably less than the nominal peak spacing of 82 meV.

We are therefore observing a progressive narrowing of the vibrational features in the I(²P_{3/2}) band for $n > 10$. On the other hand, the peak widths in the I(²P_{1/2}) band (~ 60 meV) appear to be largely independent of n up to $n = 12$, so this peak narrowing effect appears to be state specific.

A possible explanation of this effect is as follows. When an I atom in its ²P_{3/2} state interacts with another closed-shell atom or molecule, the atomic state degeneracy is removed, yielding two levels with $\Omega = 1/2$ and $3/2$.¹⁷ If this fine structure splitting is smaller than the CO₂ bend frequency, but is not resolved in the experimental spectrum, then the vibrational peaks in the I(²P_{3/2}) band will consist of overlapping transitions to the two Ω values and will be somewhat broader than those in the I(²P_{1/2}) band. Higher resolution spectra of I⁻(CO₂) recently obtained in our laboratory confirm that the peaks in the I(²P_{3/2}) band are split by this interaction.¹⁴ A similar effect was seen in the photoelectron spectra of the XHI⁻ bihalide anions [X = F, Cl, and Br].¹⁸

These considerations may explain why the peaks in the I(²P_{3/2}) band are broader in many of the cluster spectra. They also suggest a possible reason for the gradual reappearance of structure in this band for $n > 10$, namely, that the solvating CO₂ molecules are beginning to form a shell of sufficient symmetry so that the fine structure splitting decreases. In this case, the continual narrowing of the peaks implies that the shell closing occurs at $n > 13$. This is a reasonable value in light of photodissociation experiments of Lineberger and co-workers¹⁹ on Br₂⁻(CO₂) _{n} and I₂⁻(CO₂) _{n} that indicate shell closings at $n = 14$ and $n = 16$, respectively. However, it is not consistent with the solvent shift results in Fig. 4 or the mass spectrum in Fig. 1. The solvent shift plot shows the stabilization energy per additional CO₂ molecule is noticeably smaller above $n = 9$ than below, implying a shell closing at $n = 9$. On the other hand, the mass spectrum in Fig. 1 implies that I⁻(CO₂)₁₂ is particularly stable. Of these three observations, the mass spectrum is perhaps the most prone to misinterpretation; using an ion source similar to ours, Johnson^{5(a)} found little correlation between mass intensity distributions and (CO₂) _{n} ⁻ structures, indicating that the anomalous mass spectral intensities may result from kinetic rather than thermodynamic effects. The solvent shift results are more difficult to explain, but it is interesting to note that the reemergence of vibrational structure in the I(²P_{3/2}) band occurs just beyond where the solvent shifts predict a shell closing. Thus, while several aspects of the data suggest the formation of such a shell is plausible, the number of CO₂ molecules which comprise the shell is unclear.

In summary, we have presented photoelectron spectra of clusters of the form I⁻(CO₂) _{$n < 13$} . The spectra exhibit vibrational progressions in the CO₂ bending mode which result from distortion of the solvent CO₂ molecules by I⁻ core. This distortion results from a small amount of charge delocalization from the I⁻ core to the surrounding solvent molecules. As the cluster size increases, the length of the CO₂ bending progression grows. This trend is explained in terms of a simple model in which all the CO₂ molecules in a given cluster anion have the same bond angle; this angle

gradually approaches 180° with increasing n . The vibrational features in the $I(^2P_{3/2}) \cdot (CO_2)_n$ band become progressively better resolved for $n > 9$. We propose that this structure results from effects accompanying formation of a closed solvation shell of at least nine CO_2 molecules around the iodine atom. Similar experiments have been performed in our laboratory for the other halogen-carbon dioxide clusters which exhibit a wide range of charge transfer from the halogen to the CO_2 molecule.²⁰ The results form an interesting chapter in research on solute/solvent interactions and their evolution as a function of cluster size.

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¹⁰Average value obtained from resolved vibrational progression spacings. Excited state peaks for both 4.66 eV spectra and $I^-(CO_2)_{n < 11}$ 5.82 eV spectra were used along with ground state peaks for $n > 12$. All of the individual spacings easily fall within the experimental error bar of 90 cm^{-1} .

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