

Resonance-enhanced two-photon ionization time-of-flight spectroscopy of cold perfluorinated polyethers and their external and internal van der Waals dimers

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Abstract

Perfluorinated polyethers of the type $R_n-(OCF_2CF_2CF_2)_n-F$, where R_n is the end group $C_6H_5-O-CH_2CH_2-O-(C=O)CF_2CF_2-$, were laser-vaporized and entrained in a pulsed jet expansion. Two photon ionization of the jet-cooled polymers via the phenoxy chromophore was combined with time of flight (TOF) mass spectrometry. Mass spectra were obtained for polymer distributions extending to 7000 Da, with minimal fragmentation. Under the appropriate expansion and desorption conditions parent masses of van der Waals dimers of these polymers were also observed. By scanning the ionization laser and monitoring particular mass-to-charge ratios, resonance-enhanced two photon ionization (R2PI) spectra were obtained for the jet-cooled polymers and their dimers near the electronic origin. Polymers with two end groups, present as an impurity in the samples, were detected exclusively in an internally dimerized form. In both the internal and external cases, the dimerization occurs only at the phenoxy chromophore. The R2PI spectra of a series of model compounds were measured and used to characterize the evolution of the spectra from phenol toward the polymer. The model compound spectra revealed the role of multiple conformations and molecular size in the polymer spectra, which are ultimately broadened by low frequency motions of multiple conformers. The results are discussed relative to the general problem of the photoionization of large molecules.

Key words: Resonance enhanced two-photon ionization; Perfluorinated polyethers; Van der Waals dimers

Introduction

Laser desorption has demonstrated great potential for the study of complex molecules through the introduction of nonvolatile material into the gas phase. Large organic molecules have successfully

been desorbed from various substrates with no or minimal fragmentation. While in a simpler version, a single laser pulse can vaporize the sample and also perform ionization, it is advantageous to separate these processes. A particularly powerful approach for the postionization step is that of resonance-enhanced two photon ionization (R2PI). When combined with time-of-flight (TOF) mass selection, this technique can provide detailed spectroscopic information about a specific molecule in a mixture and is very sensitive in

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favorable cases. To capitalize on the strengths of R2PI detection it is necessary that the desorbed molecules be cooled by effective entrainment in a supersonic expansion. One advantage of cooling the internal degrees of freedom is the reduction in fragmentation, since less internal energy is available. A second advantage is an increase in sensitivity and selectivity, resulting from the cooling of molecules to the lower rotational and vibrational states, causing narrowed spectral lines and allowing the exciting laser line to interact with a larger fraction of the molecular population.

A disadvantage of this technique is that the molecule of interest may not absorb light at a convenient wavelength. Perfluorinated polyethers (PFPEs) are an example of such a case. To overcome this problem, a chromophore attached to the polymer can serve as a tag for R2PI studies. This approach has been demonstrated for DNA with an anthracene tag [1] and for non-aromatic peptides derivatized with a phenyl-containing chromophore [2].

Whereas many groups have successfully desorbed extremely large molecules into the gas phase [1,3–5], fewer have used jet-cooling techniques. Schlag and co-workers have produced mass spectra of a variety of large, jet-cooled molecules [6–8], including peptides [9,10] and polyenes [11]. These mass spectra are often dominated by parent ions, with the degree of fragmentation controllable with the intensity of the ionizing laser. Lubman and co-workers have also used similar techniques to study a variety of derivatized peptides [2] and aromatic polymers [12]. However, the mass spectra obtained for the aromatic polymers were dominated by the monomer unit that makes up the polymer or by fragment ions, with large oligomers rarely seen.

Even fewer examples exist where the ionization wavelength was scanned to generate the R2PI spectrum of jet cooled species. To date, this technique has been successfully applied to molecules of moderate size only, typically with masses of several hundred atomic mass units and below. Cable et al. have obtained spectra of cold dipeptides and

tripeptides containing the amino acid tryptophan, which served as the chromophore [13,14]. These spectra provide information regarding the molecular conformations in the vicinity of the chromophore and serve as a nice complement to fluorescence studies [15,16]. Li and Lubman have measured the spectra of tyrosine-containing molecules cooled in a supersonic expansion [17]. Meijer et al. have obtained the jet-cooled spectra of a number of large organic molecules and their dimers [18–21].

Several factors related to molecular size make application of these techniques more difficult as the target molecules become larger. With increasing number of atoms in a molecule comes an increase in the number of degrees of freedom and low frequency vibrational modes. As a result, substantially more vibrational states remain populated after cooling in the molecular beam than for molecules of a smaller size cooled to the same temperature. Metastable conformations also appear [22]. These effects multiply and ultimately broaden the R2PI spectrum.

Schlag and co-workers have cited several factors expected to impede the photoionization of larger molecules [23,24]. The leading one is delayed ionization. In this picture, the electronic energy needed to eject the electron to form the ion is tied up in vibrational motion before ionization, allowing other processes such as bond dissociation to compete. Other factors that may impede ionization of large molecules include unfavorable Franck–Condon factors, attachment of the ejected electron to another part of the molecule and excessive internal energy that dissociates the parent ion. In the current work we have not found these factors to present a significant impediment to photoionization of long-chain polymers with terminal chromophores.

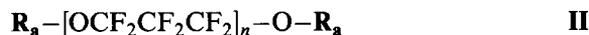
In this paper we report the extension of the technique of R2PI–TOF mass spectrometry with laser-vaporization and jet-cooling to perfluorinated polyethers (PFPEs). These polymers serve as important industrial lubricants because of their chemical inertness, thermal stability and very low

vapor pressure. We have studied polymers functionalized with an end group that contains a phenyl ring which serves as a chromophore:



where \mathbf{R}_a is the aromatic end group $\text{C}_6\text{H}_5-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-(\text{C}=\text{O})-\text{CF}_2\text{CF}_2^-$. These polymers are available as Demnum SP[®] from Daikin Industries and will be referred to as type I. We have obtained mass spectra that extend to 7000 Da and are dominated by the parent ions of these polymers using ionization wavelengths fixed at 193 nm and near 274 nm.

We have measured the R2PI wavelength spectra in the vicinity of the S_{0-0} transition (near 274 nm) of unfragmented polymers with masses up to about 2000 Da. We also studied polymers with the same repeat unit, but with two aromatic end groups:



which we will refer to as type II polymers, as well as some with branched repeat units. Under appropriate expansion and desorption conditions, spectra of van der Waals dimers of the polymers were obtained as well. In order to better understand the polymer spectra, we also studied the R2PI spectra of smaller model molecules representing various lengths of the phenoxy end of the polymers. Figure 1 shows the various compounds that we studied, starting with phenol and evolving in complexity toward the PFPE. From trends in observed spectral shifts conclusions can be drawn about the structure and the dynamics of PFPEs, which will be discussed below.

Experimental

The laser desorption jet-cooling apparatus was described in detail before [21,25] and is shown schematically in Fig. 2. Molecules are desorbed from a sample bar on the vacuum side of a pulsed supersonic nozzle. Typically the desorption spot is positioned about 1 mm in front of the nozzle opening, which corresponds to a position 2 nozzle diameters downstream in the expansion. In the current

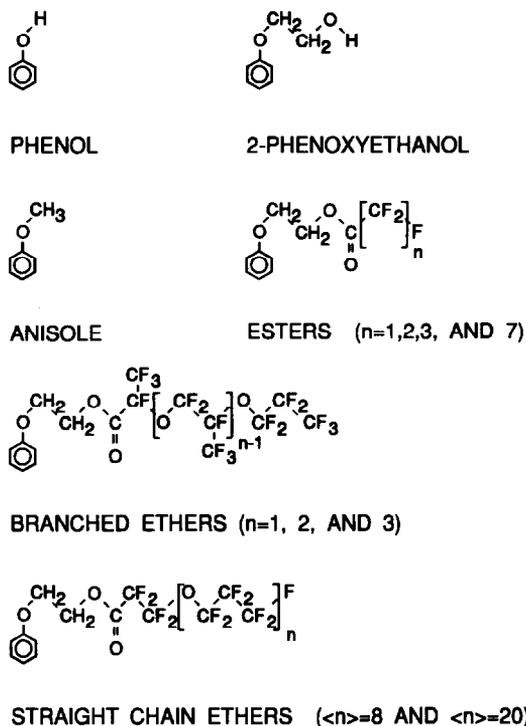


Fig. 1. Model compounds studied in this work.

studies we used the frequency-doubled output (532 nm) of a pulsed Nd:YAG laser for desorption. Most samples were applied to a substrate of activated charcoal. This provided a surface film, which was replenished between successive laser shots from the subsurface bulk of the porous carbon. Using a gas pulse from the molecular beam source timed to entrain the desorbed material, the molecules were cooled by collisions with the carrier gas. Xenon, at a stagnation pressure of 8 atm, was found to give the best cooling and most effective entrainment of the heavier molecules.

This method of sample introduction was used for all the molecules studied, with the exception of the anisole dimers. In this case, the charcoal would not hold enough of the more volatile anisole near its surface to create a high enough density to form dimers by laser desorption. Instead, the anisole was seeded in 1.5 atm of xenon in the pulsed jet.

The molecules in the beam were interrogated downstream by a pulse from a second laser, which was timed to ionize them by two photon

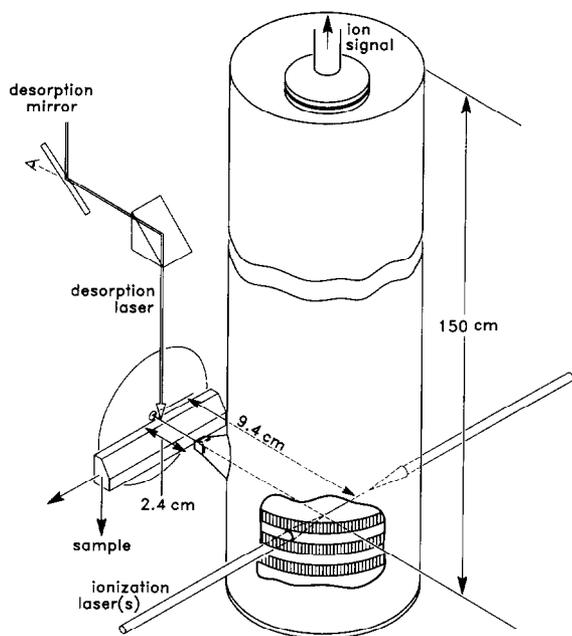


Fig. 2. Experimental apparatus.

absorption in the source of a linear time of flight mass spectrometer. Mass spectra were obtained using the 193 nm output of an ArF excimer laser or the doubled output of a fixed wavelength from a tunable dye laser. One color, R2PI spectra were collected by scanning the frequency-doubled output of the dye laser while monitoring ion masses of interest. In our setup several masses can be monitored simultaneously during a single scan to conveniently collect spectra as a function of chain length in a polymer mixture.

In most cases the signal to noise ratio of the R2PI spectra was limited by the shot-to-shot variation in the intensity of the desorption laser. This translates into fluctuations in the amount of material vaporized with each laser pulse and directly into signal variations. Improvements in the signal-to-noise ratio can be made by independently monitoring the amount of material present in the beam for each shot and normalizing the signal to this quantity after each shot. Efforts are underway to incorporate this approach into the present apparatus.

The smaller model compounds (phenol, anisole

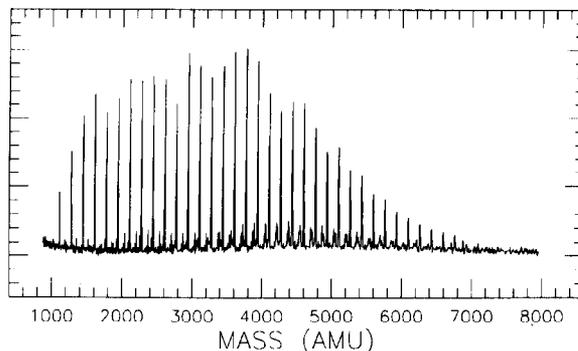


Fig. 3. Mass spectrum of the type I PFPE sample with $\langle n \rangle = 20$ ionized at 193 nm. The major peaks are parent masses spaced by 166 Da and range from 1114 Da ($n = 5$) to 6924 au ($n = 40$). The origin of the minor peaks is described in the text.

and 2-phenoxyethanol) were obtained commercially and the esters with the perfluoroalkyl and branched ether chains were synthesized for this study. The PFPE sample with the shorter chain length distribution was provided as a gift by Daikin Industries and the longer PFPE was a commercial sample from the same manufacturer.

^{19}F NMR analysis of the sample of the shorter chain PFPE showed it to be $26 \pm 2\%$ nonfunctionalized (type I with R_a replaced by $\text{CF}_3\text{CF}_2\text{CF}_2^-$), $66 \pm 2\%$ monofunctionalized (type I) and $7 \pm 2\%$ bifunctionalized (type II). The composition of the sample of the longer chain PFPE was found by the same technique to be $57 \pm 2\%$ monofunctionalized and $43 \pm 2\%$ nonfunctionalized.

Results

Mass spectra

Figure 3 shows the mass spectrum obtained using 193 nm ionization of a sample of the type I PFPE consisting of a distribution of chain lengths. The predominant peaks correspond to parent ions and are spaced apart by 166 Da, the mass of a repeat unit. They range from $m/z = 1114$ Da

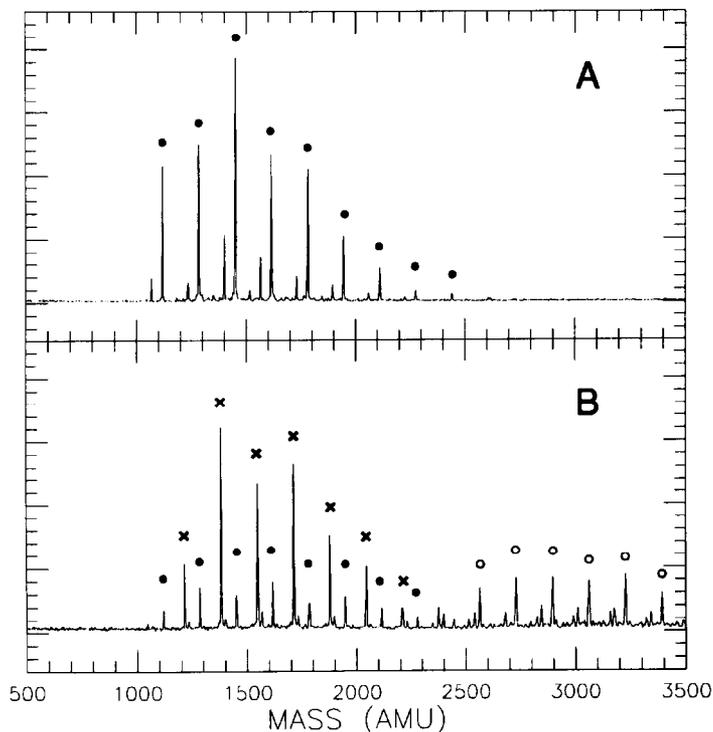


Fig. 4. Mass spectra of the type I PFPE sample with $\langle n \rangle = 8$. (A) Ionization at 273.5 nm yields predominantly parent ions of the type I PFPE, (●). (B) Ionization at 274.8 nm favors ionization of the type II polymers present as an impurity in the sample (×) and van der Waals dimers of the type I polymers (○). Peaks due to these two components of the mass spectrum are not visible in panel A. The parent masses of the type I polymer are again indicated by ●.

($n = 5$) to $m/z = 6924$ Da ($n = 40$). Minor peaks are due to several components. Polymers that contain one repeat unit or an end group that has two rather than three CF_2 units are shifted down from the main peaks by 50 Da. Some polymers are functionalized at both ends, containing two aromatic end groups, and appear as peaks shifted up 262 Da from the main peaks. At the higher end of the mass range, peaks due to van der Waals dimers of the polymers are observed. Polymers with up to 40 repeat units and a mass of the order of 7000 Da are readily measured with no observable fragmentation. The intensity distribution does not necessarily reflect the exact molecular weight distribution of the sample since entrainment and detection efficiencies may not be mass-independent over such a long mass range. However, we note that the observed mass distribu-

tion resembles distributions obtained in this laboratory from similar samples by a laser desorption–cationization technique [26].

Figure 4 shows mass spectra of another sample, which contained a mixture of shorter chain PFPEs of type I. Here, the ionization laser was the doubled dye laser operating at a fixed wavelength. In this case, the first ionization step is the absorption of a photon near the electronic origin. As a result molecules are selected that have absorption bands coinciding with the laser wavelength. Panel A shows the mass spectrum when ionizing with 273.5 nm radiation. This wavelength is resonant with polymers of type I and the mass spectrum is again dominated by parent ions, reflecting the shorter and narrower mass distribution of this sample, ranging from five ($m/z = 1114$ Da) to 13 ($m/z = 2442$ Da) repeat units. Parent masses

of the type I polymers are indicated by the solid circles.

The mass spectrum in panel B was obtained with the ionizing laser tuned to 274.8 nm. Type I polymers no longer dominate the mass spectrum. Instead, a new set of peaks (indicated by the crosses) appears that was not apparent in panel A. The new peaks correspond to polymers with two aromatic end groups, the type II polymers. This ionizing wavelength favors these polymers, whose parent ions now dominate the spectrum. In addition, parent ions of the van der Waals dimers of polymer I, indicated by the open circles, appear at the higher mass end of the spectrum. Thus, the wavelength that favors ionization of the polymers with two end groups also favors ionization of the dimers of the single end group compound. This suggests that the chromophores in the two species are similar. The reason for this similarity will be discussed below. In none of the mass spectra do we find evidence of delayed ionization, which would be indicated by tailing peaks.

Wavelength spectra

By monitoring a particular mass-to-charge ratio in the mass spectrum while tuning the wavelength of the ionization laser, a R2PI spectrum is obtained. Figure 5 shows R2PI spectra of a series of molecules of increasing size and complexity which were chosen to model the chromophore end of the polymer and converge to the structure of the PFPEs. We assign the main features in these spectra to the respective S_{0-0} transitions for two reasons. (1) In each case the peak is close to the wavelength of the known S_{0-0} transitions of phenol and anisole and (2) no other spectral feature which can be assigned to the electronic origin is observed when scanning at least 1300 cm^{-1} to the red. Panel A shows the spectrum of phenol; panel B, anisole; and panel C, 2-phenoxyethanol. Panels D through G show 2-phenoxyethyl esters of perfluorinated carboxylic acids, with increasing length of the perfluoroalkyl chain. In H through J a series of esters with branched perfluorinated polyether

chains is shown. Finally panels K through N show spectra of straight chain perfluorinated polyethers found in the PFPE sample with the shorter chain distribution. Generally, the spectra evolve smoothly from phenol to the polymers. The transition shifts to higher energy in going from phenol (A) to the first ester (D). In D, E, and F, structure is observed that may be related to several electronic origins corresponding to different conformations of the molecule. In proceeding from the esters to the branched ethers (H–J) the spectra shift back slightly toward lower energy. The straight chain polymers (K–N) show no further shift or broadening. It appears that the spectra have converged to a limiting value at three ether oxygens in the chain (J) and the branched and straight chain polyethers have similar spectra.

When material is desorbed with high enough density into the early part of the supersonic expansion it is possible to form small van der Waals clusters. Figure 6 shows spectra of the dimers of type I PFPEs, obtained from the sample with the lower average molecular weight. Since the sample contained a distribution of chain lengths, each peak in the mass spectrum is due to a mixture of dimers. Each dimer mass can only be assigned in terms of the sum of two monomer chain lengths. For example, a dimer mass peak corresponding to a chain length of 16 can contain contributions of monomers with n and m repeat units in any combination for which $n + m = 16$. When a dimer peak in the mass spectrum is monitored during the wavelength scan, the resulting spectrum is a superposition of mixed dimers with the same molecular weight. The panels in Fig. 6 are labelled accordingly. All the dimer spectra show a broadening and a characteristic redshift of about 110 cm^{-1} from the monomer wavelength. Although the sample contains 26% nonfunctionalized polymers in addition to 66% of the monofunctionalized ones, no mixed dimers involving a nonfunctionalized polymer were observed. Dimers of the nonfunctionalized polymers are, of course, not observable.

For comparison with the polymer clusters, we measured the spectrum of the anisole dimer. The spectrum showed a sharp origin shifted -215 cm^{-1}

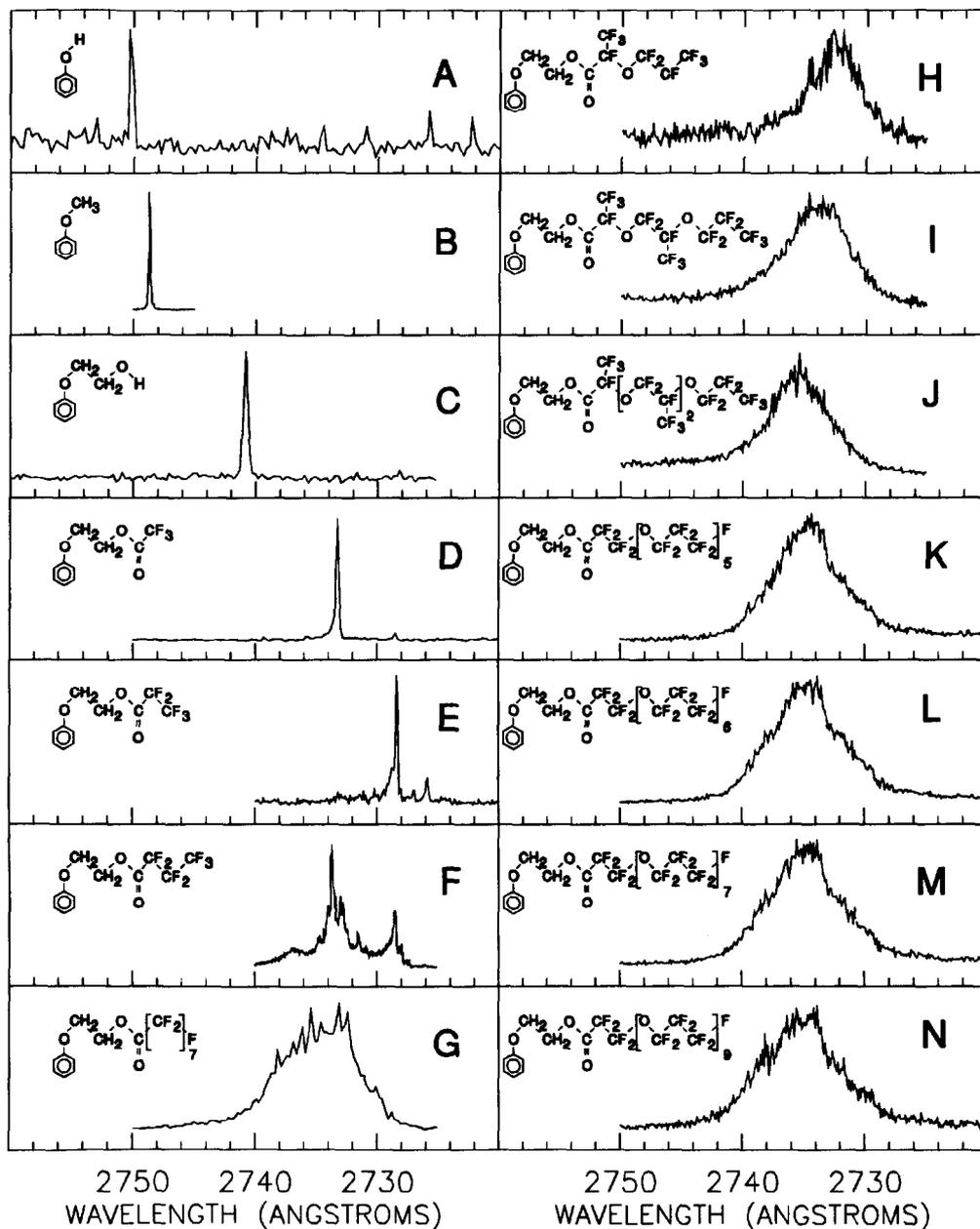


Fig. 5. R2PI spectra of the series of model compounds and PFPEs illustrated in Fig. 1: (A) phenol; (B) anisole; (C) 2-phenoxyethanol; (D–G) 2-phenoxyethyl esters of perfluorinated carboxylic acids: perfluoroacetate, perfluorobutyrate, perfluoropropionate and perfluorooctanoate; (H–J) 2-phenoxyethyl esters with branched ether chains: $n = 1, 2$ and 3 ; (K–N) type I PFPE with $n = 5, 6, 7$ and 9 .

from anisole monomer. The trimer absorbed in the same region, but gave a much broader signal (about 100cm^{-1} full width at half maximum) without any sharp structure.

Figure 7 shows the R2PI spectra of doubly functionalized PFPEs of type II for a number of chain lengths. These spectra exhibit broadening and redshifts remarkably similar to those of the

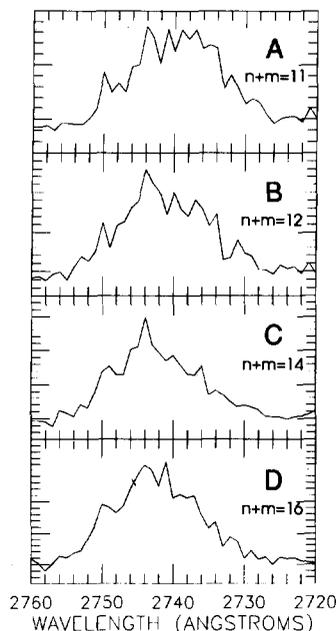


Fig. 6. R2PI spectra of van der Waals dimers of type I PFPE. Panels A–D are for $n + m = 11, 12, 14$ and 16 , respectively, where $n + m$ represents the sum of the number of units in the two polymer chains.

dimer spectra. The similarity between the spectra of the dimers of the type I polymers and the isolated, doubly functionalized type II polymers leads to the conjecture that the chromophore environment in both cases is similar, which is the case if the type II polymer chromophores are intramolecularly dimerized. When comparing the wavelength spectra of monomers (Fig. 5) and dimers (Figs. 5 and 6) with the mass spectra (Fig. 4), it is important to bear in mind that the dimer absorption is much weaker than that of the monomer due to lower concentration. Also the ratio of the type I dimer to type II absorption depends on the density of material injected in the molecular beam, that is, on the desorption laser intensity and the height of the sample relative to the pulsed jet orifice.

To explore the dimer spectra more fully, the dimers of the shorter chain branched ethers were studied. Figure 8 shows R2PI spectra of dimers of the branched polymers with varying numbers of repeat units. At $n = 3$ the spectrum is remarkably

similar to the dimers of the type I polymers (Fig. 6), but at lower values of n a double-peaked structure appears.

Discussion

Ionization of large molecules

The data reported here represent an extension of R2PI spectroscopy to heavier molecules, i.e. those with masses between 1000 and 2000 Da. There are a number of reasons why application of the laser desorption jet-cooling spectroscopy to larger molecules is more challenging. Foremost is the fact that the large increase in the number of internal degrees of freedom and low frequency modes with number of atoms may increase the number of very low frequency vibrational states populated in a jet-cooled molecule. This then broadens the spectrum, which reduces sensitivity and specificity of detection.

There is current interest in possible fundamental limitations on the size of molecules that can be efficiently ionized [23,24]. Schlag and co-workers have proposed that the origin of this limitation is related to the number of vibrationally excited levels that are coupled to the ionizing level. For a large molecule there is a very large number of non-ionic, superexcited states that are isoenergetic with the initially excited ionic state. It has been proposed that the loss of electronic energy (needed to eject the electron) to vibrational degrees of freedom as a result of coupling to these states can interfere with ionization. This is the ionization analog to internal conversion in fluorescence experiments.

A molecule excited above the ionization threshold, but having its energy in the wrong degrees of freedom for ejecting the electron, may undergo other processes. First, the molecule may auto-ionize, resulting in delayed ionization. Second, the energy-rich molecule may undergo bond dissociation, which competes with ionization. Third, the electron may attach to a remote part of the molecule, forming a zwitterion.

We find no evidence for delayed ionization in the

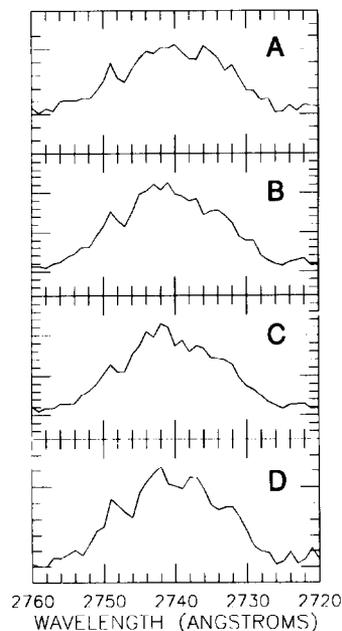


Fig. 7. R2PI spectra of the doubly functionalized type II PFPE. Panels A–D are for $n = 4, 5, 7$ and 9 , respectively.

current results, which include ionization of molecules up to 7000 Da. Nor do we find evidence of a gross decline in ionization efficiency with molecular size.

Our results also show that other factors thought to impede R2PI of large molecules are not significant in the examples studied here. First, a decline in the ionization efficiency due to increasingly unfavorable Franck–Condon factors with increasing molecular size is not germane. The sharp, isolated electronic origin of the chromophore indicates a vertical transition. The chromophore in the molecules studied here is fairly isolated from the rest of the polymer and is insensitive to changes in polymer size beyond a certain point (see Panels H–N in Fig. 5). Second, we find no evidence for the attachment of the ejected electron to the rest of the molecule. Dissociative attachment of electrons to PFPEs is a favorable process [26]. The separation of a negatively charged fragment [27] would result in positively charged ions with the polymer chain severed. We find no evidence of this in the PFPE mass spectra. Although the examples studied here may be classified as a special case (terminal chromophores attached to a perfluorinated chain), their

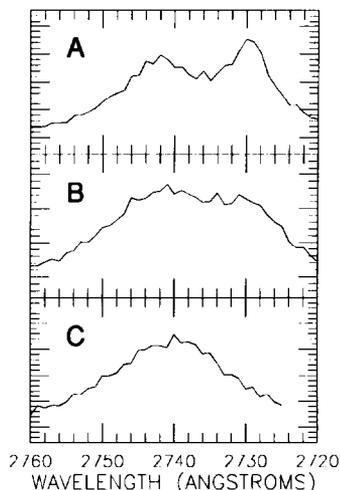


Fig. 8. R2PI spectra of van der Waals dimers of the branched chain ethers. Panels A–C are for $n = 1, 2$, and 3 in the polymer chain, respectively.

behavior should be considered in general theories of photoionization of large molecules.

Evolution of the PFPE R2PI spectrum

The sequence of compounds in Fig. 5 represents a systematic series of molecules containing the phenoxy chromophore, from phenol to the perfluorinated polyethers. The spectral shift in going from phenol to the PFPEs covers roughly 200 cm^{-1} . In the first step, from phenol (panel A) to anisole (panel B), the spectrum does not change appreciably, with the single line corresponding to the electronic origin of the first excited electronic state shifting 32 cm^{-1} to higher energy, as has been previously determined [28–30]. The single line in each case indicates a single molecular conformation, as reported for anisole by Breen et al. [30]. In their study of ethoxybenzene, workers from this group also reported a single molecular conformation, whose electronic origin is shifted 9 cm^{-1} to lower energy for anisole [31]. In panel C, we find that the spectral shift due to the addition of the OH group to ethoxybenzene, to form 2-phenoxyethanol, is 104 cm^{-1} to higher energy (relative to ethoxybenzene). Again, a single molecular conformation is observed.

The sequence of spectra in panels D–F is particularly remarkable, suggesting that the preferred conformation in the jet-cooled molecule depends critically on the number of carbons attached to the ester linkage. In panel D, the spectrum for 2-phenoxyethyl perfluoroacetate shows the first evidence for multiple conformations. The predominant conformer exhibits an additional 104 cm^{-1} shift from 2-phenoxyethanol. Minor peaks are observed at shifts of -77 cm^{-1} , -34 cm^{-1} and $+67\text{ cm}^{-1}$ from the major peak. That the minor peak at the $+67\text{ cm}^{-1}$ shift is indeed another conformer is indicated by the striking change in the spectrum going from the perfluoroacetate in panel D to the perfluoropropionate in panel E. By simply increasing the length of the perfluoroalkyl chain by one CF_2 unit, the major conformer now corresponds to the one shifted $+67\text{ cm}^{-1}$ from the major one in the perfluoroacetate.

With an additional CF_2 in the chain, the spectrum of the perfluorobutyrate (panel F) now resembles a combination of panels D and E. The major conformation has changed back to the one of the perfluoroacetate, but a significant contribution still comes from the one predominating in the perfluoropropionate. Additional peaks appear in panel F which we interpret as additional minor conformations that are shifted slightly from the major ones. We also expect a contribution from transitions that arise from molecules that are not in their vibrational ground state. With increasing size, the increasingly lower frequency torsional and bending modes remain populated at the low temperature of the molecular beam. Transitions from these states tend to further congest the spectrum.

The appearance of the spectrum of the 2-phenoxyethyl perfluorooctanoate shown in panel G can be interpreted as arising from multiple conformations broadened by transitions from molecules left with vibrational energy remaining in the long perfluoroalkyl chain. The predominant conformations seem to be built on the same geometry that resembles the important ones in panel D and F, which would explain the position of the center of the band. Pre-

sumably, a combination of a range of conformers and broadening due to thermal congestion produces the spectral width in panel G. Note that the bandwidth of this spectrum (about 100 cm^{-1} full width at half maximum) roughly matches the range spanned by the features in panel F for the perfluoropropionate.

The preceding discussion of the spectra in panels A–G showed the development of the spectrum as the molecule is built up through the ester linkage. The simplest ester was shown in panel D, with E–F showing the effect of increasing chain length. Panels H–N in the second column of Fig. 5 explore the effect of including ether linkages and then building the chain towards the PFPEs. Note that the structure of the chromophore end of these molecules through the ester linkages are identical to the esters discussed above. The spectra in panels H–J are of branched ethers, with increasing number of ether oxygens. In panels K–N the spectra are shown of straight chain PFPEs with 5, 6, 7 and 9 repeat units from the polymer mixture whose mass spectrum is shown in Fig. 4.

The trend in the spectral shift in the branched ethers is a slight shift back towards the lower energy as the number of ether oxygens increases in panels H–J. The spectral width is again presumably due to a combination of multiple conformations, absorbing at different wavelengths, and congestion due to transitions from molecules not in their vibrational ground state. These effects do not change significantly with length in this series.

A comparison of the branched polyether in panel J with the straight chain polyether (with two more additional repeat units) in panel K suggests that there is no difference in the spectra of the branched and straight chain polymers. The progression through panels K–N, corresponding to increasing the number of repeat units, indicates that both the position and width of the spectra are insensitive to chain length in this range.

In general, the spectral shift has reached its limit at the perfluoroacetate (panel D). Although an anomalous shift does appear in the perfluoropropionate (panel E), the larger molecules seem

to prefer a conformation closer to one that resembles the perfluoroacetate. The spectral width seems to have converged with the first branched ether (panel H). The PFPE spectrum (position and width) seems to have converged at three repeat units, assuming no difference in branched and straight chain spectra, as the data suggest. Apparently, additional repeat units beyond three are too remote from the chromophore to induce additional shifts. The additional units also do not significantly affect the ionization efficiency. With increasing length of the ether chain, vibrations involving low frequency torsional and bending motions that remain populated in the beam must continue to increase in number and decrease in vibrational frequency. Transitions originating from these vibrational levels certainly add additional congestion to the spectrum. However, they must have small shifts relative to those already present in the spectrum and add unobservable broadening to the already broadened peaks.

We note that the increasing spectral bandwidth with increasing molecular size observed in Fig. 5, should serve as a caution about comparing ionization efficiencies at fixed wavelength. An apparent decline in ionization efficiency may be due to sampling a smaller fraction of the molecular population as the molecules get larger and the broadening effects cited above become important.

Internal and external van der Waals dimers

As seen in Fig. 4, the PFPE sample that is nominally a mixture of the singly functionalized type I polymers contains a small fraction consisting of the doubly functionalized type II polymer. We expected the wavelength spectra of the singly and doubly functionalized polymers to be the same, because in an extended polymer chain the chromophore groups cannot interact. Since the data in Fig. 5 show that the spectral shift and width are essentially unaffected by additions to the molecule beyond the ester linkage and are certainly not sen-

sitive to the length of the PFPE chain, a chromophore at one end of a molecule with an extended chain would not be affected by the termination at the remote end of the chain. This expectation of independent chromophores at the ends of the type II polymer chains was not borne out by the experimental results.

The first indication that the two chromophores are not independent in the type II polymers is seen in Fig. 4. If the type II polymers in fact had independent chromophores, they would appear with the type I polymers in the mass spectrum in panel A, which was taken with the ionization laser tuned to 273.5 nm, near the peak of the type I polymer absorption. Instead, they are most pronounced in the mass spectrum shown in panel B of Fig. 4, taken at 274.8 nm, the ionization wavelength that favors the van der Waals dimers.

The similarity between the chromophores in the van der Waals dimers of the type I polymers and the isolated type II polymers is clearly seen in the wavelength spectra shown in Figs. 6 and 7. In Fig. 6, the spectra of the van der Waals dimers are seen as broad peaks (about 200 cm^{-1} wide) centered at 274.4 nm, shifted -100 cm^{-1} for the type I polymer. Recall that only the total number of repeat units is known for a given dimer mass, how they are distributed between the two chains is undetermined. In Fig. 7 the wavelength spectra for type II polymers of several chain lengths are seen. There is no apparent variation with chain length and the similarity of the spectra to those of the van der Waals dimers is unmistakable. The type II polymer spectra certainly resemble the van der Waals dimer spectra in Fig. 6 rather than the type I PFPE spectra in panels K–N of Fig. 5. (Note that all spectra are plotted with the same wavelength range.)

The spectra in Figs. 6 and 7 indicate that the chromophores in the isolated type II polymers and the van der Waals dimers of the type I polymers are similar. One way of achieving this similarity is to form an *intramolecular* complex in the type II polymers that resembles the *intermolecular* complex in the van der Waals dimer. This would

involve interactions between pairs of chromophores in each case.

To support this idea, first consider the structure of the external van der Waals dimer. This complex could form through (1) interaction of polymer tails on each member, interaction of polymer tails and chromophores such that (2a) one chromophore interacts with the chain on the other polymer or (2b) both chromophores interact with the polymer chain on the other member of the dimer, or (3) interaction between chromophores on each.

The last possibility, (3), is strongly supported by the dimer redshift. A useful benchmark for comparison is the shift in the anisole dimer. We have measured the dimer S_{0-0} transition shifted -215 cm^{-1} from the anisole monomer. This compares favorably with -100 cm^{-1} for the broad PFPE dimer peak, falling within the observed range of shifts and showing that interaction of the chromophores is a plausible explanation for the source of the spectral shifts in the PFPE dimer spectra. The two shifts do not match exactly because anisole only approximates the chromophore and the polymer chain may restrict the dimerization geometry from matching that in the anisole dimer.

We argue that the first two possibilities, (1) and (2a), can be immediately eliminated, since each would give rise to a significant feature in the spectrum near where the “free” chromophore absorbs in the type I polymer (273.5 nm), which is not observed.

In (2b), where there is strong interaction between the chromophore and the polymer chain, each chromophore would be bound to a chain, also giving rise to no “free” chromophore. The spectral shift for this interaction is unknown, but this possibility can be eliminated by considering chromophore–chain interactions in other species. While for type I polymers, this interaction could be with the other member of the dimer, for type II polymers it would require the chromophores to complex with the chain of their own molecule. If so, the chromophores of an isolated type I molecule should complex with its own chain just as easily,

but the spectrum shows that it does not. There is no reason to believe that type II polymers form intramolecular chromophore–chain complexes while type I polymers do not.

The possibility of dimers forming due to chromophore–chain interactions can also be eliminated by the absence of dimers between type I polymers and nonfunctionalized polymers in the mass spectrum in Fig. 4. Since the polymer mixture contains 28% of the nonfunctionalized polymer, strong interaction between the chromophore and the chain would result in a significant portion of the dimers involving one functionalized and one nonfunctionalized member. These were not observed. We conclude, therefore, that the van der Waals complex must be formed by intimate interaction between the chromophores.

If the intramolecular and intermolecular complexes are formed in the same way, as their wavelength spectra suggest, we expect that they both involve interaction of the chromophore ends. This scenario has two prerequisites. First, the chains must be flexible enough so that during the jet expansion they can efficiently bend to bring the chromophores together. In other words, the barriers to internal rotation must be low enough for the polymers to explore many conformations while they are being cooled, since the experiments suggest that the two ends of the molecule find each other with high efficiency. Second, the interaction between chromophores must be strong enough to effectively form the intramolecular complex once the chromophores are brought together.

The barriers to internal rotation around the bonds in these perfluorinated ether chains are not known accurately. Investigations on the interconversion of conformers during a supersonic expansion showed that barriers to internal rotation greater than 400 cm^{-1} were not effectively relaxed by helium, neon, argon or krypton [22]. Unfortunately, barriers to internal rotation in perfluorinated ethers have not been measured. High quality *ab initio* calculations for a model ether compound, 1,2-dimethoxyethane, predict barriers in the range of 500 to 800 cm^{-1} [32]. Ana-

logous barriers for the perfluorinated compound are expected to be similar or lower [33]. Once reliable barriers for the internal motions of these chains become available, better predictions related to polymer flexibility may be made.

The strength of the ground state interaction between chromophores, the second aspect of efficient dimer formation, has also not been measured. Here, the binding energy of van der Waals dimers of smaller molecules may be used as a guide. To our knowledge, the binding energy of the anisole dimer, a useful model of our case, has not been measured. However, binding energies of the benzene dimer and the benzene–anisole complex have been determined. For the benzene dimer, the binding energy is $560 \pm 80 \text{ cm}^{-1}$ [34]. In the benzene–anisole complex it increases to $1360\text{--}1520 \text{ cm}^{-1}$, a strong interaction [35]. It is reasonable to expect that the binding energy for the anisole dimer, containing two polar molecules, would be even larger.

We believe it is significant for the formation of the intramolecular dimer of the type II polymer that the chromophore dimer binding energy is substantially larger than the torsional barrier heights. When the polymers are laser-vaporized from the surface they must have an internal temperature equal to room temperature or higher. At this stage they have sufficient internal energy to surmount the barriers to internal rotation and freely explore many conformations. A certain fraction of these conformations bring the chromophore ends together, but at this point the molecules may be too energetic to form a complex.

As the internal energy of the molecules is reduced during the expansion, there comes a stage when there is still sufficient energy for the conformations to interconvert, but the chromophores begin to get trapped in the dimer geometry if they happen to come together. If the dimer binding energy is larger than the critical barrier heights, there is still sufficient vibrational energy in the chain for conformational changes after the dimers have begun to form. As the internal energy continues to drop, the chain conformations are eventually frozen in, but only after almost all the

chromophores have formed intramolecular dimers. Since the torsional barriers are likely larger than 400 cm^{-1} , we expect to see metastable conformations, in agreement with our observations for some of the model compounds.

If this scenario is correct, a chromophore with dimer binding energy equal to or less than the barrier heights should show incomplete or no intramolecular dimer formation. For example, a type II polymer with 2-phenylethyl rather than 2-phenoxyethyl esters in the end groups, would be predicted to have a substantially lower binding energy, comparable with the barriers to internal rotation. In this case, conformations with free chromophore groups would be expected to freeze before being converted to dimers, resulting in a free chromophore spectrum.

Combinations of polymer chains of variable flexibility with different chromophores will provide an interesting arena for making predictions based on barriers to internal rotation and binding energy. Gas phase spectroscopic measurements, similar to those reported here, of the interaction between chromophores at remote positions on polymer chains may be excellent tests of those predictions. It may be possible to gauge the internal barrier heights with a sequence of chromophores of ranging dimer strength.

To further explore the energetics of the formation of the internal dimer, we have performed molecular mechanics calculations [36]. This was done to investigate the energy required to bend the polymer chain to form the internal dimer. If this energy was found to be prohibitive, then the strength of the chromophore bond would be immaterial in the dimer formation. Preliminary results show that for the type II polymer with $n = 4$ the energy of the molecule with the extended chain is similar to that of the internally dimerized molecule. In fact, the internal dimer may be several kilocalories per mole lower in energy. Although we have not explored the low energy pathways between the extended and ring geometries, these results indicate that the internal dimer geometry is not unreasonable.

A separate but related issue is the dissipation of the energy released in the complex formation. The formation of dimers of small molecules is accompanied by stabilizing third body collisions that carry away the energy released when the complex is formed. In the polymer, the abundant low frequency modes may facilitate complex formation by providing a sink for the dissipation of energy released in complex formation. This may result in the formation of a metastable complex that is later stabilized by collisions.

Van der Waals dimers of the branched chain ethers

To better characterize the dimers of the polymers discussed above, we also studied the dimers of a series of branched ethers. These were the same ethers shown in panels H–J of Fig. 5. One advantage of using these samples to study the dimers was that they contain molecules of only a single chain length. There was therefore no ambiguity in the length of the chains in the dimer, as there was in the case of the dimers formed from the mixture of type I polymers. Unfortunately, due to the limited availability of starting materials for the synthesis we were forced to use branched ethers. The monomer spectra discussed above showed that the branched and straight chain ethers have similar spectroscopy of the chromophore. However, previous studies of similar branched perfluorinated polyethers in this laboratory showed an enhanced propensity for forming complexes with gas phase metal cations compared to the straight chain counterparts [26]. This enhancement was attributed to the dipole moment of the repeat units due to the polarity of the CF–CF₃ bond. Ab initio calculations showed that the repeat unit in the branched perfluorinated polyether has a dipole moment of 1.2 D, whereas the repeat unit in the straight chain (type I) polymer has a dipole moment near zero [37,38]. Different polarity may affect the formation of the van der Waals dimer relative to the straight chain species discussed above.

The wavelength spectra of the dimers of the three

branched ethers are shown in Fig. 8. In some of these spectra two peaks appear, unlike the spectra of the dimers of the type I straight chain polymers, which only have one. The first appears near the monomer absorption and a second is redshifted by about 130 cm⁻¹ from the monomer. The two features are most pronounced in the dimer of the shortest ether ($n = 1$, where n is the number of ether oxygens), shown in panel A. Proceeding to the $n = 2$ ether (panel B) the two features are less prominent, yet the spectrum is broad enough to consist of both. For the $n = 3$ ether in panel C, the redshift continues and the spectrum is beginning to resemble that of the dimers of the type I polymers in Fig. 6. A single broad feature is observed, shifted -60 cm⁻¹ from the $n = 3$ monomer, with no apparent peak in the vicinity of the monomer of this ether.

We interpret the two features in the spectrum in panel A as arising from (1) chromophores that are interacting, giving rise to the redshifted feature, and (2) free chromophores that occur in dimers that are bound together by the branched ether part of the chain. There may also be some contribution in the spectrum from chromophores that are complexed by the polar branched ether part of the molecule. The observed trend in the spectrum towards chromophores that are complexed as the size of the ether gets larger, can be explained by arguments similar to those used to explain the increased thermal congestion with size in the monomer spectra. Again, the increasing number and decreasing vibrational frequencies of the low frequency modes of the larger branched ethers results in molecules that survive with vibrational energy in these modes. A significant fraction of this energy will be in the low frequency modes that involve torsional and bending motions. This energy may be available for motion within the cluster as it is being formed, in a sense annealing it to its lowest energy geometry. Presumably, this is the structure with the two chromophores interacting in the cluster. The presence of the longer chains in the cluster may also facilitate the interconversion to the lower energy geometry by

providing a low energy path with intermediate geometries that involve bonding with the chain. In this picture, the smaller ethers may form dimers that do not have the chromophores interacting and cannot rearrange to the other geometry.

With increasing length of the branched PFPE chain, the appearance of the spectrum converges towards that of the dimers of the longer chain polymers of type I. With the present data it is impossible to completely separate the effect of having branched units in the molecule from the effect of the chain length in the PFPE chain. This is because there is no example where the chain length is the same for both the straight and branched ethers.

The spectra of all the dimers studied, including both internal and external ones, exhibit bandwidths considerably broader than the corresponding monomers. This broadening arises from two sources. First, the dimers have additional vibrations involving the van der Waals bond. These are extremely low frequency vibrations that may remain populated in the cooled molecules and broaden the spectrum. A second effect arises from different conformations that have varying chromophore dimer geometries and, therefore, different spectral shifts from the monomer that contribute to a broadened spectrum.

Summary

We have demonstrated that it is possible to generate parent mass spectra of distributions of functionalized perfluorinated polyethers extending to 7000 au using laser desorption, jet-cooling and two photon ionization via a terminal chromophore. That the ionization technique is gentle is reinforced by the observation of weakly bound complexes of the polymers. The sensitivity of this technique is sufficient for the measurement of R2PI spectra for the polymers ranging in size to 1778 au by scanning the ionization wavelength in the vicinity of the electronic origin of the first excited electronic state and monitoring the ion signal at a particular mass-to-charge ratio.

These results show that factors thought to limit the R2PI detection of molecules of this size are not significant for these polymers. We see no evidence of tailing peaks in the mass spectrum which would indicate delayed ionization due to coupling of the electronic and vibrational degrees of freedom. There is also no evidence that the ejected electron is attaching to the polymer chain. This would be plausible for the PFPE chain, but the expected dissociative attachment would result in chain scission, which was not observed. The problem of increasingly unfavorable Franck–Condon factors with increasing molecular size is probably not relevant for these molecules, since the transitions seem to be essentially vertical and the spectrum does not change beyond a certain molecular size.

To better understand the polymer R2PI spectra, we studied a series of model compounds that show the evolution of the spectrum from the simplest molecule, phenol, representing the chromophore in the functional end group of the polymer, through intermediate model compounds representing portions of the polymer of increasing length, to the polymers themselves. In going from phenol towards the straight chain polymer the total wavelength shift is about 200 cm^{-1} . The spectral shift is essentially insensitive to structural changes more than six atoms removed from the chromophore, with the bandwidth also saturating. For the polyethers, no further change is seen in the spectrum for polymers containing three or more repeat units and there seems to be no sensitivity to the structural difference between the branched and straight polymer chains. Conformations for the three smaller esters in this series show a very interesting sensitivity to the length of the perfluoroalkyl chain.

The R2PI spectra of the van der Waals dimers of the straight chain polymers and the spectra of the polymers with two phenoxy end groups show a striking similarity, suggesting an accompanying similarity in structure. We argue that in both cases van der Waals complexes are formed between the two chromophores, which are *intermolecular* for the dimer and *intramolecular* for the bifunctionalized chains. The formation of the

intramolecular complex is an indication of the flexibility of the polymer chains and the strength of the interaction between chromophores. The barriers to internal rotation in the polymer must be low enough to allow the two ends of the chain to hook together before the conformations are frozen. This requires a chromophore dimerization energy which is substantially larger than the critical barrier heights.

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References

- R.J. Levis, L.J. Romano, J. Rajan, D. Schilke and M. DeWitt, personal communication, (1992).
- L. Li and D.M. Lubman, *Appl. Spectrosc.*, 42(3) (1988) 411.
- F. Hillenkamp, M. Karas, R.C. Beavis and B.T. Chait, *Anal. Chem. A*, 63 (1991) 1193.
- C. Köster, J.A. Castoro and C.L. Wilkens, *J. Am. Chem. Soc.*, 114 (1992) 7572.
- D.M. Schielz, C.W. Chou, C.W. Luo, R.M. Thomas and P. Williams, *Rapid Commun. Mass Spectrom.*, 6(10) (1992) 631.
- J. Grottemeyer and E.W. Schlag, *Acc. Chem. Res.*, 22 (1989) 399.
- U. Boesl, R. Weinkauff and E.W. Schlag, *Int. J. Mass Spectrom. Ion Processes*, 112 (1992) 121.
- U. Boesl, J. Grottemeyer, K. Müller-Dethlefs, H.J. Neusser and E.W. Schlag, *Int. J. Mass Spectrom. Ion Processes*, 118/119 (1992) 191.
- G.R. Kinsel, J. Lindner and J. Grottemeyer, *J. Phys. Chem.*, 96 (1992) 3157; 3162.
- G.R. Kinsel, J. Lindner, J. Grottemeyer and E.W. Schlag, *J. Phys. Chem.*, 95 (1991) 824.
- M. Dey, F. Moritz, G.H. Atkinson, J. Grottemeyer and E.W. Schlag, *J. Chem. Phys.*, 95(6) (1991) 4584.
- D.A. Lustig and D.M. Lubman, *Int. J. Mass Spectrom. Ion Processes*, 107 (1991) 265.
- J.R. Cable, M.J. Tubergen and D.H. Levy, *J. Am. Chem. Soc.*, 110 (1988) 7349.
- J.R. Cable, M.J. Tubergen and D.H. Levy, *Faraday Discuss. Chem. Soc.*, 86 (1988) 143.
- J.R. Cable, M.J. Tubergen and D.H. Levy, *J. Am. Chem. Soc.*, 111 (1989) 9032.
- S.J. Martinez III, J.C. Alfano and D.H. Levy, *J. Mol. Spectrosc.*, 156 (1992) 421.
- L. Li and D.M. Lubman, *Appl. Spectrosc.*, 42(3) (1988) 418.
- G. Meijer, M.S. de Vries, H.E. Hunziker and H.R. Wendt, *J. Chem. Phys.*, 92 (1990) 7625.
- G. Meijer, M.S. de Vries, H.E. Hunziker and H.R. Wendt, *J. Chem. Phys.*, 94 (1990) 4394.
- G. Meijer, G. Berden, W.L. Meerts, H.E. Hunziker, M.S. de Vries and H.R. Wendt, *Chem. Phys.*, 163(2) (1992) 209.
- G. Meijer, M. S. de Vries, H.E. Hunziker and H.R. Wendt, *Appl. Phys. B*, 51 (1990) 395.
- R.D. Ruoff, T.D. Klots, T. Emilsson and H.S. Gutowsky, *J. Chem. Phys.*, 93(5) (1990) 3142.
- E.W. Schlag, J. Grottemeyer and R.D. Levine, *Chem. Phys. Lett.*, 190(6) (1992) 521.
- E.W. Schlag and R.D. Levine, *J. Phys. Chem.*, 96 (1992) 10608.
- P. Arrowsmith, M.S. de Vries, H.E. Hunziker and H.R. Wendt, *Appl. Phys. B*, 46 (1988) 165.
- E.F. Cromwell, K. Reihls, M.S. de Vries, S. Ghaderi, H.R. Wendt and H.E. Hunziker, *J. Phys. Chem.*, 97(18) (1993) 4720.
- S.M. Spyrou, I. Sauers and L.G. Christophorou, *J. Chem. Phys.*, 78 (1983) 7200.
- S.J. Martinez III, J.C. Alfano and D.H. Levy, *J. Mol. Spectrosc.*, 152 (1992) 80.
- H. Abe, N. Mikami and M. Ito, *J. Phys. Chem.*, 86 (1982) 1768.
- P.J. Breen, E.R. Bernstein, H.V. Secor and J.I. Seeman, *J. Am. Chem. Soc.*, 111 (1989) 1958.
- E.R. Bernstein, H-S Im and M.A. Young, *J. Org. Chem.*, 56 (1991) 6059.
- G.D. Smith, R.L. Jaffe and D.Y. Yoon, *J. Phys. Chem.*, (1993) in press.
- D.Y. Yoon, personal communication, (1993).
- H. Krause, B. Ernstberger and H.J. Neusser, *Chem. Phys. Lett.*, 184 (1991) 411.
- F. Lahmani, C. Lardeux-Dedonder, D. Solgadi and A. Zehnacker, *J. Phys. Chem.*, 93 (1989) 3984.
- MMX calculations, PCMODEL-PI, Serena Software, Bloomington, IN.
- J. Pacansky, M. Miller, W. Hatton, B. Liu, A. Scheiner and R. Waltman, *J. Am. Chem. Soc.*, 113 (1991) 329.
- R. Waltman and J. Pacansky, personal communication, (1992).