COMMUNICATIONS

Characterization of the I$_3$ radical by anion photoelectron spectroscopy

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The ground and first excited states of the I$_3$ radical are characterized by photoelectron spectroscopy of I$_3^-$ and Ar·I$_3^-$ at 266 nm. The electron affinity of I$_3$ is 4.226±0.013 eV. Based on the recently determined bond dissociation energy of I$_3^-$, the I$_3$ ground state is bound by 0.143±0.06 eV. The first excited state of I$_3$ lies 0.27 eV above the ground state. A vibrational progression is seen in the ground state band of the I$_3^-$ photoelectron spectrum. The addition of an argon atom to I$_3^-$ reduces the contribution of hot bands to the photoelectron spectrum, facilitating the interpretation of the vibrational structure. Simulations indicate that the I$_3$ ground state is linear with a symmetric stretch frequency of 115±5 cm^{-1} and is likely to be centrosymmetric. © *1999 American Institute of Physics.* [S0021-9606(99)02016-4]

INTRODUCTION

The triiodine radical, I$_3$, has been proposed to play a key role in one of the most fundamental reactions in gas phase kinetics, the recombination of I atoms to form I$_2$, via the following mechanism:[1–6]

$$I + I_2 \rightarrow I_3,$$
$$I + I_3 \rightarrow 2I_2. \qquad (1)$$
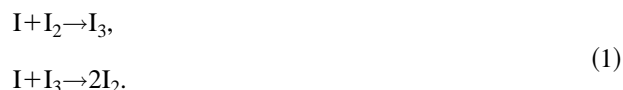
However, in spite of considerable effort,[7] neither I$_3$ nor any other homonuclear trihalogen (X$_3$) has ever been spectroscopically identified. In fact, the only gas-phase experimental evidence that any of these species is thermodynamically stable comes from the mass-spectrometric observation of Br$_3$ as a photodissociation product from (Br$_2$)$_2$.[8]

In this Communication we use anion photoelectron spectroscopy of I$_3^-$ to show that I$_3$ is a covalently bound molecule and probe its vibrational spectroscopy. Further, we demonstrate that the contribution of hot bands to the photoelectron spectrum is reduced by the addition of an argon atom to form the Ar·I$_3^-$ cluster. This results in a clearer analysis of vibrational structure in the photoelectron spectrum of I$_3^-$ than would otherwise be possible.

Several other studies have indirectly estimated the thermodynamic stability of triiodine.[3–5] Because iodine is the least electronegative halogen, I$_3$ should be the most stable trihalogen and is the most likely to be linear.[9,10] There are no high level *ab initio* calculations available for I$_3$, however, calculations by Morokuma and co-workers[7] on isovalent Cl$_3$ show its ground state to be a highly asymmetric Cl·Cl$_2$ van der Waals complex with a low-lying linear, centrosymmetric excited state.

The triiodide anion is considerably better characterized than the I$_3$ radical. I$_3^-$ is a hypervalent 22 electron triatomic violating the Lewis octet rule. In Walsh's 1953 paper,[9] I$_3^-$ was predicted to be linear and all subsequent *ab initio* calculations have shown that it is both linear and centrosymmetric.[11–19] While many experimental studies of I$_3^-$ have been performed, nearly all of these have been limited to the solid and solution phases. In the gas phase, Do *et al.*[20] recently carried out collision induced dissociation experiments in which they determined the I$^-$+I$_2$ binding energy to be 1.31±0.06 eV. Time-resolved studies of I$_3^-$ photodissociation in the gas phase have recently been carried out in our laboratory;[21] in that work, a low-resolution photoelectron spectrum of I$_3^-$ was presented. The higher resolution work presented here offers a much more detailed picture of the energetics and spectroscopy of I$_3$.

EXPERIMENT

The anion photoelectron spectrometer used in this study has been described in detail previously.[22,23] In the work presented here, argon carrier gas (2 psig) is passed over crystalline I$_2$ and supersonically expanded through a pulsed piezoelectric valve. Anions are generated by crossing a 1 keV electron beam with the molecular beam. The negative ions pass through a skimmer into a differentially pumped region. They are extracted perpendicular to their flow direction by a pulsed electric field and injected into a linear reflectron time-of-flight (TOF) mass spectrometer,[24,25] affording a mass resolution $m/\Delta m$ of 2000. The ions of interest are selectively photodetached with the fourth harmonic of a pulse Nd:YAG laser (266 nm, $h\nu = 4.657$ eV). The electron kinetic energy (eKe) distribution is determined by TOF analysis. The energy resolution is 8 meV at 0.65 eKE and degrades as (eKE)$^{3/2}$ at higher eKE. The laser polarization can be rotated by means of a half-wave plate defining a polarization angle θ as the angle between the electric vector of the photon and the direction of electron detection.
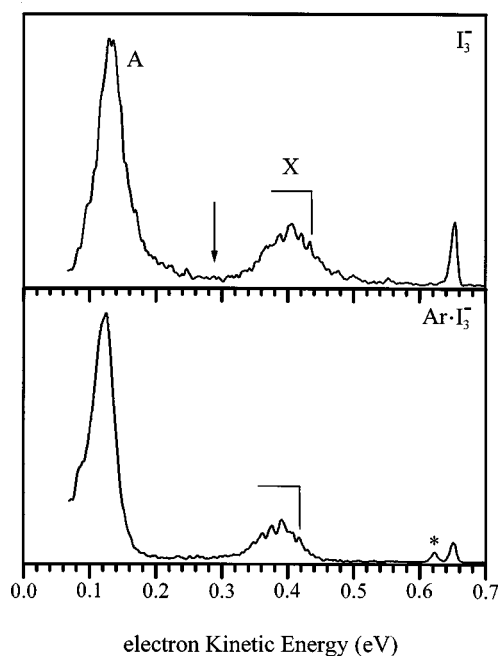
FIG. 1. Photoelectron spectrum of I_3^- (top) and $Ar \cdot I_3^-$ (bottom) taken at the photodetachment wavelength of 266 nm (4.657 eV). Laser polarization angle is 90° with respect to the direction of electron collection.

RESULTS

Figure 1 shows the anion photoelectron spectra of I_3^- (top) and $Ar \cdot I_3^-$ (bottom) taken at 266 nm (4.657 eV) and a polarization angle of $\theta = 90°$. In these photoelectron spectra the electron kinetic energy, eKE, is related to the internal energy of the neutral and anion by $eKE = h\nu - EA - E^0 + E^-$. Here $h\nu$ is the photon energy, EA is the adiabatic electron affinity, E^0 is the internal energy of the neutral, and E^- is the internal energy of the anion.

The three features observed in the photoelectron spectrum of I_3^- are centered at 0.652, 0.402, and 0.132 eV eKE. The highest energy feature is due to a two-photon process, photodissociation of I_3^- to form $I^- + I_2$ followed by photodetachment to the $^2P_{1/2}$ spin–orbit state of atomic iodine (photodetachment to the $^2P_{3/2}$ state is observed but not shown in Fig. 1). Features X and A at lower eKE correspond to detachment to the ground and first excited states of I_3, respectively. We estimate the energy separation between features X and A to be 0.27 eV by taking the difference in the vertical detachment energies. Feature X is 60 meV wide showing a partially resolved vibrational progression with a frequency of ~14 meV. Feature A is 40 meV wide and shows no vibrational structure. Comparison with the photoelectron spectrum taken at $\theta = 0°$ yields anisotropy parameters β of -0.7 and -0.4 for features X and A, respectively.[26]

The bottom panel of Fig. 1 shows the anion photoelectron spectrum of the $Ar \cdot I_3^-$ cluster. In this cluster, the internal energy of the I_3^- moiety must be less than the dissociation energy, or predissociation to $Ar + I_3^-$ will occur. As a result, features X and A are narrower, the baseline between them is flatter, and the vibrational structure in feature X is more regular and somewhat better-resolved. These effects are all attributed to a vibrationally colder I_3^- chromophore; similar

results were seen in the photoelectron spectrum of $Ar \cdot I_2^-$.[27] In the $Ar \cdot I_3^-$ photoelectron spectrum, features X and A are centered at slightly lower eKEs, 0.385 eV and 0.121 eV, respectively, due to stronger binding of the argon in the anion than in the neutral.

In addition to the three features seen in the I_3^- spectrum, the $Ar \cdot I_3^-$ spectrum shows a peak 28 meV below the I $^2P_{1/2}$ two-photon feature labeled with an (∗). This peak is from detachment of $Ar \cdot I^-$, which is known to have an electron affinity 26.7 meV higher than that of I^-.[28] Hence, both $Ar \cdot I^-$ and I^- result from photodissociation of $Ar \cdot I_3^-$ at 266 nm in about a 1:2 ratio.

DISCUSSION

First we show that the ground state of I_3 is bound with respect to dissociation. Any feature in the photoelectron spectrum at a higher electron kinetic energy than $eKE_{max} = h\nu - D_0(I_2 \cdots I^-) - EA(I)$ corresponds to a transition to a state of I_3 that lies below the $I + I_2$ asymptote. From the I_3^- dissociation energy of 1.31 ± 0.06 eV measured by Do et al.[20] and the electron affinity of atomic iodine, 3.059 038 eV,[29] we find $eKE_{max} = 0.288 \pm 0.06$ eV. This energy is indicated with an arrow in the top panel of Fig. 1. Feature X lies entirely above this value, so the ground state of I_3 is thermodynamically stable.

The vibrational structure in feature X of the I_3^- spectrum is somewhat irregular, and it is not obvious where the origin lies. Contributions from vibrational hot bands are considerably reduced in the $Ar \cdot I_3^-$ spectrum, so the intensity should fall off more rapidly to the high eKE side of the origin in the $Ar \cdot I_3^-$ spectrum than in the I_3^- spectrum. Based on this expectation and the fairly clear correspondence between several vibrational features in the two spectra, the vibrational origins are assigned as shown in Fig. 1.

Feature X in the $Ar \cdot I_3^-$ spectrum shows a vibrational progression of 115 cm^{-1}. No experimental or theoretical frequencies of I_3 are available for the purpose of assigning this progression. A recent calculation of the I_3^- vibrational frequencies at the CCSD(T) level of theory[18] yields $\omega_1 = 107.8$ cm^{-1}, $\omega_2 = 58.2$ cm^{-1}, and $\omega_3 = 129.3$ cm^{-1}, suggesting that the active I_3 mode is a stretching mode rather than the bending mode. This indicates that the neutral is linear, since the anion is linear. If I_3 were linear but highly asymmetric, such as the $Cl \cdot Cl_2$ van der Waals complex predicted to be the ground state for Cl_3,[7] then one would expect an extended progression in the I_2 stretch with a frequency comparable to that of diatomic I_2, 214 cm^{-1}, which is clearly too high. On the other hand, if I_3 were linear and centrosymmetric, the dominant progression would be in the symmetric stretching mode. This is the most reasonable interpretation of the observed 115 cm^{-1} progression, although a small barrier at the centrosymmetric geometry cannot entirely be ruled out.

Figure 2 shows a Franck–Condon simulation of the $Ar \cdot I_3^-$ spectrum superimposed on the experimental data. Only the symmetric stretch was considered; the gas phase value of 112 cm^{-1} for I_3^- was used here.[21] The simulation
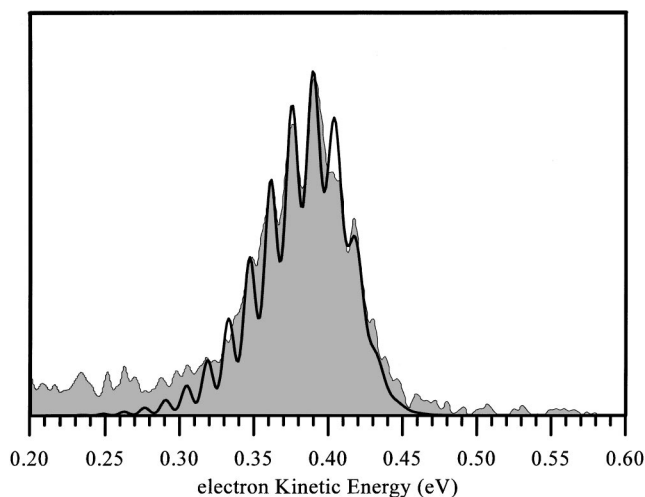
FIG. 2. Simulation of the $Ar \cdot I_3^-$ photoelectron spectrum (solid line) superimposed on the experimental data (gray filled area).

yields a neutral frequency of 115 ± 5 cm^{-1}, a vibrational temperature of 95 K, and an electron affinity of 4.239 ± 0.010 eV for $Ar \cdot I_3$.

The best simulation of the I_3^- spectrum (using a single vibrational mode) was obtained by shifting the origin by $+13 \pm 3$ meV and increasing the vibrational temperature to 205 K. However, agreement with experiment was not nearly as good as in the $Ar \cdot I_3^-$ spectrum, presumably because of increased contributions from sequence bands involving excited bending and antisymmetric stretching modes in the anion. Nonetheless, on the basis of the origin shift we find the electron affinity of I_3 to be 4.226 ± 0.013 eV. The electron affinity has been experimentally estimated by Do et al.[20] to be 4.15 ± 0.12 eV and theoretically estimated to be 3.6 eV at the X_α DVM level by Gutsev.[15] With our measurement of the electron affinity the dissociation energy D_0 for $I_3 \rightarrow I_2 + I$ is 0.143 ± 0.06 eV. This value can be compared with the experimental estimates of 0.23 and 0.24 eV by Blake et al.[5] and Bunker et al.,[3] respectively.

The increase in electron affinity of I_3 upon addition of an Ar atom, 13 meV, is considerably less than the increases for I and I_2, which are 26.7 and 29.4 meV, respectively.[27,28] These shifts are related to the difference in the neutral and anion solvation energies via

$$EA(Ar \cdot I_p) - EA(I_p) = SE(Ar \cdot I_p^-) - SE(Ar \cdot I_p), \quad p = 1-3, \quad (2)$$

where $SE(Ar \cdot I_p^-)$ and $SE(Ar \cdot I_p)$ are defined as the Ar binding energies in the anion and neutral complexes, respectively, and p indicates the number of iodine atoms. The anomalously small shift for $Ar \cdot I_3$ suggests that the anion solvation energy is considerably lower than for the smaller species. In $Ar \cdot I^-$ and $Ar \cdot I_2^-$, the Ar atom is adjacent to all I atoms in the anion ($Ar \cdot I_2^-$ is T-shaped) and can interact strongly with all charge centers. However, the HOMO in I_3^- is a nonbonding π_u orbital with a node at the central I atom.[30] Thus, regardless of whether the Ar atom is bonded to the central I atom or one of the end atoms, its overall interaction with the excess charge on the I_3^- should be weaker than in $Ar \cdot I^-$ or $Ar \cdot I_2^-$, consistent with the experimental results.

In this Communication we have shown that the ground state of I_3 is stable and have characterized its vibrational spectroscopy, dissociation energy, and electron affinity via photoelectron spectroscopy of I_3^-. Furthermore, we have shown that the addition of an argon atom significantly cools the I_3^- chromophore, resulting in better-resolved vibrational structure in the photoelectron spectrum. This may prove invaluable in investigating the photoelectron spectroscopy of other anions in which progressions in low-frequency vibrations occur.

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