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A REMPI study of styrene$(Ar)_n$, $n = 4$–12 clusters

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Abstract

New experimental spectra for styrene$(Ar)_n$, $n = 4$–12 clusters have been recorded using the technique of resonant one-color two-photon ionization and time-of-flight mass spectrometry. Transition energies and spectral shifts relative to styrene have been determined and are reported. These spectra are discussed in terms of progressive solvation dynamics. © 2000 Published by Elsevier Science B.V.

1. Introduction

An understanding of microsolvation at the molecular level has been a long-term goal of cluster science. An important area of this research has been the study of the interaction of aromatic molecules with small solvent molecules [1,2]. There are two aspects to these studies. One is a detailed understanding of the positions and interactions of the first few solvent molecules [3–5]. Another aspect, however, is the stepwise evolution of this interaction over the addition of a sufficiently large number of solvent molecules [6–9]. This will give insight into the variation of interactions as the system evolves to the solvated state.

Styrene and substituted styrenes have been useful in several of these studies [10–17]. The unsaturated side chain provides a site for π interaction with solvent molecules, in competition with the aromatic ring. However it does not substantially increase the polarity of the aromatic compound, as do the amine or chlorine substituents in aniline and chlorobenzene.

Resonance enhanced multiphoton ionization spectroscopy (REMPI) and time-of-flight mass spectrometry (TOF-MS) have contributed significantly in these studies. The REMPI technique allows energetic information about the interaction to be extracted. Time-of-flight mass spectrometry provides a means of relating this energetic information to a particular cluster size, and permits the variation in the energetics with varying cluster size to be studied. Generally, in these techniques, clusters of the species under study are produced using either a pulsed or cw supersonic expansion nozzle source. The clusters are resonantly excited with pulsed laser light and then ionized using either the same pulsed laser light source (one color), or a second pulsed laser (two color). We have recorded one color REMPI spectra of styrene$(Ar)_n$, $n = 4$–12 clusters using a recently constructed REMPI-TOF-MS apparatus.

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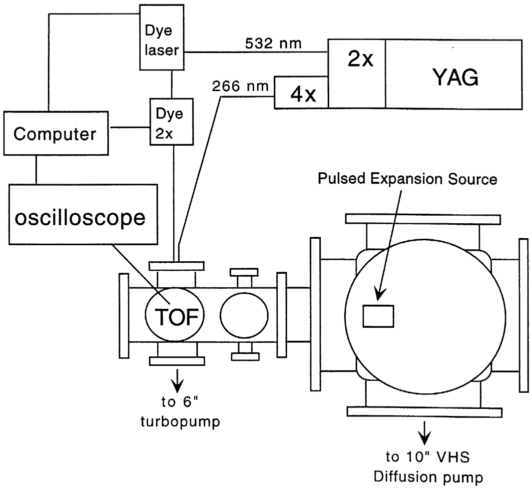

Fig. 1. Schematic diagram of the REMPI apparatus.

2. Experimental

A schematic diagram of this recently constructed beam apparatus is shown in Fig. 1. In this apparatus, a cluster beam is produced by expanding a gas mixture through a pulsed valve (General Valve #9) with a 0.8 mm nozzle. Clusters are formed in the cold, condensation prone region of the expansion on the high vacuum side of the nozzle. In these experiments, the valve was operated with 1 to 3 atmospheres of argon gas seeded with 1 to 10 torr of styrene vapor. The pulsed nozzle is operated at 10 Hz, with the valve actually open for about 140 μs to 400 μs per pulse. (This corresponds to an open duration setting of 290 μs to 550 μs on our general valve controller. Upon this apparatus becoming oper-

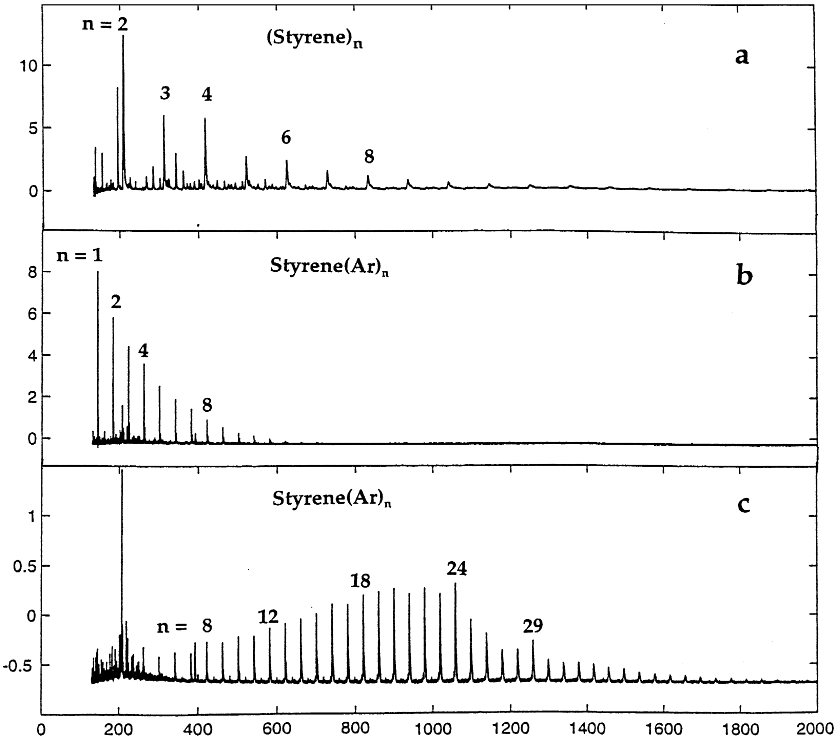

Fig. 2. Mass spectra of styrene-argon clusters recorded using varying source conditions: (a) room temperature (28°C) styrene, a nozzle open time of 200 μs, and a 1.945 ms delay between the pulsed nozzle opening and the laser Q-switch firing, (b) cold (10°C) styrene, a nozzle open time of 380 μs and a 1.475 ms delay between the pulsed nozzle opening and the laser Q-switch firing (c) cold (10°C) styrene, a nozzle open time of 380 μs and a 1.945 ms delay between the pulsed nozzle opening and the laser Q-switch firing. All spectra were recorded with 25 psia of argon as a carrier gas and an ionization wavelength of 266 nm.

ational, we noted that ~ 150 μs of the open duration setting seemed to be needed before the valve actually opened. This was confirmed by varying the nozzle open to ionization laser Q-switch delay while monitoring styrene ion signal as a diagnostic of the actual time length of the expansion pulse.) The expansion chamber is pumped with a Varian 10″ VHS diffusion pump equipped with a water cooled baffle (2500 L/s) and achieves a working pressure of $\sim 2 \times 10^{-5}$ torr under the above expansion conditions.

The expanded pulse passes through a 1 mm diameter skimmer (Beam dynamics) 25 mm downstream of the nozzle and passes into a differentially pumped spectroscopy chamber. The neutral cluster beam travels 32 cm in the spectroscopy chamber and enters the extraction region of a 2 stage, Wiley–McLaren type ion source of a linear time of flight mass spectrometer. Here, a tunable laser pulse resonantly excites and ionizes the neutral clusters. The ionized clusters are extracted perpendicularly into the TOF-MS, travel 40 cm up the flight tube and impact a 40 mm dual microchannel plate (MCP) detector. The detector signal is time resolved, digitized and integrated by a LeCroy 9350 digital oscilloscope. Resulting mass spectra were transferred to a personal computer (Macintosh 7200) via GPIB where the ion intensity data were normalized to the laser pulse energy and compiled versus wavelength. The spectroscopy chamber (and TOF-MS) is pumped by a 6″ Turbo pump (Leybold TMP 361, 350 L/s) which maintains a pressure below 2×10^{-6} torr under operating conditions. The TOF-MS is a Wiley–McLaren type with a 2 stage acceleration source. Typical extraction and acceleration voltages were 240 V and 3760 V, respectively. These conditions produce mass resolution of $m/\Delta m \sim 150$.

The tunable UV excitation and ionization pulse used for the REMPI spectra was generated by a frequency doubled dye laser (Dakota Technologies Inc.) pumped by the 2nd harmonic of a Q-switched Nd:YAG laser (Quantel Brilliant B) operating at a pulse repetition rate of 10 Hz. The visible output of the dye laser was passed through a frequency-doubling crystal mounted on a computer controlled rotational stage. For each wavelength, the angle of the rotation stage was scanned while the power of the frequency doubled output was monitored. The phase matching angle of the doubling crystal was then set to maximize the UV output power at that wavelength. The energy of the tunable UV pulse was typically 200 μJ with a 5 ns pulse length and a spectral width of < 1 cm^{-1}. The mass spectra in Fig. 2 were generated using the Nd:YAG 4th harmonic (266nm).

3. Results and discussion

Mass spectra of styrene clusters produced under a variety of source conditions are shown in Fig. 2. When the liquid styrene is held at room temperature (~ 25 °C, corresponding to an equilibrium vapor pressure of 8 torr) and expanded with 1 atmosphere of argon, styrene clusters predominate (Fig. 2a). Cooling the liquid styrene with cold tap water (~ 2°C, corresponding to an equilibrium vapor pressure of 1–2 torr) the styrene clusters are suppressed, and styrene$(Ar)_n$ clusters are produced (Fig. 2b). The styrene$(Ar)_n$ cluster distribution can be shifted to larger cluster sizes by increasing the argon gas pressure or increasing the open time of the pulsed nozzle. Photoionizing later in the gas pulse by increasing the delay between the nozzle open and laser Q-switch also shifts the cluster size distribution to larger cluster sizes, as shown in Fig. 2c.

The REMPI spectra of styrene and styrene$(Ar)_n$, $n = 1$–3, near the origin of the $S_1 \leftarrow S_0$ electronic transition, have been recorded and are shown in Fig. 3. These spectra are similar to previously reported spectra [4,13,14] and were helpful in tuning and calibrating our new instrument. The styrene(Ar) and styrene$(Ar)_2$ origin transitions are red shifted 32 cm^{-1} and 63 cm^{-1}, respectively, relative to styrene. Essentially, red or blue shift indicates the differences between the amount the upper, excited state is stabilized by cluster formation relative to the amount the ground state is stabilized. If the upper excited state is stabilized by clustering more than the ground state, the spectrum is red shifted. Thus, in styrene(Ar), the excited state is stabilized by cluster formation 32 cm^{-1} more than the ground state, while the excited state of styrene$(Ar)_2$ is stabilized 63 cm^{-1} more than the ground state. These first two argon clusters of styrene obey the additivity rule [1,14]: that is the spectral shift varies linearly with the number of

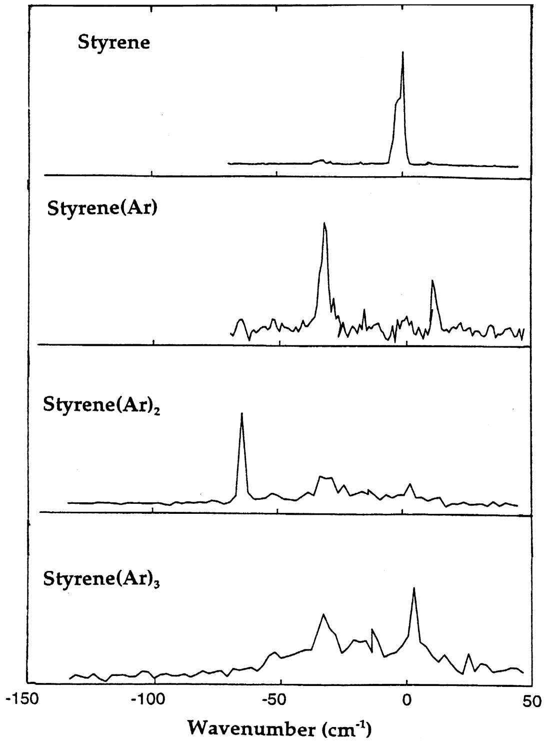

Fig. 3. The mass resolved resonant 1 color, 2 photon, ionization spectra of styrene and styrene$(Ar)_n$, $n = 1$, 2, 3. The zero wavenumber (cm^{-1}) point corresponds to the styrene origin transition at 34,764.1 cm^{-1}.

adatoms. This is reasonable in that it is likely they occupy equivalent sites which will prevent them from interacting strongly with each other. Consalvo, et al. [14] explained these shifts as argon atoms adding first above, and then below the plane of the styrene aromatic ring. The spectrum of styrene$(Ar)_3$, also previously published by Consalvo, et al. [14], is more complicated, containing both sharp and diffuse features. This is likely caused by the presence of more than one isomer.

These spectra are scanned over the range 0 to -100 cm^{-1} relative to the styrene $S^1 \leftarrow S^0$ origin transition at 34,764.1 cm^{-1}. The ionization potential of styrene is 68,267 cm^{-1} and styrene(Ar) is 68,151 cm^{-1} [10]. Since a one color technique is used, two excitation photons are 1100 to 1400 cm^{-1} greater than the ionization potential of the cluster, and up to this amount of excess energy can be deposited in the cluster upon photoionization. It should be noted that some of this energy must be carried away by the ionized electron, and not all will remain within the ionized cluster. However, excess energy could cause cluster fragmentation, and cluster fragmentation on a sub-microsecond time scale can lead to spectral contamination of clusters smaller than the fragmenting parent cluster ion. It is unlikely that fragmentation is making a significant contribution to the spectral features in these spectra. While some features in the spectra of styrene$(Ar)_n$ $n = 0$–3 suggest some fragmentation, these features are very small and do not obscure or complicate the spectral assignment.

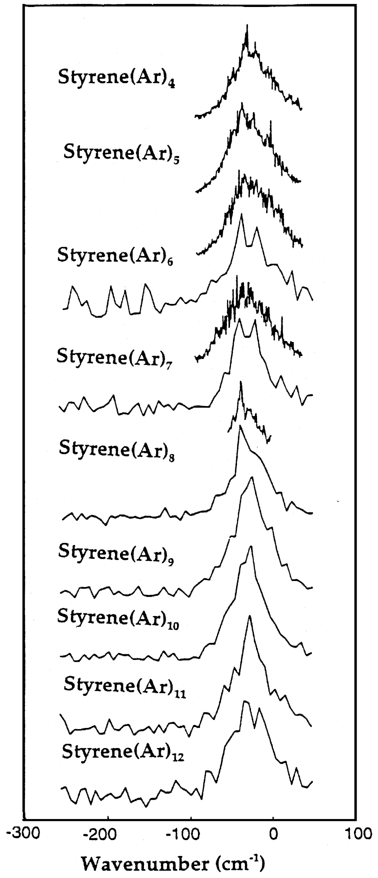

Fig. 4. The mass resolved resonant one color, two photon ionization spectra of Styrene$(Ar)_n$, $n = 4$–12. For the spectra of Styrene$(Ar)_n$ $n = 4$–8, the upper trace is a higher resolution (1-2 cm^{-1}) scan of the main peak. The zero wavenumber (cm^{-1}) point corresponds to the styrene origin transition at 34,764.1 cm^{-1}.

The REMPI spectra of larger styrene-argon clusters, styrene(Ar)$_n$, $n = 4$–12, have also been recorded and are presented in Fig. 4. Energies for the origin transitions observed for these species are listed in Table 1. These spectra are dominated by a single band, red shifted from the styrene origin transition by 24–37 cm^{-1} and with a FWHM of ~ 50 cm^{-1}. Higher resolution scans of several of the clusters have been included in Fig. 4. The spectra of styrene(Ar)$_n$, $n = 4$–8 clearly contain partially resolved features. Shifts and transition energies for these spectra were measured from the two most prominent features near the peak of the band.

While all of the bands in the spectra of styrene(Ar)$_n$, $n = 4$–12, are red shifted relative to the styrene origin transition, this red shift is essentially constant with increasing cluster size over this range. The larger argon clusters no longer exhibit spectral shift additivity. This is similar to spectral shifts observed in the REMPI spectra of phenylacetylene(Ar)$_n$ and paraxylene(Ar)$_n$ clusters by Dao and Castleman [6,7]. From styrene(Ar)$_4$ to styrene(Ar)$_8$, there is a small, gradual shift of several wavenumbers to the red, while styrene(Ar)$_9$ through styrene(Ar)$_{12}$ have shifted back to the blue by about the same amount. This is comparable to the progression observed by Faltin, et al. [5] in which the REMPI spectra of fluorostyrene(Ar)$_n$ clusters exhibit a small blue shift for $n \leqslant 15$.

Table 1
Transition Energies and spectral shifts relative to styrene of the clusters, styrene(Ar)$_n$, $n = 4$–12. The red and blue indicates the two small features at the top of the peak of several of the spectra

		Transition energy (cm^{-1})	Shift (cm^{-1}) (reltive to styrene)
Sty(Ar)$_4$	red	34732	−32
	blue	34743	−21
Sty(Ar)$_5$	red	34728	−36
	blue	34742	−22
Sty(Ar)$_6$	red	34728	−36
	blue	34743	−21
Sty(Ar)$_7$	red	34728	−36
	blue	34739	−25
Sty(Ar)$_8$	red	34725	−38
	blue		−27
Sty(Ar)$_9$		34737	−27
Sty(Ar)$_{10}$		34727	−27
Sty(Ar)$_{11}$		34727	−27
Sty(Ar)$_{12}$		34727	−27

In solvatochromic theory, solvation shifts with nonpolar ($\mu_s = 0$) solvents are related to the difference between the dipole moments of the solute ground and excited states, the polarizability of the solute, and the dielectric constant and refractive index of the solvent [18,19]. Styrene in the ground state has a negligible dipole moment [20], while the change in dipole moment upon excitation is ± 0.13 D [21]. A red (bathochromic) solvation shift is generally indicative of an increase in the dipole moment upon excitation. It is reasonable to think that the dipole moment would increase upon excitation, due to the increased participation of the ethylenic p orbitals with the ring π system. Effects of the solvent dielectric constant and refractive index are often best analyzed by comparison to solvents with similar values for these parameters and known solvation shifts. Pentane is a solvent with appropriate, although slightly larger, constants; however the effect of the difference in molecular geometry between argon and pentane is more difficult to estimate, and is not addressed in solvatochromic theory. The solvation shift of styrene in pentane was measured by UV–Vis absorption to be 335 cm^{-1}. The solvation shift, adjusted for the slightly smaller dielectric constant of argon, is approximately 250 cm^{-1}.

Although the spectral shift is relatively constant over the $n = 4$ to $n = 12$ range observed, it is still an order of magnitude less than expected on the basis of solvatochromic theory. Perhaps these cluster beam spectra are representative of an ensemble of one or several rigid isomeric structures, which are a poor comparison with the fluid environment of solutions. Another possible explanation is temperature. The internal temperature of the clusters is likely to be very low; Consalvo et al. [14] estimate 10 to 15 K for their comparable spectra. These very cold species might not be directly comparable to room temperature solutions [18]. A more appropriate comparison for these spectra might be with rare gas matrix isolated aromatic chromophores.

4. Conclusion

We have reported new experimental spectra for styrene(Argon)$_n$, $n = 4$–12 clusters. These spectra were recorded using a newly constructed cluster beam time-of-flight mass spectrometer. Transition energies and spectral shifts relative to styrene have been determined from these spectra and are reported. Essentially, clusters in this size range have origin transitions red shifted 36–27 cm^{-1} relative to styrene monomer.

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