

# Solvent effects on the vibrational frequency of $I_2^-$ in size-selected $I_2^-(Ar)_n$ and $I_2^-(CO_2)_n$ clusters

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(Received 10 August 1998; accepted 30 September 1998)

The vibrational frequency of the  $I_2^-$  chromophore in size-selected  $I_2^-(Ar)_n$  and  $I_2^-(CO_2)_n$  clusters has been measured to wave-number accuracy. The frequencies are determined by creating a coherent superposition of vibrational levels with a femtosecond laser pulse via a resonance impulsive stimulated Raman scattering process. The resulting wave-packet oscillations are detected with femtosecond photoelectron spectroscopy. Blueshifting of the frequency occurs upon solvation, with larger shifts observed for solvation with  $CO_2$ . The nature of the shifting is discussed and related to specific cluster geometries. © 1998 American Institute of Physics.

[S0021-9606(98)02246-6]

## INTRODUCTION

Solvation plays a dramatic role in chemical physics, and its effect on the photodissociation dynamics, branching ratios, and product energy distributions has been explored in experiments with chromophores solvated in liquids,<sup>1-5</sup> solids,<sup>6-10</sup> and size-selected clusters.<sup>11-14</sup> Solvation not only has the ability to remove energy and redirect motion on potential surfaces, but can also modify the potentials themselves. One way to quantify this effect is to monitor the frequency shift of a chromophore as a function of cluster size, as has been done in high-resolution studies of  $Ar_nHF$ .<sup>15-18</sup> Presumably, when enough solvent species are attached, the frequency will match that of the chromophore in a condensed phase environment.<sup>19,20</sup> However, in neutral species it is difficult to determine unambiguously the number of solvent atoms for larger clusters. In studies of ion clusters, on the other hand, there is no ambiguity concerning the size of the clusters since they are readily mass selected. In addition, the solvent-solute interactions are considerably stronger than in van der Waals clusters. In this communication we probe the effects of solvation on the ground electronic state of a diatomic anion by measuring the vibrational frequency of  $I_2^-$  in size-selected  $I_2^-(Ar)_{n=6,12,18}$  and  $I_2^-(CO_2)_{n=4,9}$  clusters.

This work represents an extension of earlier experiments in which the vibrational frequency of bare  $I_2^-$  was determined using resonance impulsive stimulated Raman scattering (RISRS) with femtosecond lasers.<sup>21</sup> We showed that by inducing coherent motion on the ground state of  $I_2^-$  with a femtosecond pump pulse and measuring the resulting oscillatory motion with femtosecond photoelectron spectroscopy (FPES), the ground-state vibrational frequency can be obtained. This information was combined with results from conventional photoelectron spectroscopy to construct an accurate Morse potential for the ground state of  $I_2^-$ . In this communication we use this method to investigate  $I_2^-$  embed-

ded in Ar and  $CO_2$  clusters, and monitor the shift of vibrational frequency with wave-number accuracy. Our results show that solvation generally results in a blueshifting of the  $I_2^-$  vibrational frequency; the blueshift increases with both the number of solvent species and the strength of the chromophore-solvent interaction. Comparison of the experimental shifts with calculated structures for these clusters suggests that the size of the shift is sensitive not only to the number of solvent species but also their configuration with respect to the  $I_2^-$  chromophore.

## EXPERIMENT

The femtosecond photoelectron spectrometer has been described previously, and only a brief summary will be given here.<sup>21,22</sup> Argon carrier gas [seeded with 1.5%  $CO_2$  when producing  $I_2^-(CO_2)_n$  clusters] is passed over crystalline  $I_2$  and supersonically expanded through a pulsed piezoelectric valve operating at a repetition rate of 500 Hz. Anions are generated by crossing the expansion with a 1 keV electron beam and are mass selected using a Wiley-McLaren time-of-flight mass spectrometer. After passing through several differentially pumped regions, the ions enter the detector chamber and are intercepted by the femtosecond pump and probe laser pulses at the focus of a ‘‘magnetic bottle’’ time-of-flight photoelectron spectrometer. Both laser pulses are generated using a commercial Ti:sapphire oscillator-regenerative amplifier laser system (CLARK-MXR). The pump pulse is centered at 780 nm with a full width at half maximum (FWHM) duration of 75 fs (sech<sup>2</sup>). A portion of the pump pulse is split off and frequency tripled to give a probe pulse at 260 nm with a FWHM of 105 fs.

## RESULTS AND DISCUSSION

As has been described earlier,<sup>21</sup> the pump pulse is in resonance with the  $I_2^-(\tilde{A}'^2\Pi_{g,1/2}) \leftarrow I_2^-(\tilde{X}^2\Sigma_u^+)$  transition. This transfers population from the  $\tilde{X}$  state to the  $\tilde{A}'$  excited electronic state. However, the pump pulse also creates a co-

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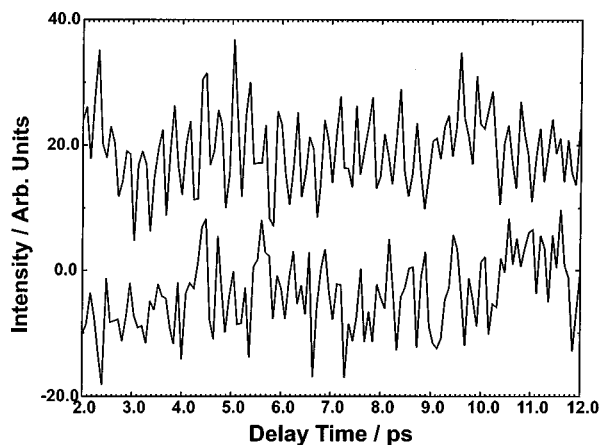


FIG. 1. Photoelectron spectra as a function of time for bare  $I_2^-$  (upper) and  $I_2^-(CO_2)_9$  (lower). The spectra are shown at electron kinetic energies of 1.45 and 0.95 eV, respectively. The oscillations are caused by coherent wave-packet motion on the electronic ground state induced by the femtosecond pump pulse.

herent superposition of vibrational states on the ground electronic state via a second-order Raman process,<sup>23–27</sup> resulting in oscillatory wave-packet motion that is apparent in the time-resolved photoelectron spectra. Figure 1 shows these oscillations for bare  $I_2^-$  and  $I_2^-(CO_2)_9$  (upper and lower spectra, respectively) taken in 80 fs steps, at electron kinetic energies of 1.45 and 0.95 eV, respectively. In bare  $I_2^-$  the oscillations are clearly apparent with a period of approximately 300 fs. For  $I_2^-(CO_2)_9$ , the oscillations are less pronounced but still apparent, with a similar period of approximately 300 fs.

Vibrational frequencies are obtained by taking the Fourier transform of the photoelectron data at the electron energy where the oscillations are most evident. For all the clusters, spectra were taken at 80 fs steps out to time delays ranging from 11 to 17 ps. Shown in Fig. 2 is the Fourier transform from our previously reported experiment on bare  $I_2^-$ , yielding a frequency of  $110.0 \pm 2.0 \text{ cm}^{-1}$  (solid).<sup>21</sup> Also shown in Fig. 2 are the Fourier transforms obtained from

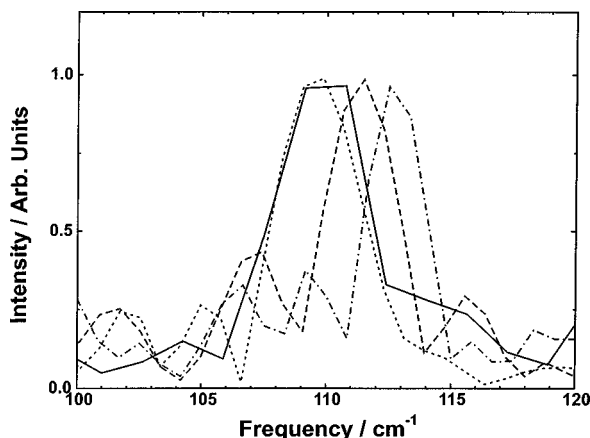


FIG. 2. Fourier transforms of oscillatory photoelectron data yielding vibrational frequencies for  $I_2^-(Ar)_n$ :  $n=6$  (dot),  $n=12$  (dashed), and  $n=18$  (dot dashed), determined at electron kinetic energies of 1.38, 1.30, and 1.25 eV, respectively. The previously reported result for bare  $I_2^-$  is also shown (solid) for comparison.

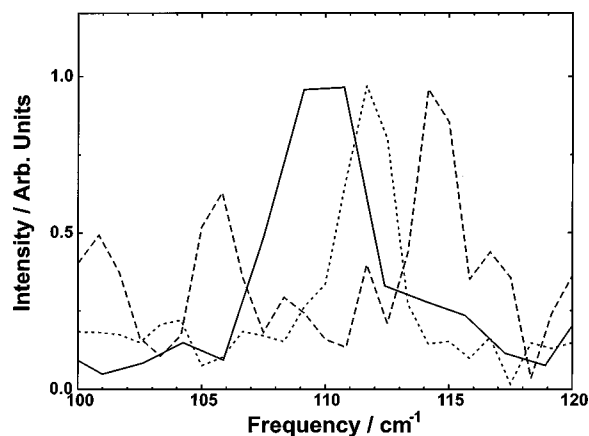


FIG. 3. Fourier transforms of oscillatory photoelectron data yielding vibrational frequencies for  $I_2^-(CO_2)_n$ :  $n=4$  (dot) and  $n=9$  (dashed), determined at electron kinetic energies of 1.08 and 0.95 eV, respectively. The previously reported result for bare  $I_2^-$  is also shown (solid) for comparison.

$I_2^-(Ar)_6$ ,  $I_2^-(Ar)_{12}$ , and  $I_2^-(Ar)_{18}$  clusters, indicating frequencies of  $109.7 \pm 2.0$ ,  $111.4 \pm 1.7$ , and  $112.7 \pm 1.5 \text{ cm}^{-1}$ , respectively. Within our resolution, the  $I_2^-(Ar)_6$  frequency is indistinguishable from that of bare  $I_2^-$ , while the  $I_2^-(Ar)_{12}$  and  $I_2^-(Ar)_{18}$  frequencies are progressively shifted to higher values. The Fourier transform of bare  $I_2^-$  is again shown in Fig. 3, along with the Fourier transforms obtained from  $I_2^-(CO_2)_4$  and  $I_2^-(CO_2)_9$ . The two clusters show frequencies of  $111.7 \pm 1.5$  and  $114.5 \pm 1.1 \text{ cm}^{-1}$ , respectively. Both are blueshifted with respect to bare  $I_2^-$ , and the degree of shifting is more pronounced than for the argon clusters, i.e., four  $CO_2$  molecules produces the same blueshift as 12 Ar atoms. The larger effect of  $CO_2$  is not surprising, given the considerably stronger binding energy of  $I_2^-$  to  $CO_2$  vs Ar; the dissociation energy of  $I_2^-Ar$  is 53 meV, whereas the average binding energy per  $CO_2$  is 240 meV for  $I_2^-(CO_2)_{n=10-22}$ .<sup>11,28</sup>

The sign of the shift and its dependence on the number of solvent species is more intriguing. Blueshifting of the  $I_2^-$  vibrational frequency can arise from electrostatic chromophore–solvent interactions, which can be visualized more easily by considering the calculated minimum energy structures<sup>29–32</sup> for the clusters shown in Fig. 4. In  $I_2^-(Ar)_6$ , the Ar atoms form a ring about the  $I_2^-$  bond.<sup>31,32</sup>  $I_2^-(Ar)_{12}$  is a ‘half-solvated’ species in which one I atom is surrounded by Ar atoms, while in  $I_2^-(Ar)_{18}$  the solvent atoms form a nearly complete shell around the  $I_2^-$  (shell closure<sup>33</sup> is expected for  $n=20$ ). As the  $I_2^-$  bond stretches during the course of a vibration, I atoms will collide with Ar atoms lying along or near the  $I_2^-$  internuclear axis; the  $I_2^-$  outer turning point is approximately 0.07 Å longer in the  $\nu=1$  level compared to the ground state. One might, therefore, expect this repulsive interaction to effectively steepen the potential at the outer turning point of the  $I_2^-$  vibration, resulting in bond compression and a higher vibrational frequency.

This picture is consistent with the trends in vibrational frequency. In  $I_2^-(Ar)_6$ , there are no Ar atoms along the internuclear axis, and no blueshift is observed. The structures in Fig. 4 show that the I atoms are progressively more con-

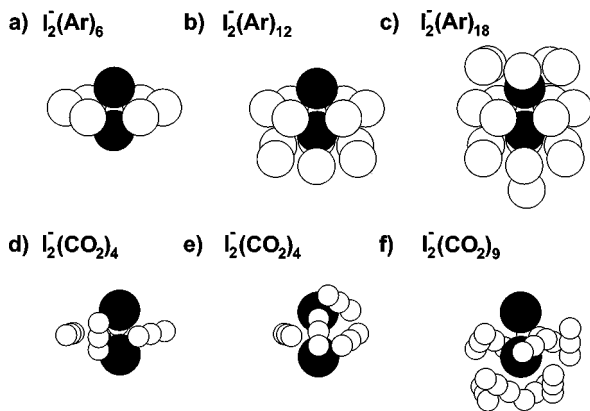


FIG. 4. Minimum energy structures for  $I_2^-(Ar)_n$  and  $I_2^-(CO_2)_n$  clusters (Refs. 29–32). For  $n=4$ , the ring and asymmetrical structures are both shown [(d) and (e), respectively]. The  $CO_2$  molecules are reduced in size for clarity.

fined along the internuclear axis for the  $n=12$  and  $n=18$  clusters, while the blueshifts are 1.4 and 2.7  $cm^{-1}$ , respectively. Note that the blueshift in  $I_2^-(Ar)_{18}$  is less than the  $\sim 5$   $cm^{-1}$  shift seen in an Ar matrix,<sup>34</sup> suggesting that the vibrational frequency in the clusters will continue to increase as a second solvent shell is added.

We, therefore, attribute the trends in vibrational frequency for  $I_2^-(Ar)_n$  clusters to repulsive interactions between the chromophore and solvent. Although attractive anion–solvent interactions could also play a role, it is difficult to understand the absence of a blueshift in  $I_2^-(Ar)_6$  in terms of attractive forces alone. Moreover, in the larger clusters studied here, one might expect attractive anion–solvent forces to soften the  $I_2^-$  potential for  $R > R_e$ , resulting in a redshifted vibrational frequency.<sup>17,18</sup>

The situation for  $I_2^-(CO_2)_n$  clusters is more complex. Two calculated minimum energy structures for  $I_2^-(CO_2)_4$  along with that for  $I_2^-(CO_2)_9$  are shown in Fig. 4.<sup>29,30,35</sup> While the ring structure in Fig. 4(d) was originally calculated to be the ground state for  $I_2^-(CO_2)_4$ ,<sup>29</sup> Parson and co-workers<sup>35</sup> find the asymmetric structure in Fig. 4(e) to be more stable by 30 meV. In  $I_2^-(CO_2)_9$ , one of the I atoms is completely solvated, as in the  $I_2^-(Ar)_{12}$  structure, and one can explain the blueshift in terms of repulsive anion–solvent interactions as described above. It is more difficult to do this for either  $I_2^-(CO_2)_4$  structure, particularly the ring. On the other hand, attractive interactions with the equatorial  $CO_2$  molecules could be sufficiently strong to compress the  $I_2$  bond, leading to a picture in which the blueshifts are due to a combination of attractive interactions with the equatorial  $CO_2$  molecules and repulsive interactions with the axial  $CO_2$  molecules.

Another possible origin for the blueshift is electron delocalization into the solvent species. The highest occupied molecular orbital in  $I_2^-$  is an antibonding  $\sigma_u^*$  orbital. Any electron delocalization would reduce the electron density in this orbital, thereby reducing the bond length and increasing the vibrational frequency. Electron delocalization in  $I_2^-(Ar)_n$  clusters seems unlikely, but it is more difficult to rule out in the  $I_2^-(CO_2)_n$  clusters, where the anion–neutral binding is stronger. Our previous study of the photoelectron spectra of

$I^-(CO_2)_n$  showed that the anion–neutral interaction was strong enough to bend the  $CO_2$  molecule by several degrees.<sup>36</sup> This could be explained solely by interaction of the  $I^-$  negative charge with the  $CO_2$  quadrupole moment, without including any electron transfer. Since the  $I_2^-CO_2$  binding energy is lower than that of  $I^-CO_2$ ,<sup>36,37</sup> we expect minimal charge delocalization in  $I_2^-(CO_2)_n$  clusters as well. Nonetheless, even a small amount of delocalization could result in blueshifts on the order of those seen here.

To summarize, we have demonstrated that our RISRS/FPES experiment yields relatively high-resolution vibrational spectra on large, size-selected ion clusters. Specifically, we find that clustering of  $I_2^-$  with Ar and  $CO_2$  results in a blueshift of the  $I_2^-$  frequency. The frequency shifts in  $I_2^-(Ar)_n$  clusters are attributed to repulsive anion–solvent interactions with axial or near-axial Ar atoms. These interactions most likely play a role in  $I_2^-(CO_2)_n$  clusters, but may be complemented by attractive interactions with equatorial solvent molecules and electron delocalization effects. These qualitative ideas can be explored more thoroughly with the aid of molecular dynamics simulations, and we hope the results presented here will stimulate such investigations. We plan to perform these experiments over a wider range of cluster sizes, and will vary both the anion and solvent species in order to gain a more complete picture of the trends in vibrational frequency with solvation.

## ACKNOWLEDGMENTS

This research is supported by the National Science Foundation under Grant No. CHE-9710243. Support from the Defense University Research Instrumentation Program under Grant No. F49620-95-1-0078 is also gratefully acknowledged. The authors would also like to thank Victor Batista, Marilyn Jacox, Jim Faeder, and Robert Parson for helpful suggestions.

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