

PERFORMANCE REPORT

High Resolution Raman Spectroscopy of Complexes and Clusters in Molecular Beams

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I. Introduction

The DoE-sponsored project in this laboratory has two facets. The first is the development of methods of nonlinear Raman spectroscopy for application in studies of sparse samples. The second is the application of such methods to structural and dynamical studies of species in supersonic molecular beams. The progress we have made in both of these areas is described below. The report is divided into five remaining sections. The first pertains to theoretical and experimental developments in Fourier transform stimulated emission spectroscopy and Fourier transform hole-burning spectroscopy. The second deals with progress in the development of ionization-detected stimulated Raman spectroscopies (IDSRS). The third describes results from the application of IDSRS methods to studies of jet-cooled benzene clusters. The fourth describes IDSRS results from studies of hydrogen-bonded complexes containing phenols. The fifth relates to studies of carbazole-(Ar)_n clusters.

II. Developments in Fourier transform stimulated emission and hole-burning spectroscopies**A. Fourier transform stimulated emission spectroscopy**

In the decade since they have been introduced ¹stimulated emission spectroscopies (SES) have proved to be powerful probes of ground-state molecular level structure, particularly in the case of small species.^{1,2} In SES schemes a pump pulse is tuned to a vibronic (or rovibronic) resonance of a species. A tunable probe pulse then induces transitions from the pump-prepared excited state to vibrationally excited levels in the ground-state manifold. Resonances in the probe-pulse spectrum deplete the population of the pump-prepared excited state. Such depletions are monitored by detecting fluorescence or photoionization signals as a function of probe-pulse wavelength.

One shortcoming of SES schemes arises when the species to be studied has a short-lived excited electronic state. To achieve appreciable SES depletions it is necessary to

employ excitation sources whose pulsewidths are less than, or comparable to, the excited-state lifetime. Short lifetimes require short-pulsed lasers. However, the shorter the laser pulse, the wider its bandwidth, and therefore the worse the resolution in a SES experiment. This situation would seem to preclude the effective application of high-resolution SES in many cases of interest.

As part of our development of Fourier transform versions of nonlinear Raman spectroscopies,^{3-7,9} we invented a Fourier transform version of SES (FT-SES).⁴ The FT-SES scheme involves sending the pump and probe laser pulses collinearly through a Michelson interferometer prior to the sample. The output of the interferometer then is directed to the sample and total fluorescence is measured as a function of the delay of the interferometer. The signal vs. delay (the "interferogram") is then Fourier transformed. A spectrum of ground-state resonances corresponding to the two-photon resonance-Raman transitions between the initial and final states in the SES process is thereby obtained. An important feature of this spectrum is that the spectral resolution depends on interferometer characteristics, not on the bandwidths of the pump and probe light sources. This fact suggested to us that the implementation of high-resolution SES with short-pulse lasers might be possible with the FT-SES technique. If so, efficient depletions would be achievable, even on species with short-lived excited electronic states, without any sacrifice in spectral resolution. Thus, a detailed theoretical and experimental study of short-pulse FT-SES was performed.¹¹ Of particular interest were questions relating to the effect of pulsewidths on spectral resolution, the influence of Doppler broadening in FT-SES spectra, the factors determining lifetime broadening in the spectra, and the way in which rotational structure is manifest.

The theoretical portion of the study is straightforward perturbation theory involving standard techniques of diagrammatic analysis applied to the calculation of density matrix elements. The approach that we took was to calculate directly the diagonal density matrix elements corresponding to the population of *excited-state* levels. This calculation of excited-state populations appears to be a novel way of analyzing the SES process.¹² However, these populations are the quantities that are directly related to the observable in the scheme and are thus the natural ones to consider. With this approach SES depletions

show up as fourth-order (negative) contributions to the diagonal, excited-state density matrix elements. The experimental portion of the study involved FT-SES measurements on jet-cooled *t*-stilbene. The experiments were implemented with pump and probe pulses having pulsewidths of about 30 psec. The results of the study are summarized below:

1. Both theory and experiment show that the resolution of FT-SES is limited by the length of the measured interferogram. The bandwidths and pulsewidths of the excitation pulses do not play a role, nor does the delay between the pump and probe pulse trains. This result means that indeed the technique can indeed be implemented at high resolution with short-pulse lasers (which are most effective at inducing depletions in species with short-lived excited states). As mentioned above, this cannot be done with frequency-domain SES.
2. Theory and experiment show that the Doppler broadening in FT-SES spectra is that which corresponds to the vibrational resonances that enter into such spectra, *not the vibronic resonances* associated with the pump and probe processes. This characteristic is different than frequency-domain SES, the Doppler broadening of which is essentially determined by the bandwidths of the pump and probe light sources.
3. Theoretical results indicate that the homogeneous broadening in FT-SES spectra is determined by the damping rates of ground-state density matrix elements. This means that the lifetimes of the pump-prepared excited states do not limit the resolution in the spectra. This same situation also obtains in frequency-domain SES.¹³
4. The experimental results show that particularly simple rotational structure – namely, an overwhelmingly dominant Q-branch feature – often characterizes a resonance in a FT-SES spectrum. Figure 1a shows such a spectrum for *t*-stilbene. This feature of FT-SES means that the vibrational linewidths even of very large species may be measured with minimal interference from rotational congestion. Furthermore, very accurate vibrational frequencies may be readily obtained.
5. Finally, unpublished experimental results show that although the manifestations of rotational structure may not be apparent in a FT-SES spectrum (i.e., only a single peak is present per vibrational resonance), such manifestations are *apparent in the interferogram associated with that spectrum*. Essentially, the information concerning

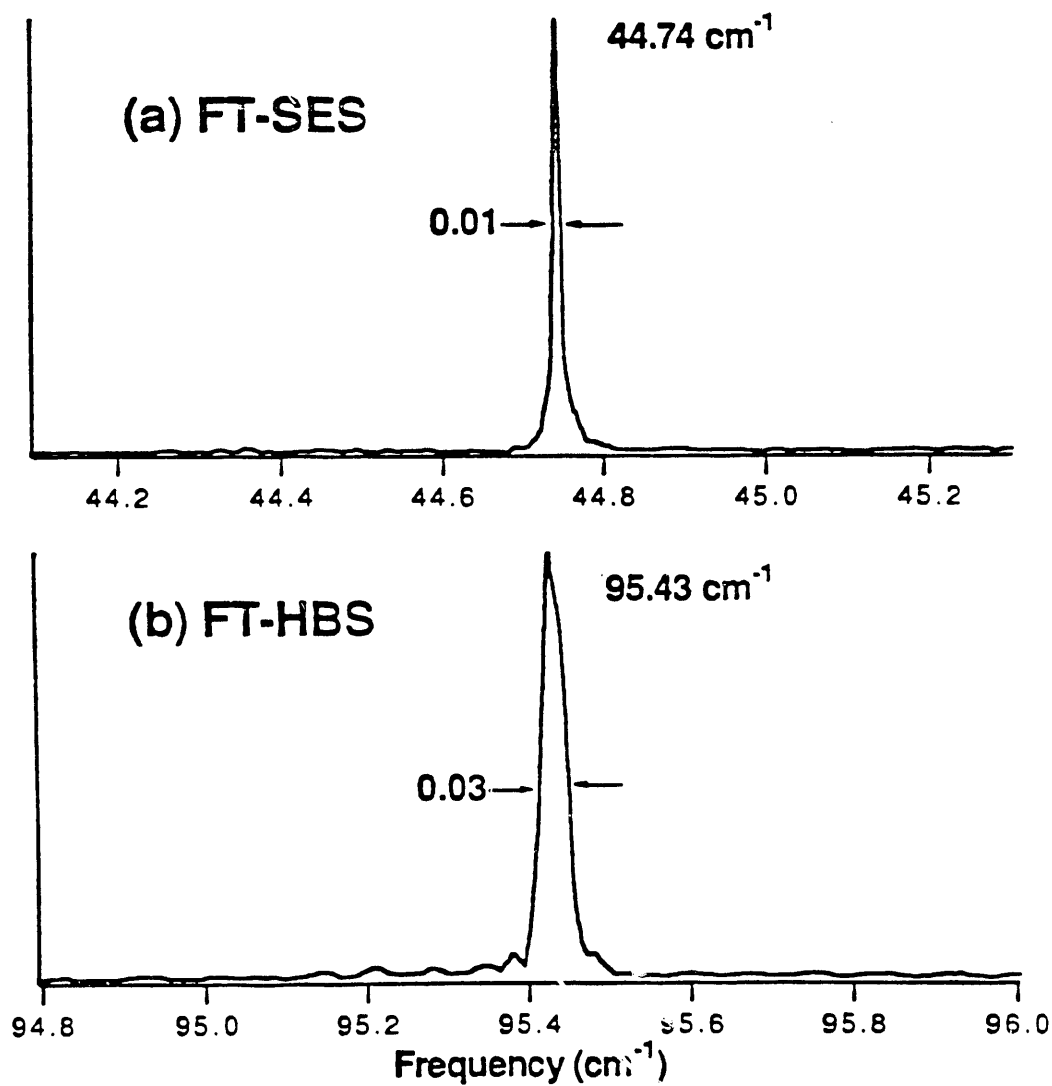


Figure 1. (a) FT-SES power spectrum corresponding to the 37_0 - 37_4 vibrational interval of jet-cooled t-stilbene. The excited intermediate state was the S_1 vibrationless level. (b) FT-HBS power spectrum corresponding to the 37_2 - 37_0 vibrational interval of t-stilbene. The pertinent ground-state level in the HBS process was the 0_0 level.

rotations is localized in the interferogram and therefore present with good signal-to-noise. In the Fourier spectrum, however, the information is delocalized throughout the spectrum and does not rise above the noise. The effect is analogous to the rotational coherence effects that enter into picosecond time-resolved results on isolated molecules.¹⁴ It could provide a means for the high resolution rotational spectroscopy of large species, just as rotational coherence spectroscopy does.¹⁴⁻¹⁸

B. Fourier transform hole-burning spectroscopy

In analyzing FT-SES we came to realize that (1) fluorescence-detected hole-burning spectroscopy (HBS)¹⁹ could be implemented interferometrically as a Fourier transform spectroscopy, (2) such an implementation could be effected with the same apparatus as used for FT-SES, and (3) the theoretical analysis of the method would be very similar to that of FT-SES. Given these facts, we undertook a theoretical and experimental study of FT-HBS the results of which will be published with the analogous results on FT-SES.¹¹ FT-HBS is implemented in precisely the same way as FT-SES except that the pump pulse and the probe pulse are tuned to two different vibronic transitions originating in the same ground-state vibrational level (see Fig. 2). The result of a FT-HBS experiment is a spectrum of excited-state resonances corresponding to the two excited state levels involved ($|e\rangle$ and $|n\rangle$) of Fig. 2). Like FT-SES this method has promise in part because it can be implemented at high resolution with any convenient light source without regard to their bandwidths. In addition, the following results regarding FT-HBS have been obtained.¹¹

1. The resolution of FT-HBS is limited by the length of the interferogram taken. Besides being independent of pump and probe bandwidths, the resolution is also independent of the corresponding pulsewidths and the delay between the pulses. This means that high resolution FT-HBS can be implemented with high repetition-rate picosecond laser sources, for example.
2. Doppler broadening in FT-HBS is proportional to the energy difference between the two excited-state levels involved in the process, and does not depend on the vibronic transition frequencies.
3. Homogeneous broadening in FT-HBS is determined by the damping rates of density matrix elements associated with the excited-state manifold.

4. Finally, just as in FT-SES we find that rotational structure in FT-IHS often is of a particularly simple form, namely a dominant Q-branch feature (see Fig. 1b). Because of this and because of the high accuracy in line position measurement that obtains in Fourier spectroscopies,³⁸ one expects that FT-IHS may be especially valuable in the measurement of very accurate excited-state vibrational intervals.

III. Developments in IDSRS

Ionization-detected stimulated Raman spectroscopies are three-color (or four-color) double-resonance schemes in which the population shifts induced by stimulated Raman scattering processes are probed by resonantly enhanced multiphoton ionization (REMPI). Two variants of IDSRS exist. The first pertains to the measurement of the increase in population of the final state in the Raman process. This scheme, invented by Esherick and Owyong,²⁰ we call ionization-gain stimulated Raman spectroscopy (IGSRS). The second involves the measurement of the population loss in the initial state of the Raman process. This method, invented by Bronner, et al.,²¹ we call ionization-loss stimulated Raman spectroscopy (ILSRS). These methods have great potential in the ground-state vibrational spectroscopy of jet-cooled species. (See, for example, Ref. 9 or section II B of the project description.) In part, such potential derives from work performed in this laboratory. We list four of the more significant developments below.

- (1.) *Implementation of mass analysis.* IDSRS schemes are very well suited to mass-selectivity given that the IDSRS observable consists of photoions. With mass-selective detection one has a powerful means by which to measure size-specific Raman spectra in cluster studies, a considerable experimental advantage in such studies. We have been the first to implement IDSRS with mass analysis.⁸ This development has been essential to the success of all our applications of IDSRS.
- (2.) *Development of Fourier transform-IDSRS.* We have shown that IDSRS schemes can be implemented interferometrically as Fourier transform spectroscopies.^{6,7,9} These schemes are analogous to the FT-SES scheme discussed above. They have the major advantage that the Raman resolution is limited by the interferometer, not by the bandwidths of the Raman excitation fields. Also significant is the fact that very accurate vibrational frequencies are readily obtained in FT-IDSRS spectra, a common feature

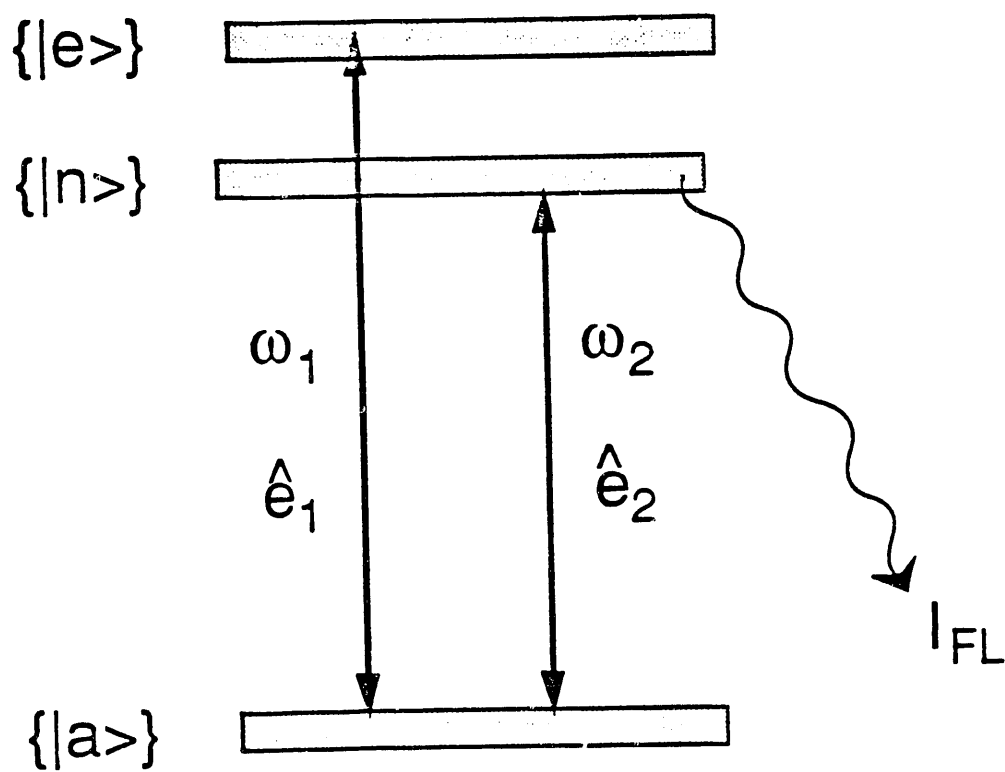


Figure 2. Energy level diagram for HBS. The $\{|a\rangle\}$ manifold corresponds to a vibrational level of the ground electronic state. The $\{|e\rangle\}$ and $\{|n\rangle\}$ manifolds correspond to vibrational levels of an excited electronic state.

of Fourier spectroscopies. We have successfully implemented FT-IDSRS with a He-Ne laser-calibrated interferometer capable of a spectral resolution of 0.05 cm^{-1} .^{9,10,22} FT-IDSRS has been very important in our studies of benzene clusters (see below).^{10,22}

(3.) *Development of ILSRS for molecular beam studies.* ILSRS is a depletion (hole-burning) spectroscopy. Because it relies on (a) the ability to effect significant population shifts by stimulated Raman processes, and (b) the ability to generate a background ion signal that is fairly stable, it was not obvious that it would find general application in molecular beam studies. We are the first to have applied ILSRS in such studies.^{6,8,9} Moreover, we have shown that it is indeed a technique with wide applicability in species-specific, medium-to-high resolution vibrational spectroscopy of jet-cooled molecules and molecular clusters. Part of the success with ILSRS derives from our implementation⁹ of a normalization scheme adapted from the clever IR-REMPI normalization method of Page, et al.²³ In addition, some intrinsic features of ILSRS are very valuable.⁹ First, the method allows for the measurement of Raman spectra even when the final state in the Raman process is short-lived due to vibrational redistribution or predissociation processes. Second, it can be used to probe the Raman resonances of all the moieties in a molecular cluster, not just the one involved in the REMPI excitation process. Thus, for example, in phenol-benzene, the Raman resonances of both phenol and benzene can be characterized (see Fig. 3).²⁴ In phenol-water, both the phenol-localized and the water-localized O-H stretch fundamentals can be probed.

(4.) *Implementation of IDSRS with two-color REMPI.* Photofragmentation is a process that can impede severely the measurement of size-specific spectra of clusters in studies based on REMPI. One way to minimize photofragmentation is to use a two-color photoionization REMPI scheme in which the species is ionized just above threshold.²⁵ We have demonstrated that IDSRS methods can be readily implemented with two-color REMPI. In many cases, this scheme will allow better species-specificity in the measurement of Raman spectra.

The developments listed above are perhaps best illustrated by a discussion of the results obtained in this laboratory with mass-selective IDSRS. Such results are the subject

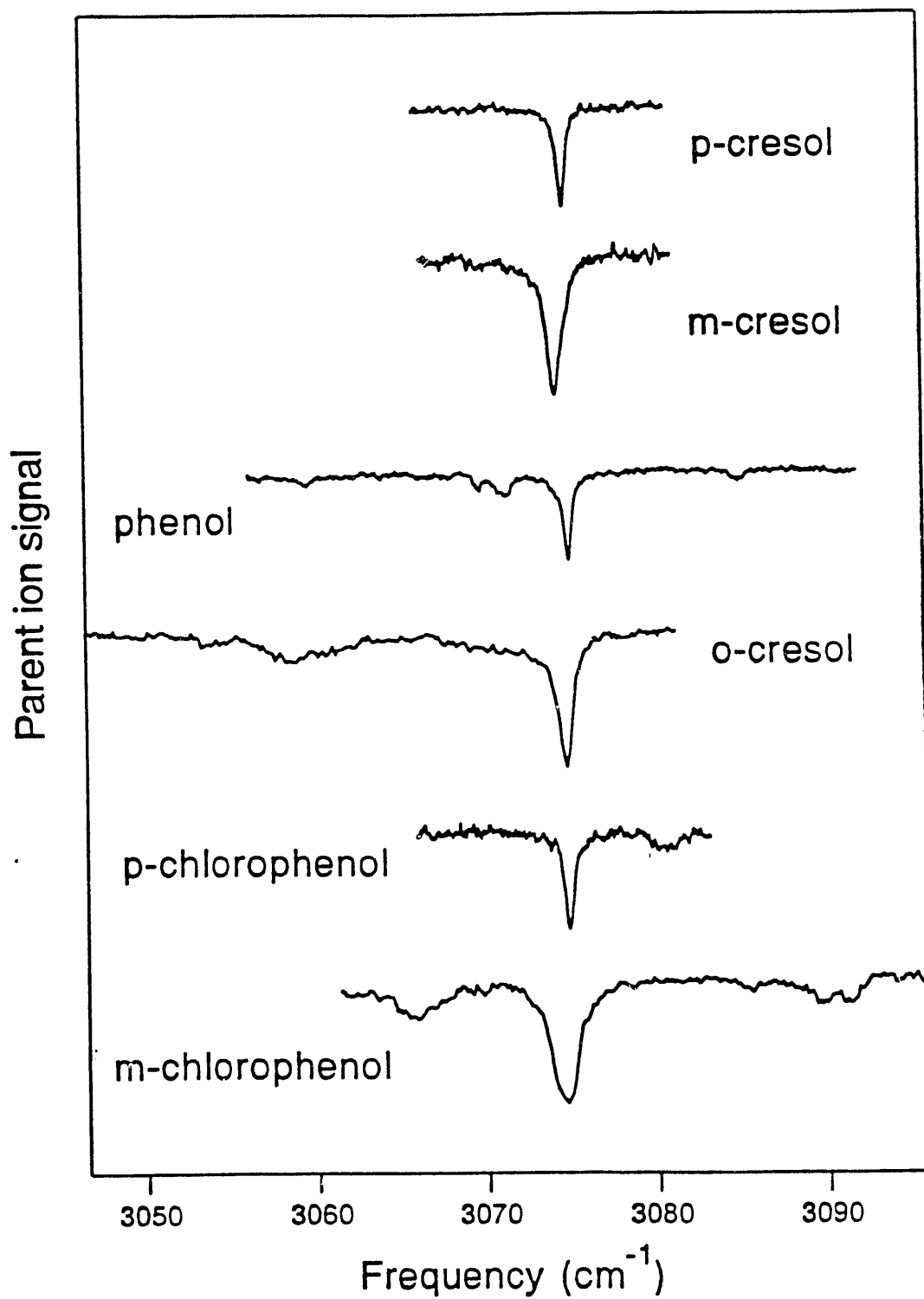


Figure 3. ILSRS spectra of the benzene-localized ν_2 mode in substituted phenol-benzene complexes. The pertinent phenol associated with each trace is given in the figure.

of the following sections.

IV. IDSRS Studies of Benzene Clusters

The spectroscopy of benzene clusters, particularly the dimer, has received considerable attention in recent years.²⁶ The motivation for such attention derives in large part from the desire to characterize the forces between aromatics. Given that benzene is the prototypical aromatic, has high symmetry, and a great deal is known about it, clusters of benzene are attractive systems for the study of such forces.

We have obtained IDSRS results on isotopically pure and mixed benzene clusters^{8,10,22} in three regions of the vibrational spectrum, that corresponding to the totally symmetric ring breathing fundamental (ν_1) of benzene in the 940 to 1000 cm^{-1} region (depending on isotopic substitution), that corresponding to the totally symmetric C-H stretch fundamental (ν_2) near 3074 cm^{-1} (2300 cm^{-1} for perdeuterated benzene), and that corresponding to the fundamental of the doubly degenerate ν_6 mode near 600 cm^{-1} in the perprotonated species. The results speak to the geometries, the vibrational dynamics, and the magnitudes of vibrational coupling matrix elements in the species. They are summarized below.

A. Benzene dimer

We have spent a lot of time studying benzene dimer and isotopomers thereof. One aspect of this species that has been of particular interest to us has been its geometry. Oddly enough, despite numerous spectroscopic studies,²⁶ there is no consensus on what the dimer geometry is. Indeed, there is disagreement on gross features of the geometry, such as whether or not the benzene moieties are symmetrically equivalent. Our Raman results^{10,22} strongly indicate that the benzenes in benzene dimer are symmetrically *inequivalent*, in contrast to interpretations made of vibronic spectroscopic results.^{26d,r}

The IDSRS evidence for inequivalent benzenes in benzene dimer consists principally of the splittings and frequency shifts of the ν_1 and ν_2 fundamentals in the various isotopomers of the species. Figure 4 shows that the $h_6 - h_6$ dimer (h_6 represents fully protonated benzene) and the $d_6 - d_6$ dimer each have two Raman resonances in the ν_1 region. The ν_2 resonances of these homodimers are also split. Such splittings might have been expected, even for a symmetrical dimer, given that excitation exchange interactions will mix the ν_1 (or ν_2) level of one benzene in the dimer with that of the other. However, analysis²²

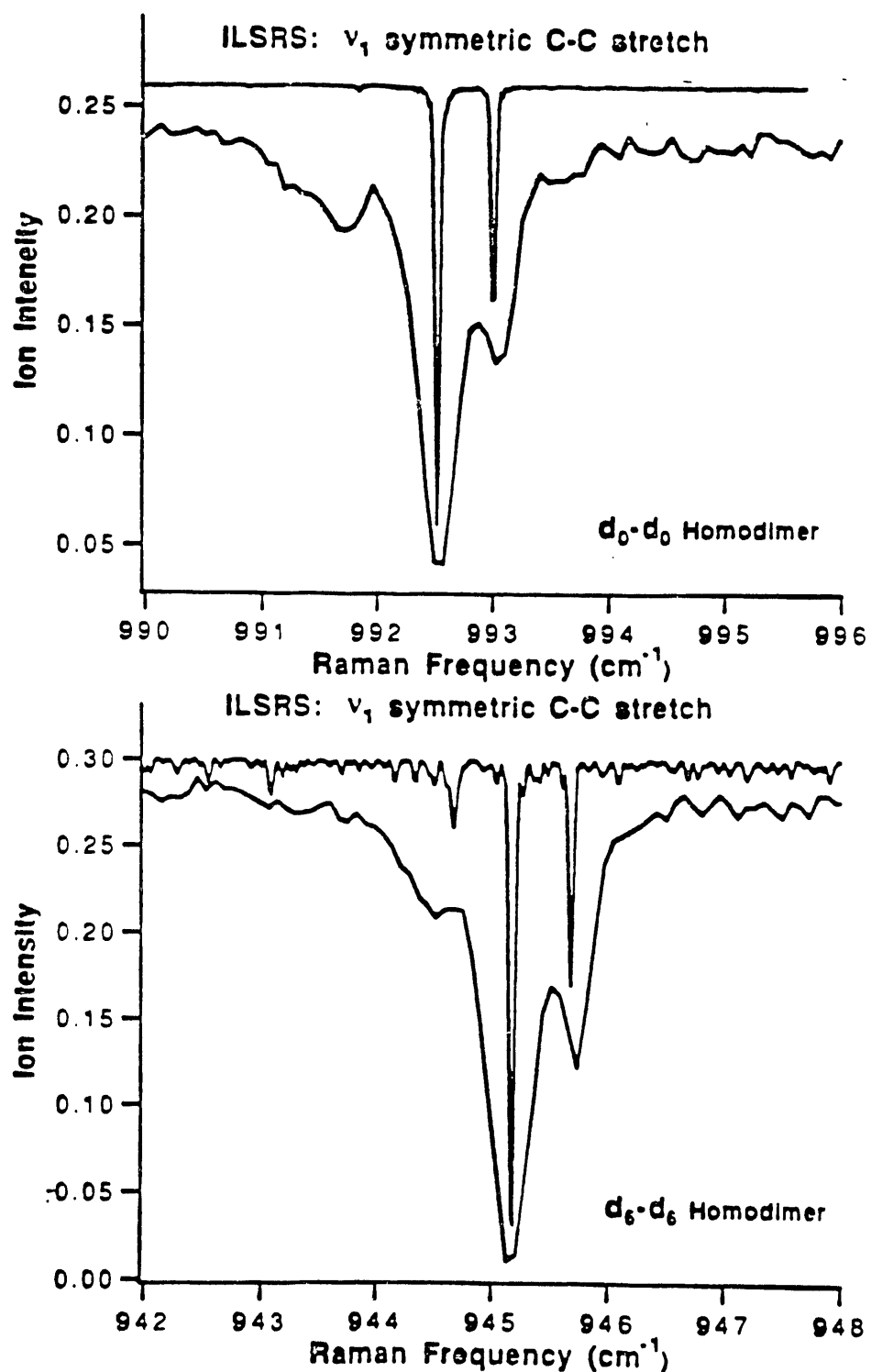


Figure 4. Top - FT-ILSRS spectrum in the region of the ν_1 fundamental of perprotonated benzene dimer. The low resolution trace is a frequency-domain trace at 0.3 cm^{-1} resolution. Bottom - Same as the top except for the perdeuterated species.

shows that such mixing in a symmetrical dimer will produce two resonances with the lower frequency one carrying all of the Raman intensity and the higher frequency one having no Raman intensity at all (in the limit where the isotropic part of the Raman polarizability tensor dominates). Thus, the homodimer results in the ν_1 and ν_2 regions indicate an asymmetrical dimer.

These results are fully supported by IDSRS measurements on the $h_6 - d_6$, $h_6 - d_1$, and $d_6 - d_1$ isotopomers. For each of these dimers we find *two resonances* in the region of the ν_1 (and ν_2) fundamentals of each of the moieties. For example, for $h_6 - d_6$ there are two resonances in the region of the h_6 -localized ν_1 fundamental (at 992.66 and 992.93 cm^{-1}) and two in the region of the d_6 -localized ν_1 fundamental (at 945.28 and 945.59 cm^{-1}). This is very strong evidence for inequivalent sites in the dimer. Moreover, if one looks at the magnitudes of the splittings of the fundamentals in the various dimer isotopomers, one finds further strong evidence for inequivalent benzenes.^{10,22} For example, the ν_1 doublets in the $h_6 - h_6$ and $d_6 - d_6$ homodimers are split by the same amount. However, the h_6 -localized ν_1 doublets in $h_6 - d_6$ and $h_6 - d_1$ are split by values smaller than in the homodimers but identical to one another. These results point to an inherent ν_1 site splitting of 0.3 cm^{-1} in all of the dimers, with an additional excitation exchange contribution in the homodimers. It is pertinent to point out that the magnitudes of these splittings are directly related to terms in the Taylor series expansion of the intermolecular potential with respect to the benzene normal coordinates.²⁷ Thus, accurate, experimentally determined splittings can provide one with a stringent test of trial intermolecular potential energy surfaces. We have done some work,²² and plan to do considerably more, toward using our experimental results in this capacity.

A final set of results that bear on the geometry of the dimer were obtained by characterizing the vibronic resonances of the vibrational levels excited by the various ν_1 resonances of the dimer isotopomers. For example, Fig. 5 shows that the vibronic spectrum in the region of the $S_1 \leftrightarrow S_0$ $1_1^0 6_0^1$ band that results subsequent to excitation of the 993.02 cm^{-1} Raman resonance in $h_6 - h_6$ has a markedly different intensity distribution than that which arises subsequent to excitation of the Raman resonance at 992.53 cm^{-1} in the same species. For the mixed isotopomers the differences are even more extreme (see

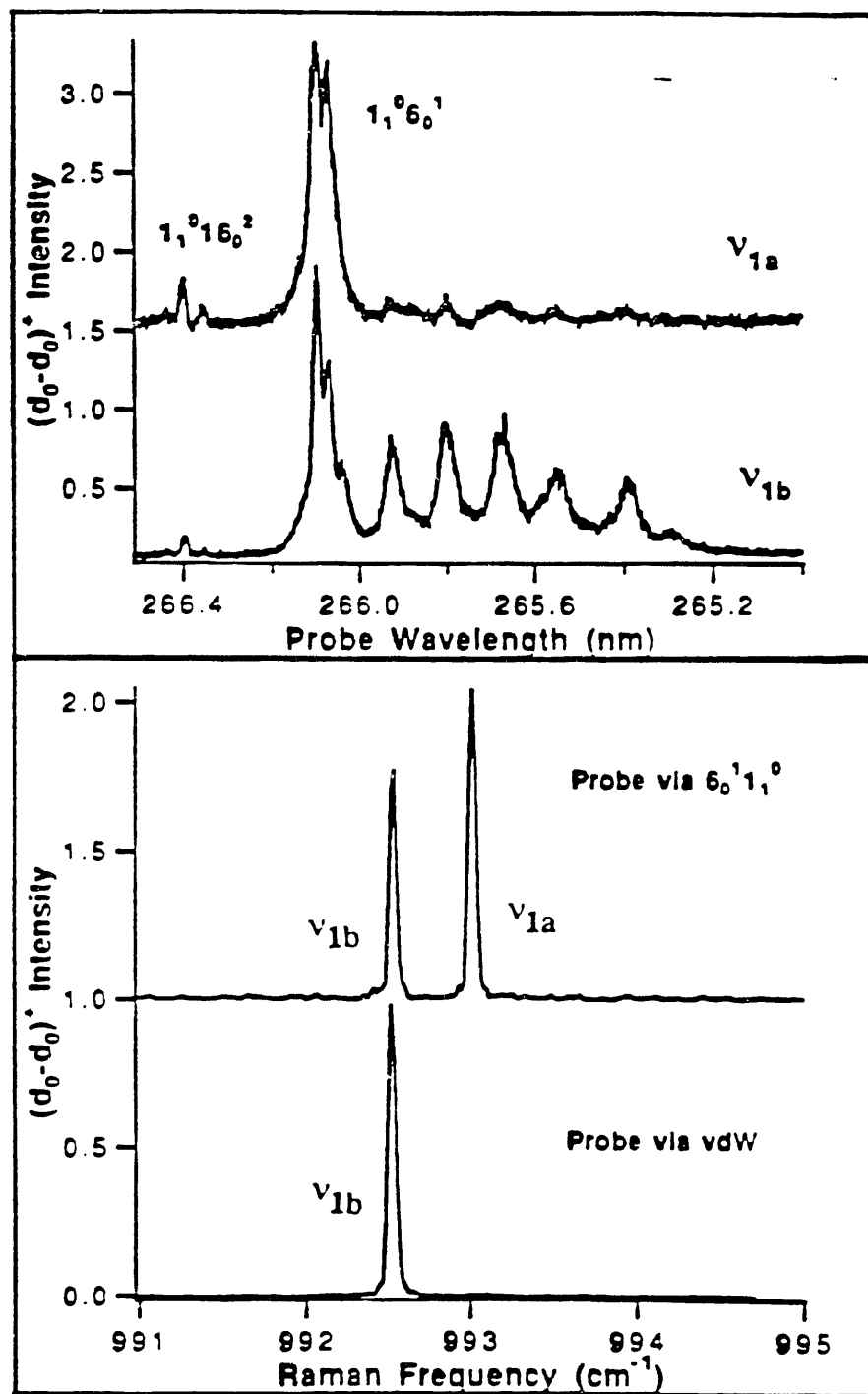


Figure 5. Top - The vibronic spectra in the $1^0_1 6^1_0$ region of perprotonated benzene dimer that arise subsequent to Raman excitation of each of the two v_1 resonances of the species (shown below).

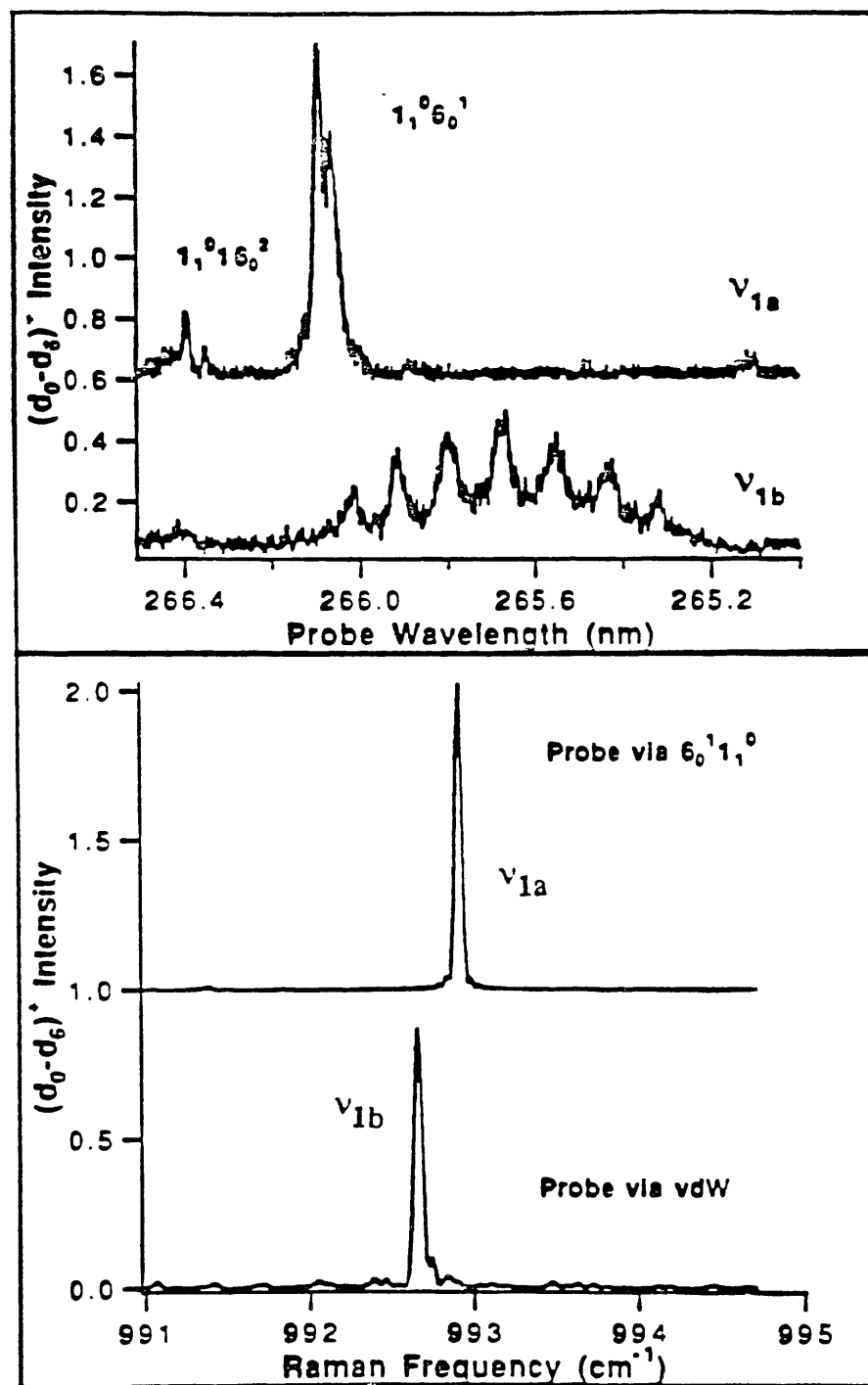


Figure 6a. Top - The vibronic spectra in the $1^0_{16}1^0$ region of the h_6-d_6 benzene dimer that arise subsequent to Raman excitation of each of the two v_1 resonances of the species (shown below).

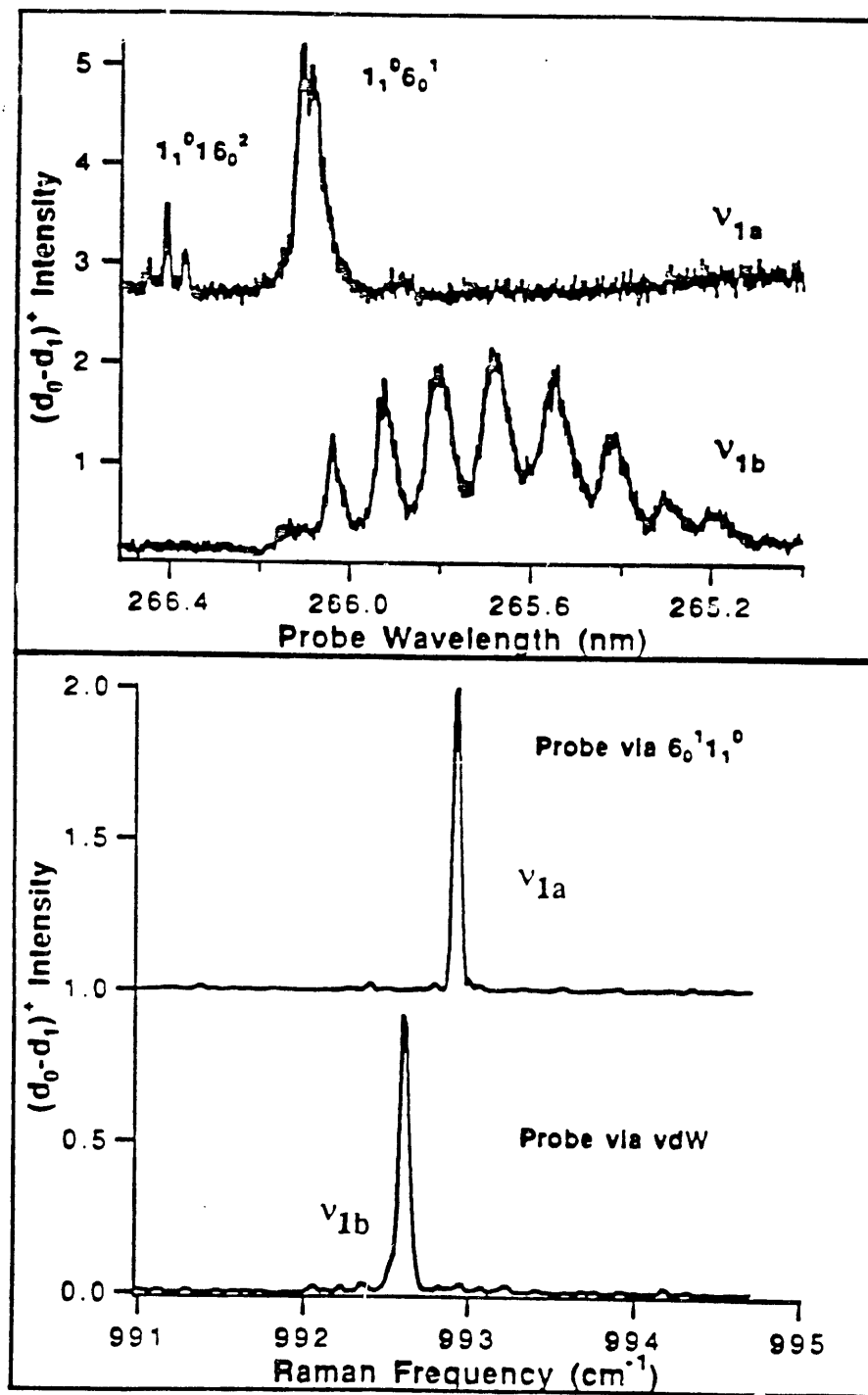


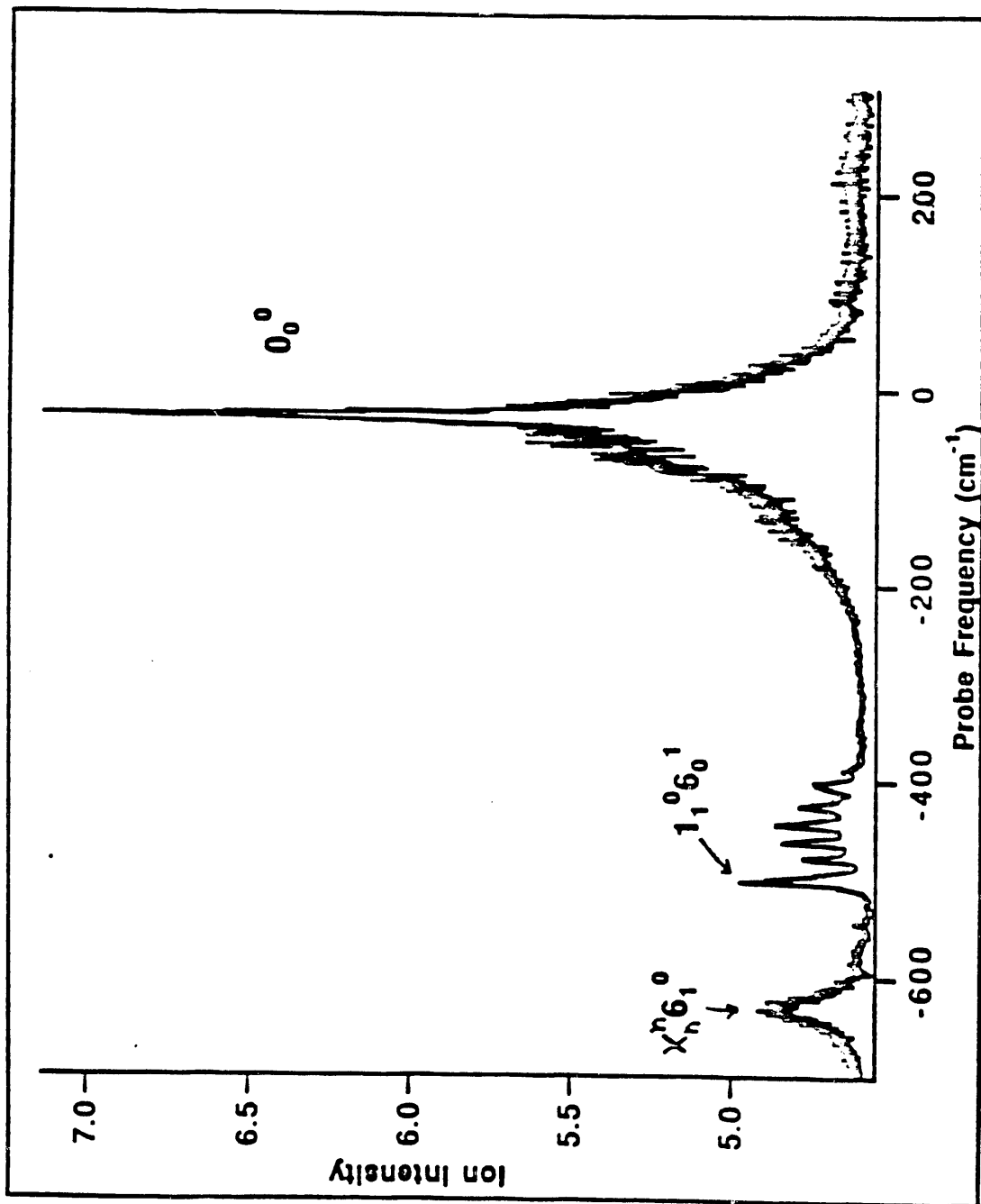
Figure 6b. Top - The vibronic spectra in the $10^0 16^1_0$ region of the h_6-d_1 benzene dimer that arise subsequent to Raman excitation of each of the two v_1 resonances of the species (shown below).

Figs. 6a and 6b). These results are readily interpreted in terms of vibronic excitations localized the different moieties of an asymmetrical dimer. A further interesting implication from these double resonance vibronic spectra is that there is a large geometry change subsequent to vibronic excitation of one of the benzene moieties in the dimer, such geometry change being reflected in the prominent progressions in low frequency intermolecular modes.

In addition to the geometry of the dimer we have also been concerned with its vibrational dynamics. Information on vibrational dynamics can be obtained in several ways by IDSR methods. First, linewidths of Raman resonances provide lower limits to the lifetimes of the states involved in the transition. Second, time-resolved IGSRS experiments can be performed in which the delay between the Raman-pump and REMPI probe pulses is varied while ion signal is monitored. Third, information regarding the "acceptor" (final) states in IVR or predissociation processes induced by Raman excitation can be obtained by exciting the Raman resonance of interest and scanning the REMPI probe frequency.

One result of interest pertains to the lifetime of the ν_1 -excited dimer. Given the presence of six, low frequency intermolecular modes in the species and the possibility for predissociation upon excitation with 1000 cm^{-1} of vibrational energy, one might expect the ν_1 -excited species to decay on a sub-nanosecond timescale. In fact, by nanosecond time-resolved IGSRS experiments, we have found that the species has a lifetime of about 30 nsec.²² We also have evidence, however, that the species does undergo an IVR process. In particular, we have found that the 6_1 level acts as an acceptor mode for such a process. A Raman-induced vibronic spectrum that provides evidence for this is shown in Fig. 7.

For vibrational excitation in the ν_2 region of the dimer we have obtained dynamical information from linewidths and from the measurement of vibronic spectra subsequent to Raman-excitation. Three results are of most interest. As mentioned above all the dimer isotopomers exhibit doublets in the region of the h_6 -localized ν_2 fundamental and in that of the d_6 -localized ν_2 fundamental. We have found that the two members of any one of these doublets have markedly different linewidths, the lower frequency resonance being about 1 cm^{-1} wide and the higher frequency one being about 0.3 cm^{-1} wide. Examples of this behavior are shown in Fig. 8 for the $h_6 - h_6$ and $d_6 - d_6$ homodimers. Such is evidence for



7. Figure 9. Vibronic spectrum of benzene dimer obtained by scanning the probe laser (ω_3) in an IGSR experiment. The Raman excitation fields were fixed to a resonance in the ν_1 region of the dimer. The $1^0_1 6^0_0$ band arises from the Raman-excited 1^0_1 level. The $X^n_n 6^0_1$ feature arises from states populated by IVR from the initially prepared 1^0_1 level.

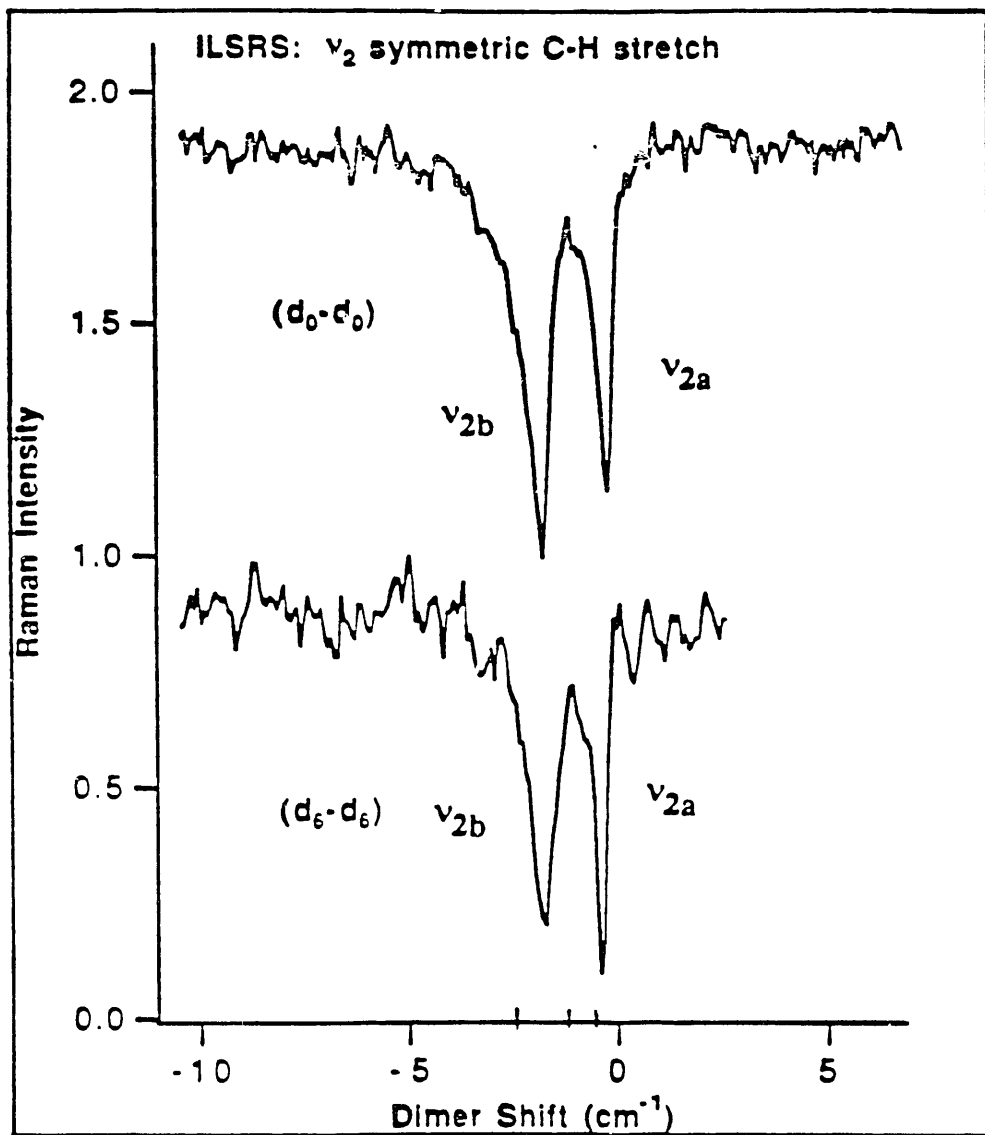


Figure 8. Frequency-domain ILSRS spectra in the ν_2 region of perprotonated benzene dimer (top) and perdeuterated benzene dimer (bottom).

mode-selective vibrational dynamics in the ν_2 region of the dimer. Apparently, ν_2 -excited benzene residing in one site of the dimer relaxes considerably faster than ν_2 -excited benzene in the other inequivalent site. A second point of interest in regard to the ν_2 dynamics of the dimer is that the lifetime lower limits derived from spectra like those of Fig. 8 are larger than one might expect. For example, lifetimes longer than 15 psec are derived from the linewidths of the ν_{2a} resonances in Fig. 8. Such lifetimes seem surprisingly long given the 3070 cm^{-1} excitation energy and the relatively large size of this weakly bound complex. A third point regarding ν_2 dynamics in the dimer is that we have obtained very limited results pertaining to the increase in population of "relaxed" vibrational states subsequent to IVR after ν_2 excitation. As in the ν_1 case, such results were obtained by scanning the REMPI probe laser with the Raman frequency set to the vibrational resonance of interest.

All of the experimental results quoted above pertain to the ν_1 and ν_2 fundamentals. We have also measured IDSRS spectra of the dimer in the region of the nontotally symmetric ν_6 fundamental of benzene. These results, for example the IGSR spectra of Fig. 9, are more difficult to obtain and to interpret than those corresponding to the totally symmetric fundamentals. They will become more useful when more becomes known about the structure of the species.

B. Benzene trimer

As for the dimer of benzene, we have made extensive IDSRS measurements relating to the ν_1 and ν_2 fundamentals of benzene trimer isotopomers. Again, the results relate to the geometry and the dynamics of this species.

Our results relating to geometry point to a *symmetrical, cyclic* structure for benzene trimer.²² This interpretation of the Raman results is at variance with the interpretation of the vibronic spectroscopy of the species, from which a "herring-bone" structure has been inferred.^{26h} Nevertheless, we feel the evidence for the cyclic structure is compelling. The evidence takes several forms: (a) the number of Raman resonances in the ν_1 and ν_2 regions, (b) the shifts of those resonances as a function of isotopic substitution, and (c) the intensities of the resonances as a function of isotopic substitution. In regard to the first point, to within our resolution, we have been able to observe only one resonance in each of the ν_1 and ν_2 regions pertinent to any one of the trimers. For example, Fig. 10 shows

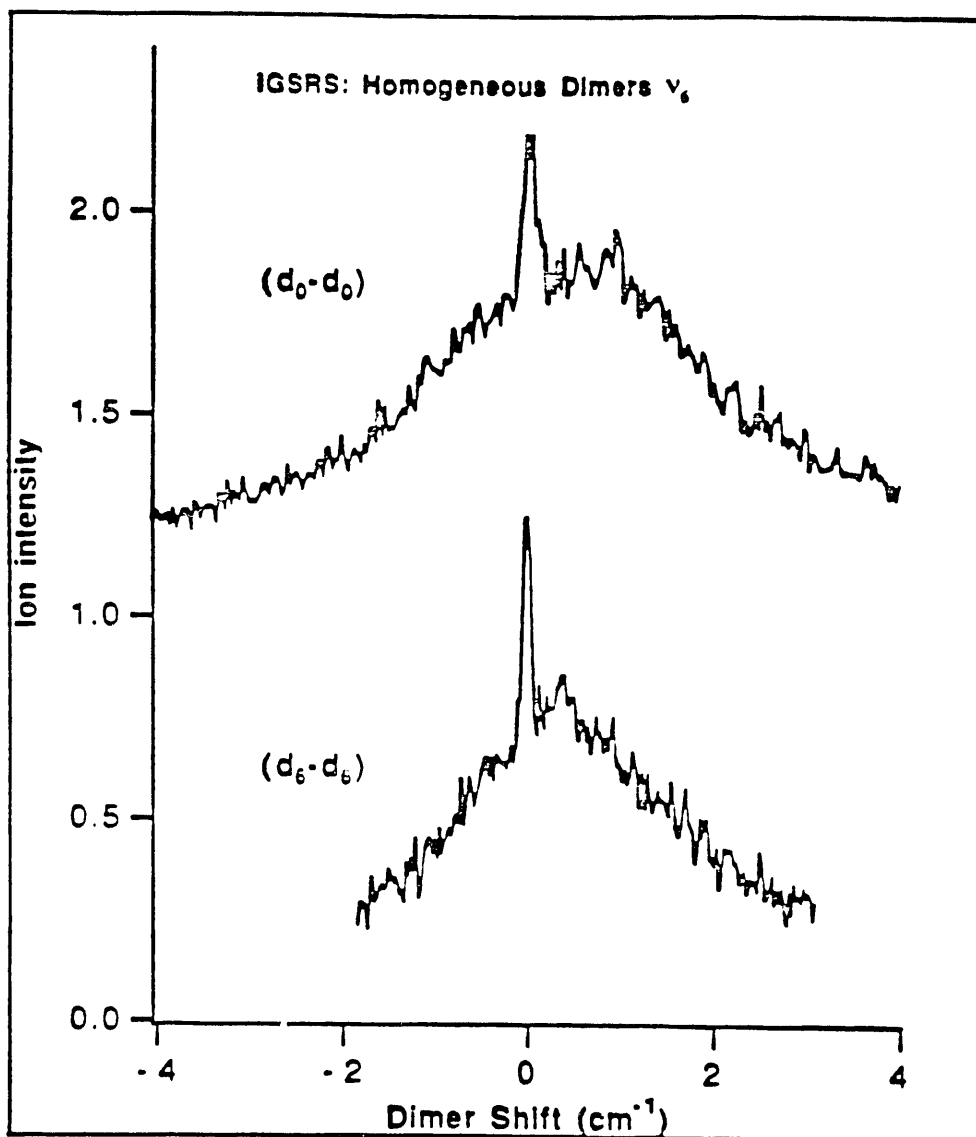
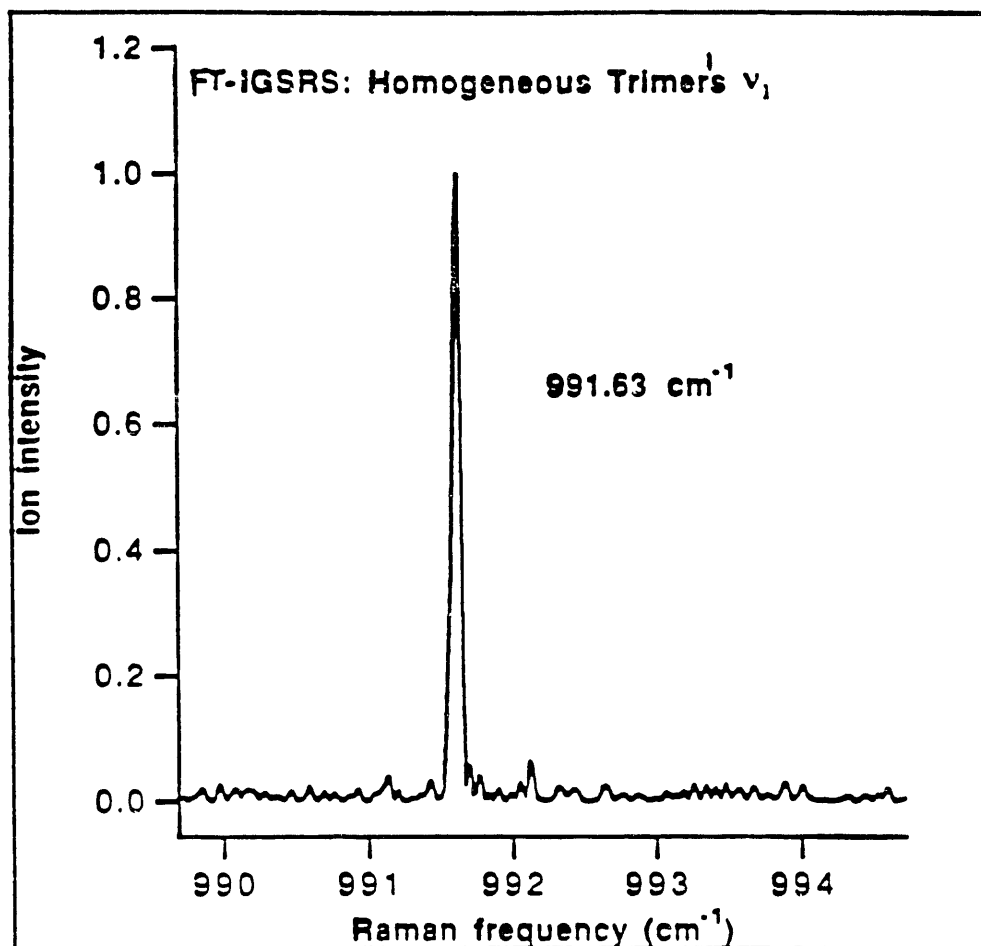


Figure 9. Frequency-domain IGSRS spectra pertaining to the ν_6 fundamentals of perprotonated benzene dimer (top) and perdeuterated benzene dimer (bottom).



10.
Figure 8. FT-IGSRS spectrum taken for jet-cooled benzene trimer in the region of the ν_1 fundamental (totally symmetric ring-breathing mode) of benzene.

a 0.05 cm^{-1} -resolution FT-IGSRS spectrum in the ν_1 region of the $(h_6)_3$ homotrimer. In regard to the shifts of these trimer resonances as a function of isotopic substitution, we find consistent trends in which the homotrimer (e.g., $(h_6)_3$) produces the lowest frequency resonance, substitution of one of the moieties with a different benzene isotopomer gives rise to a shift to the blue, and substitution of two of the moieties produces a further shift to the blue. For example, Fig. 11 shows the shift behavior of the d_6 -localized ν_1 resonances in ILSRS spectra of $(d_6)_3$, $(d_6)_2h_6$, and $d_6(h_6)_2$. Finally, Fig. 11 also provides a representative example of observed trends in relative intensities with isotopic substitution. Namely, the intensity of the fundamental associated with a given isotopic moiety decreases monotonically as the number of such moieties present in the trimer decreases. A perturbation theory analysis²² of the vibrational states in a weakly bound trimer shows that each of these trends is entirely consistent with a trimer structure in which all of the benzene moieties reside in symmetrically equivalent sites. Moreover, the coupling matrix elements derived from such an analysis as applied to our Raman results are consistent from isotopomer to isotopomer and consistent with what one would expect based on the IDSRS results for the dimer. In contrast, structures involving inequivalent benzene sites can only reproduce the Raman results for unreasonably large values of the coupling parameters. In regard to our interpretation of the trimer structure, it is pertinent to point out that recent binding energy measurements of benzene clusters also indicate a cyclic, symmetric form for the trimer geometry.²⁸ Moreover, minimum-energy geometry calculations in which a semi-empirical intermolecular potential was employed also predict such a trimer structure.²⁹

Results pertaining to the vibrational dynamics of the ν_1 -excited trimer have been obtained by nanosecond time-resolved IGSRS. Such experiments reveal that the vibrationally excited species lives for greater than 10 ns.²² As for the dimer, this is somewhat of a surprise. Given the size of the trimer and its twelve intermolecular vibrational modes, one might have expected IVR rates in the sub-nanosecond range at 1000 cm^{-1} vibrational energy. In the region of the ν_2 fundamentals the information on dynamics that we have obtained derives from Raman linewidth measurements. We find that the ν_2 -excited trimer lives for at least as long as 8 ps. It would appear that the coupling of the excited ν_2 vibra-

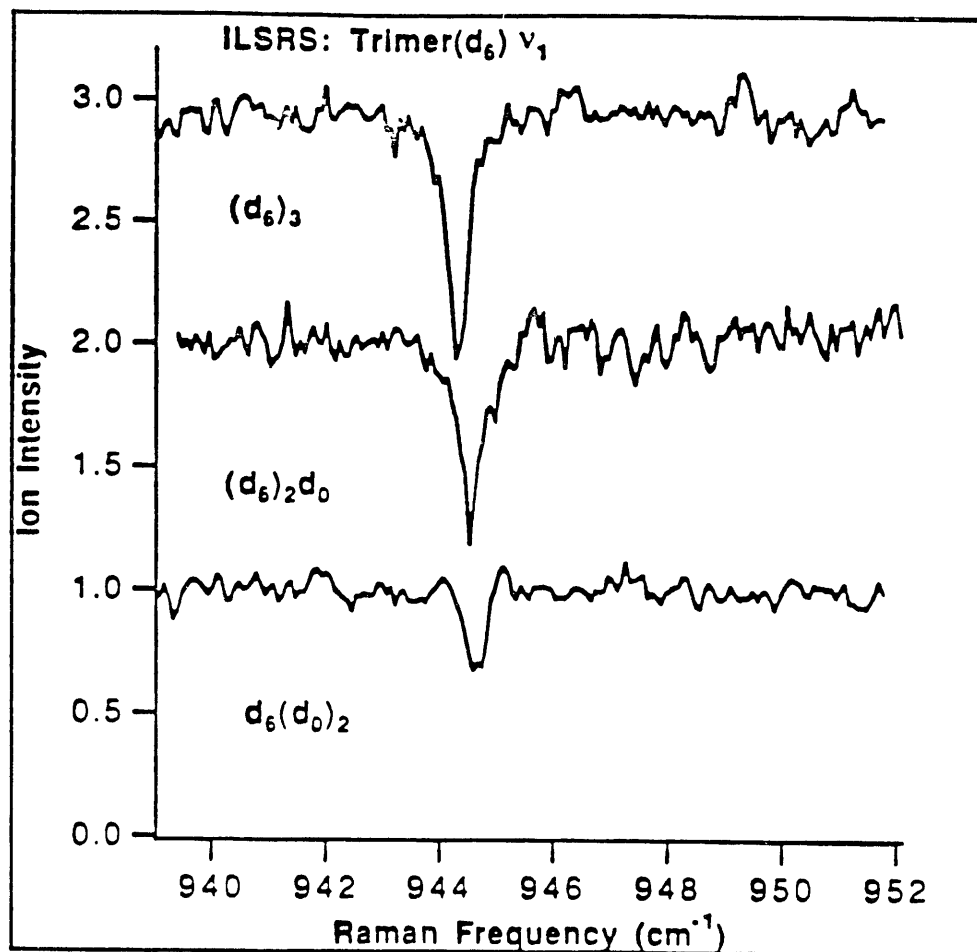


Figure 11. Frequency-domain ILSRS spectra in the d_6 -localized ν_1 region of fully deuterated benzene trimer (top), the $(d_6)_2h_6$ isotopomer (middle), and the $d_6(h_6)_2$ isotopomer (bottom).

tion of the trimer into the bath of vibrational levels dominated by excited intermolecular modes is not very strong.

C. Higher clusters of benzene

The IDSRS experiments we have done on clusters of benzene larger than the trimer are much less extensive than those pertaining to the dimer and trimer.²² A large part of the reason for this is because with our nanosecond laser sources we cannot perform IGSRs experiments on the species – their vibrational relaxation rates are apparently too fast.³⁰ (IGSRs should be possible on at least some of these species with a picosecond implementation of IDSRS.) Nevertheless, we have measured spectra in the ν_1 and ν_2 regions for fully protonated and fully deuterated clusters. One series of spectra is given in Fig. 12. From these spectra one qualitative conclusion that emerges is that the tetramer, pentamer, and hexamer (and probably the heptamer and octamer, as well) have benzene sites that are symmetrically inequivalent. The partially resolved structure in the tetramer, pentamer, and hexamer spectra of Fig. 12, compared with the single peak associated with the trimer, argue strongly for this conclusion. A second point in regard to the tetramer, at least, is a recurring theme in the benzene cluster studies, namely fairly slow IVR rates. Figure 13 shows a FT-ILSRS spectrum of the fully protonated tetramer in the ν_1 region. The spectrum is somewhat noisy, yet it is clear that the linewidth of the main peak in the spectrum is limited by the resolution of the apparatus (about 0.05 cm^{-1}). Such a width implies an excited vibrational state lifetime of at least 100 psec.

We plan further work on benzene clusters in the future. A sampling of some of this work is described in the accompanying proposal. I should point out that we have very recently made improvements to our molecular beam apparatus (a new, much better pulsed beam valve, a better pumping arrangement for the TOFMS) that have very significantly enhanced our capabilities for IDSRS. These changes will greatly facilitate further benzene cluster studies and IDSRS experiments in general.

V. IDSRS studies of phenol complexes

Van der Waals complexes containing phenol or phenol derivatives are of interest for several reasons. First, the hydrogen-bonding (H-bonding) interactions of phenol can serve as prototypes for the interaction of larger aryl alcohols. Second, clusters in which phenol is

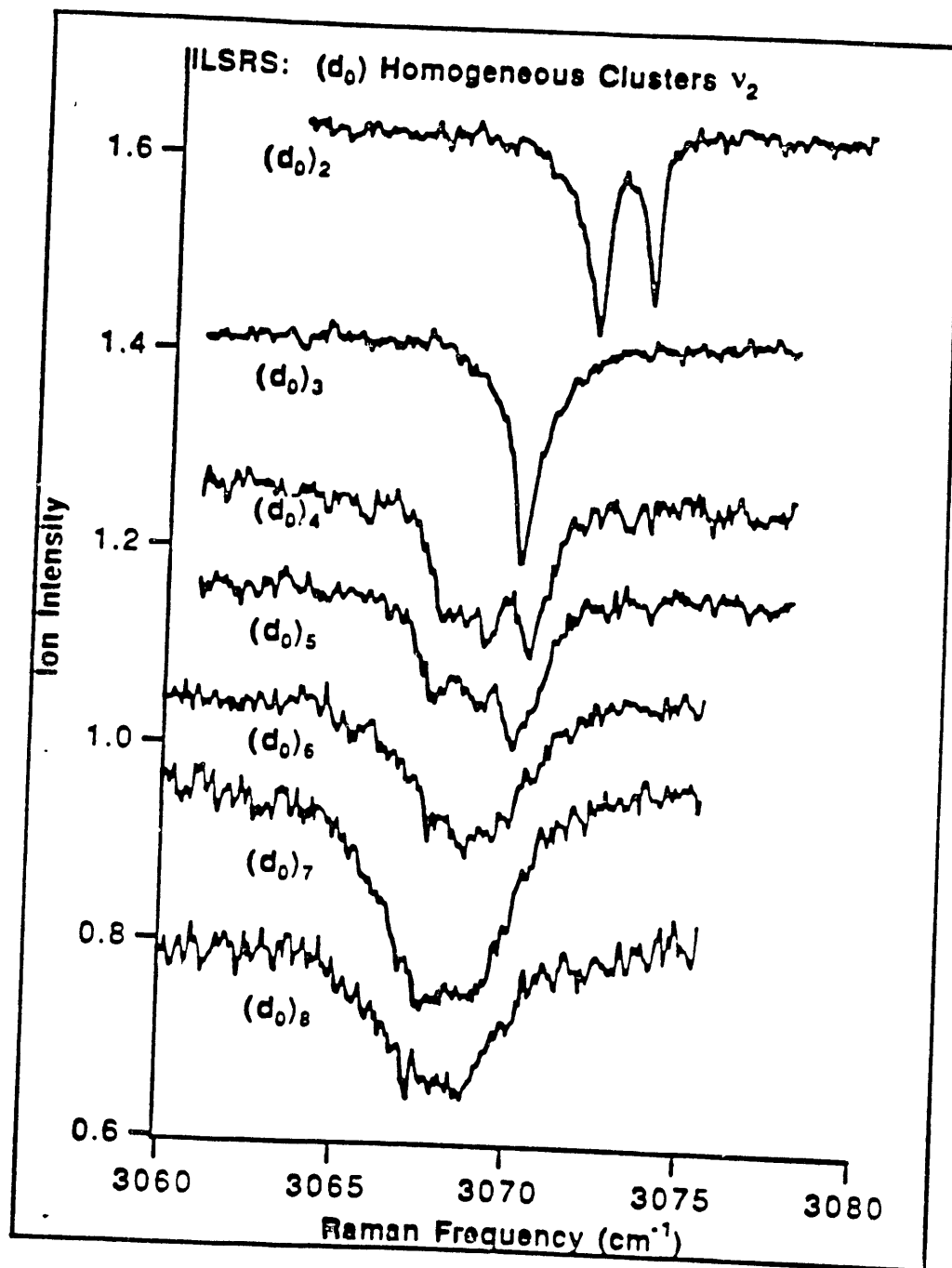


Figure 2. Frequency-domain ILSRS spectra for the series of jet-cooled perprotonated benzene clusters ranging from the dimer (top) to the octamer (bottom). The spectra are in the region of the ν_2 (totally symmetric CH stretch) fundamental of benzene.

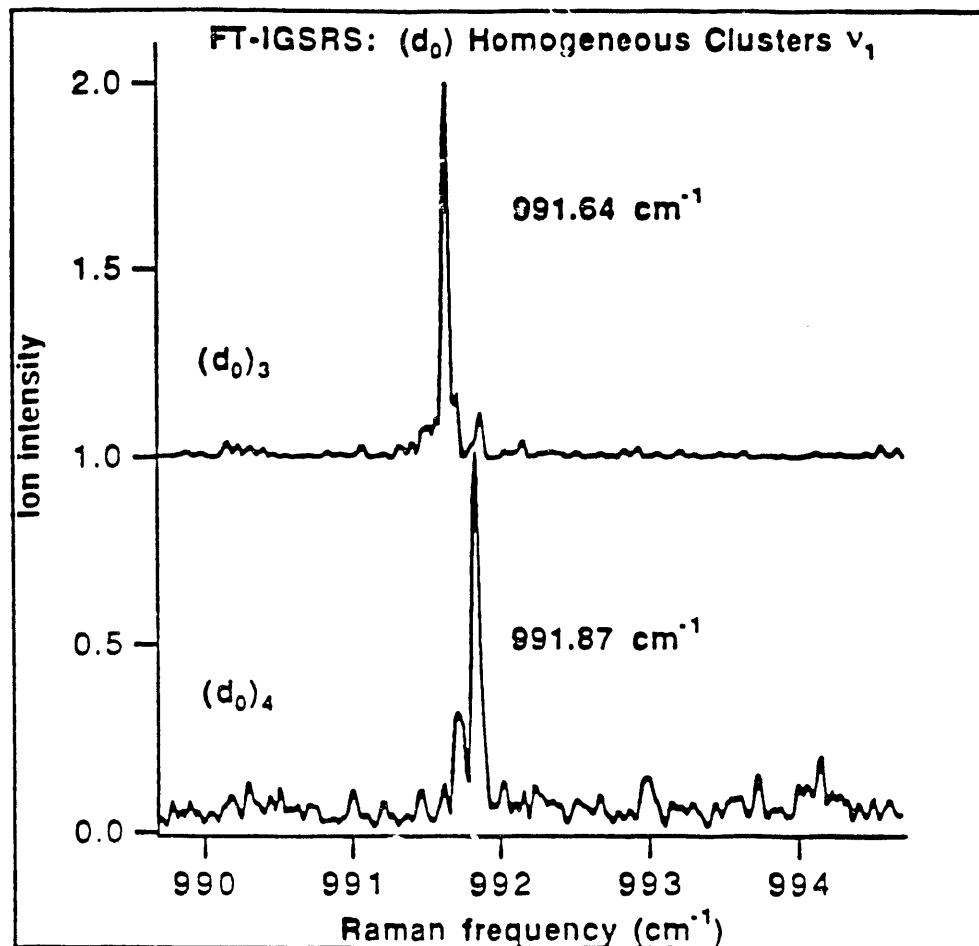


Figure 13. FT-ILSRS spectra in the ν₁ regions of fully protonated benzene trimer (top) and tetramer (bottom).

solvated by proton acceptors (ammonia, for example) exhibit excited-state proton transfer from the phenol moiety to the solvent species.³¹ Thus, these species provide the opportunity to study a very important type of reaction on a microscopic level. Third, there is a great deal of information pertaining to phenol H bonding in condensed phase systems.³² The study of phenol van der Waals complexes provides an opportunity to make connections between the condensed phase results and results on smaller systems. Fourth, phenol-M complexes are attractive systems in regard to their experimental accessibility (they are easy to make, the lowest energy, allowed electronic transition in phenol is at a convenient wavelength, etc.). Thus, these species are good model systems for the study of dynamical processes such as vibrational energy flow and predissociation in medium-to-large weakly bound complexes.

We have performed extensive frequency domain ILSRS experiments on jet-cooled, phenol-containing van der Waals complexes.²⁴ The experiments were undertaken for the reasons mentioned above and to obtain background information necessary for future studies of dynamics in these species. The results are also good examples of the capabilities of ILSRS.

Spectra were measured for phenol and monomethyl- and monochloro-phenols in combination with water, methanol, ethanol, diethyl ether, ammonia, benzene, N₂, methane and argon. The spectra encompass four spectral regions: the C-C stretch region (800 to 1050 cm⁻¹), the phenolic C-O stretch region (near 1260 cm⁻¹), the aromatic C-H stretch region (near 3070 cm⁻¹) and the O-H stretch region (~ 3500 to 3700 cm⁻¹). Full details regarding the experiments and results are given in a paper in press.²⁴ We summarize some of the principal results below.

A. Spectroscopic results

Figures 14 to 16 show ILSRS results for a variety of phenol complexes in three regions of the vibrational spectrum. The results are significant in several respects. First, they clearly show that mass-selective ILSRS is applicable in molecular beam vibrational spectroscopy at sub-wavenumber resolution throughout the vibrational fundamental region. Second, the spectra can be used to identify and characterize quantitatively "fingerprint" vibrational resonances for phenol - that is, phenolic resonances whose frequencies shift

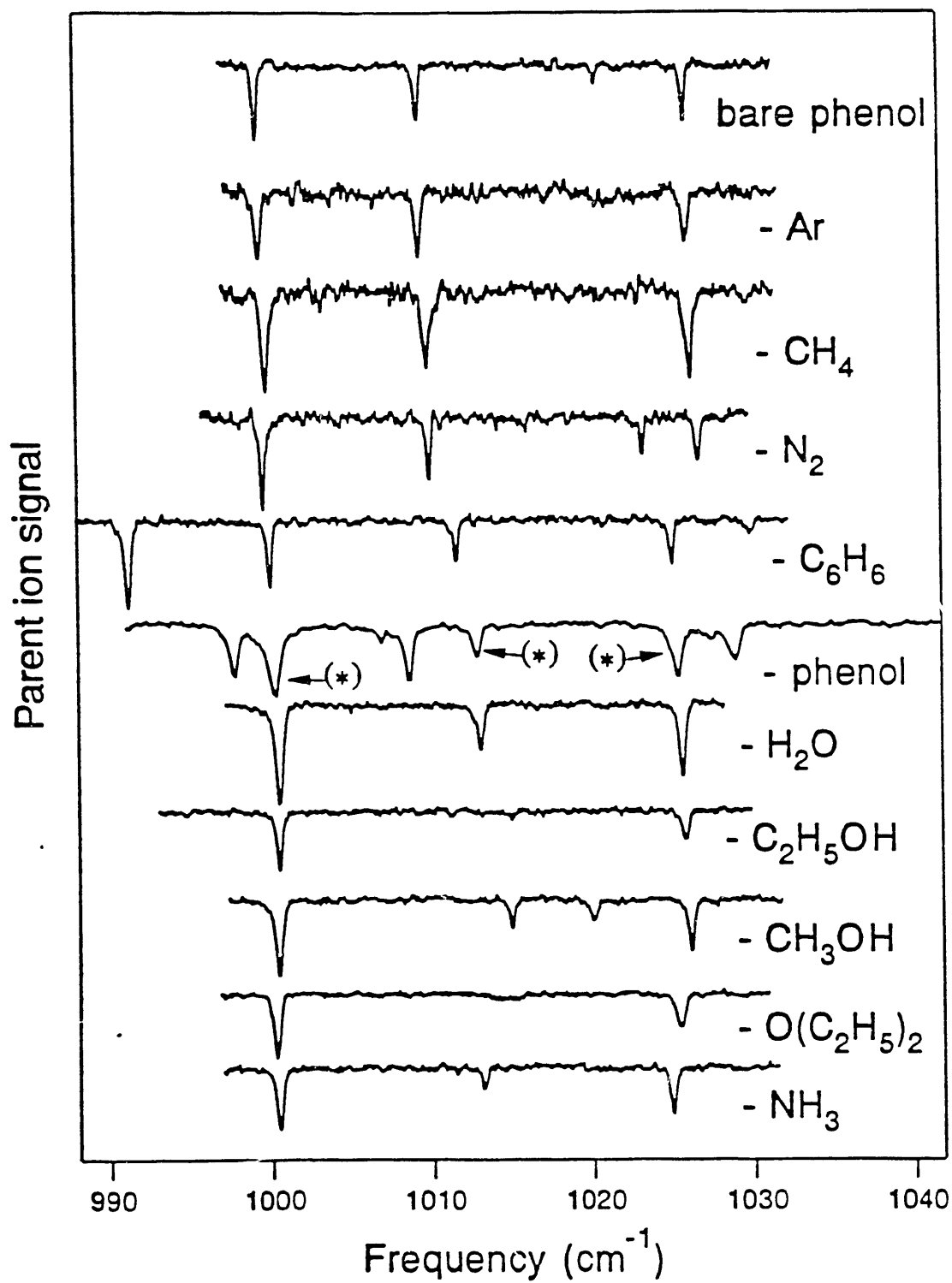


Figure 14. ILSRS spectra of H-bonded and van der Waals complexes of phenol in the 1000 cm^{-1} region of the vibrational spectrum. Given in the figure is the complexing partner associated with each spectrum.

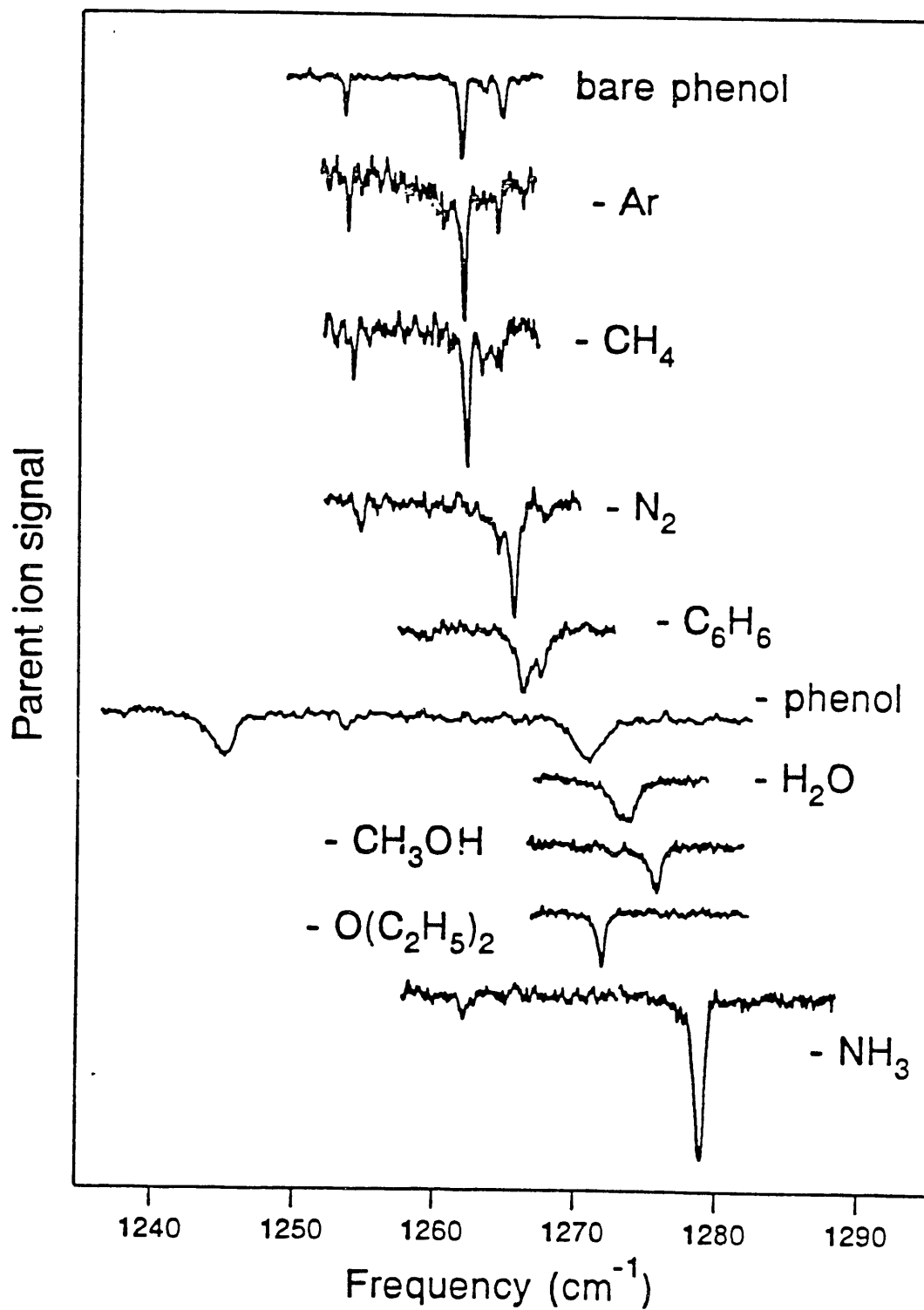


Figure 15. ILSRS spectra of H-bonded and van der Waals complexes of phenol in the region of the C-O stretch fundamental of phenol. Given in the figure is the complexing partner associated with each spectrum.

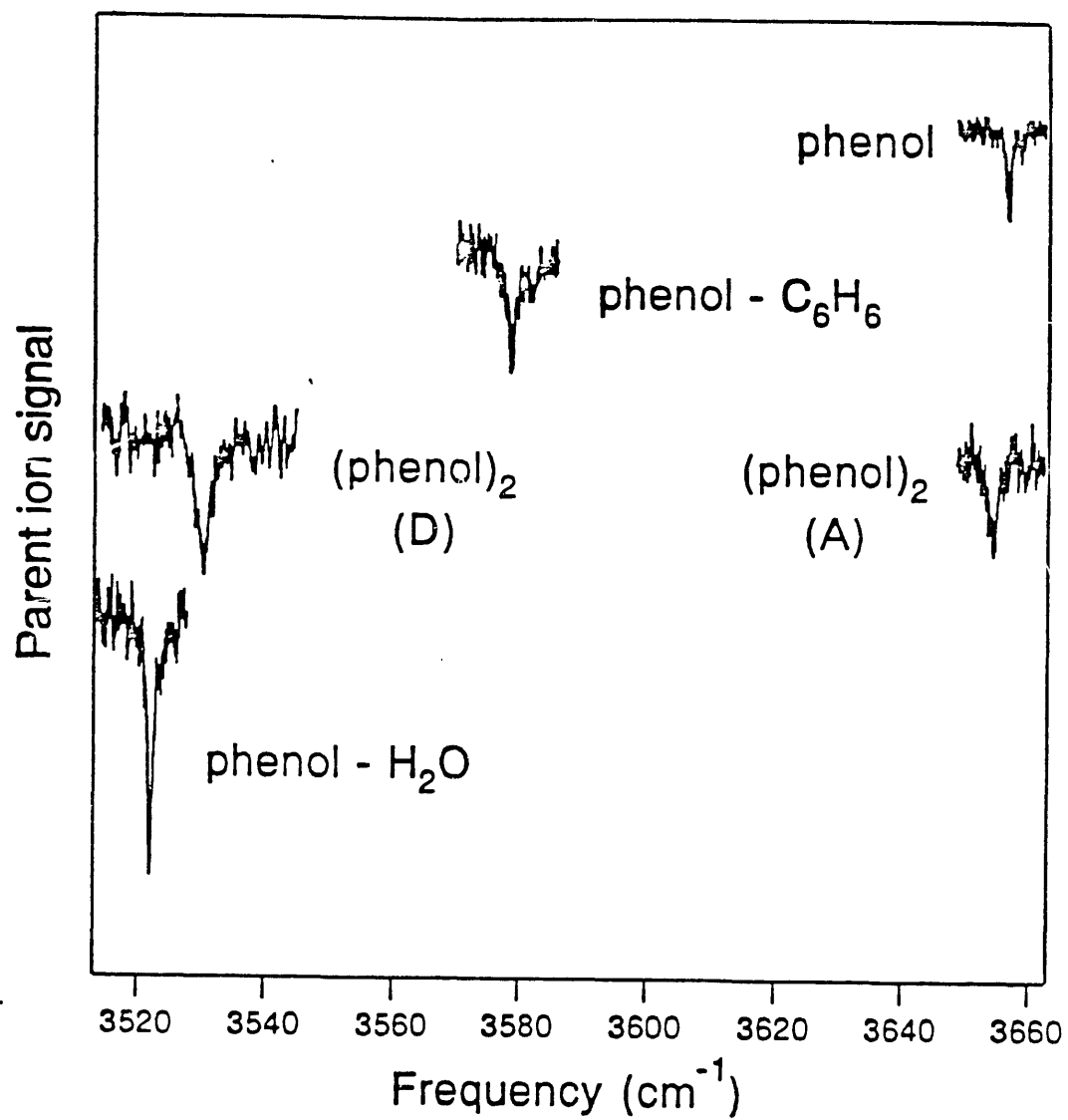


Figure 16. ILSRS spectra of H-bonded complexes of phenol in the region of the O-H stretch fundamental of phenol. Given in the figure is the complexing partner associated with each spectrum.

in a regular way upon H bonding. For example, the C-O and O-H stretch fundamentals shift blue and red, respectively upon H-bonding – see Figs. 15 and 16. These resonances have been used as probes of the local environment of phenols in condensed phases. Our molecular beam results provide previously unknown information as to the inherent H-bond induced shifts of the resonances. Third, with advances in the theoretical treatment of intermolecular interactions, one expects that the results of Figs. 14 to 16 may provide useful data with which to compare theoretical predictions. Fourth, in some cases the ILSRS results provide valuable information in regard to the geometries of the complexes. For example, the phenol dimer results in the O-H stretch region (Fig. 16) strongly suggest that the species is such that one phenol is a proton donor and the other is a proton acceptor via its oxygen atom. This information was used in conjunction with results from high resolution rotational spectroscopy to arrive at a geometry for the species.³³ Fifth, the ILSRS spectra of Figs. 14 to 16 represent background information essential to future studies that we plan to undertake in regard to the vibrational energy flow and predissociation dynamics of these species.

Figure 17 shows spectra that pertain not to phenol-localized vibrational resonances but to resonances localized in the water moiety of phenol-water and substituted phenol complexes. These spectra, and analogous ones for phenol-benzene and phenol-ammonia complexes, are further examples of the capability of ILSRS to probe the vibrational resonances of all the moieties that make up a molecular complex or cluster. Of particular note regarding Fig. 17 are the small shifts of the water-localized O-H symmetric stretch frequencies away from the value corresponding to free water ($\sim 3656 \text{ cm}^{-1}$). Such small shifts contrast with the very much larger red shift of the proton-accepting moiety in water dimer (about 50 cm^{-1}).³⁴ The reason for this large difference in species that presumably have similar H-bonding interactions is not clear. The spectra of Fig. 17 are also valuable in that they will be used as background information for future studies of IVR and predissociation in the H-bonded complexes. (See the accompanying proposal.)

B. Results pertaining to dynamics

Information on dynamics was obtained by nanosecond time-resolved IGSRS experiments and by linewidth measurements. From nanosecond-resolved IGSRS we have found

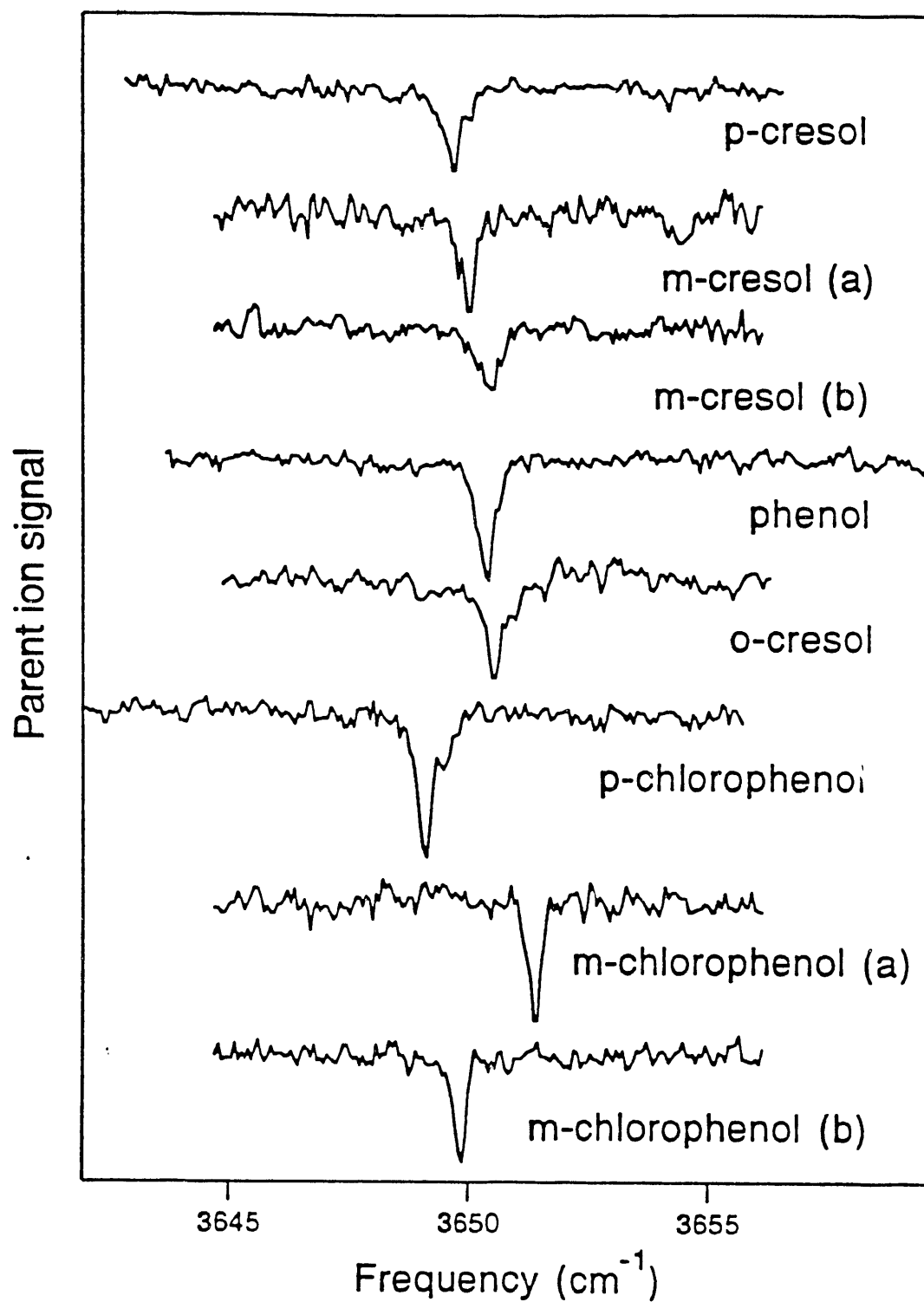
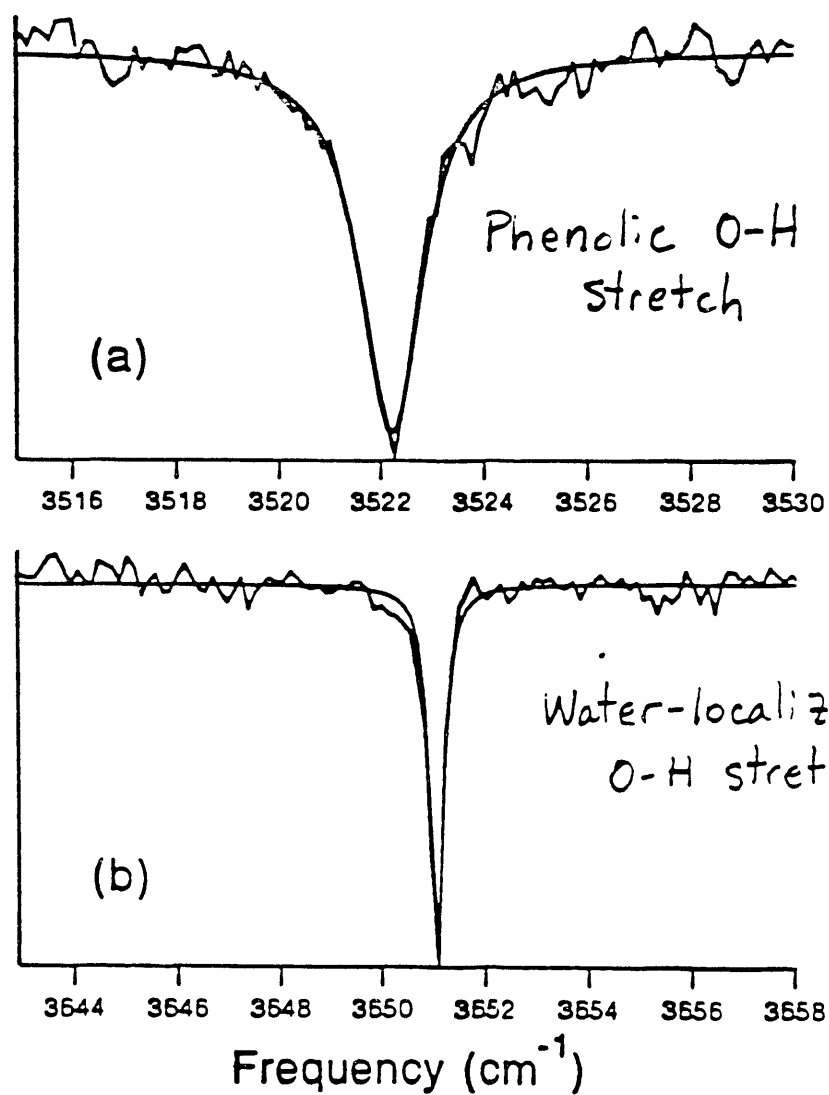


Figure 17. ILSRS spectra pertaining to the water-localized O-H symmetric stretch in substituted phenol complexes. The pertinent substituted phenol for each spectrum is given in the figure.

for all of the phenol-M complexes held together by a H bond, that the lifetimes of Raman-prepared vibrational states at energies greater than 1000 cm^{-1} are significantly less than the pulsewidths of the lasers used (about 7-10 ns). Such lifetimes were inferred from the failure to observe IGSRS signals from these species.^{9,24} In contrast, IGSRS signals were obtained upon excitation of phenol-Ar and phenol-CH₄ (species not H-bonded) to the same phenol-localized vibrational levels, indicating nanosecond-lived excited vibrational levels in these species. One's conclusion is that IVR from phenol-localized vibrations to the bath of intermolecular modes is considerably faster in the H-bonded complexes than it is for the complexes without H bonds. Evidently, the vibrational coupling of phenolic modes with H-bond modes is considerably stronger than the coupling of phenolic modes with the intermolecular modes in the Ar and CH₄ van der Waals complexes. Also of note is the disparity between the vibrational lifetimes of the phenol H-bonded complexes and the considerably longer lifetimes of the benzene dimer and trimer upon excitation to similar energies (see previous section). The source of this disparity, whether it be the nature of the intermolecular bonding, the intrinsic properties of the monomers involved, or some combination of the two, is an interesting issue. Also of interest is the question of which, if either, of these two classes of species has dynamics that is most representative of other species of similar size. Answers to such questions await more detailed results on these systems (e.g., those from picosecond IGSRS experiments) and results on more and varied complexes.

Much of the information we have obtained on vibrational dynamics in phenol-M complexes derives from linewidth measurements. Several such results are of particular interest. First, we have observed behavior that is very suggestive of mode-selective dynamics in the O-H stretch region of phenol-H₂O and substituted phenol-H₂O complexes.²⁴ Specifically, the linewidths of the water-localized O-H symmetric stretch fundamental in these species are about a factor of four to five narrower than the phenolic O-H stretch resonances in the same species, even though the latter occur at lower frequencies. In phenol-water, for example, the linewidth of the water-localized O-H stretch implies a lifetime longer than 17 ps, whereas that for the phenolic O-H stretch gives a lifetime longer than 4 ps (see Fig. 18). Such behavior, which is analogous to behavior in smaller H-bonded complexes,³⁷ implies

ILSRS ON
Phenol-Water



18,
Figure 7. Frequency-domain ILSRS spectra of the phenol-water complex. (a) The fundamental associated with the phenol-localized O-H stretch. (b) The fundamental associated with the totally symmetric O-H stretch of the water. Note the large difference in linewidths between the two resonances.

that the proton-donating O-H stretch of phenol couples more effectively with the H-bond intermolecular modes than does the proton-accepting O-H stretch of the water. Second, spectra in the region of the C-O stretch of H-bonded and non-H-bonded complexes suggest that H-bonding produces an enhanced relaxation of the excited C-O stretch vibration in phenol (see Fig. 15). Such an enhanced relaxation might be expected given the likelihood of substantial coupling between this vibration and the low frequency intermolecular modes in the H-bonded complexes. Third, the linewidths of the totally symmetric N-H stretch of ammonia in phenol-ammonia and substituted phenol-ammonia complexes suggest that this vibration relaxes significantly faster than the water-localized symmetric O-H stretch in phenol-water complexes, even though the latter are at higher energies (e.g., compare Figs. 17 and 19). Whether this linewidth behavior is truly reflective of a difference in dynamics is still open to question. Picosecond IDSRS experiments would settle the question definitively. In any case, these results suggest that there may be significant differences in the way in which ammonia and water interact dynamically with a proton-donating solute.

VI. IDSRS studies of carbazole-(Ar)_n clusters

Very recently we have begun a study of the vibrational spectroscopy of carbazole-(Ar)_n clusters. These species have been studied in some detail both experimentally and theoretically.³⁵ They are of interest because they represent a convenient model system for the study of the microscopic details of solvation. Our interest in them is two-fold. First, we wonder if the vibrational spectroscopy of the species is consistent with conclusions drawn from the results of vibronic spectroscopy.³⁵ Second, we are interested in the vibrational dynamics of the carbazole moiety and, in particular, how the dynamics changes as a function of cluster size (i.e., degree of solvation). At this time we have progressed to the point where we are confident that reasonably high quality ILSRS spectra can be measured even for fairly large clusters. For example, Fig. 20 shows ILSRS spectra in the 1320 cm⁻¹ region of the Raman spectrum as a function of the number of Ar atoms involved in the cluster. Three points are noteworthy. First, it is clear that size-specific vibrational spectra can be measured by ILSRS for this system. Second, there are spectral changes in this region as the cluster grows. (The resonance at about 1322 cm⁻¹ is particularly sensitive to the degree of solvation.) Just what these changes mean is unclear

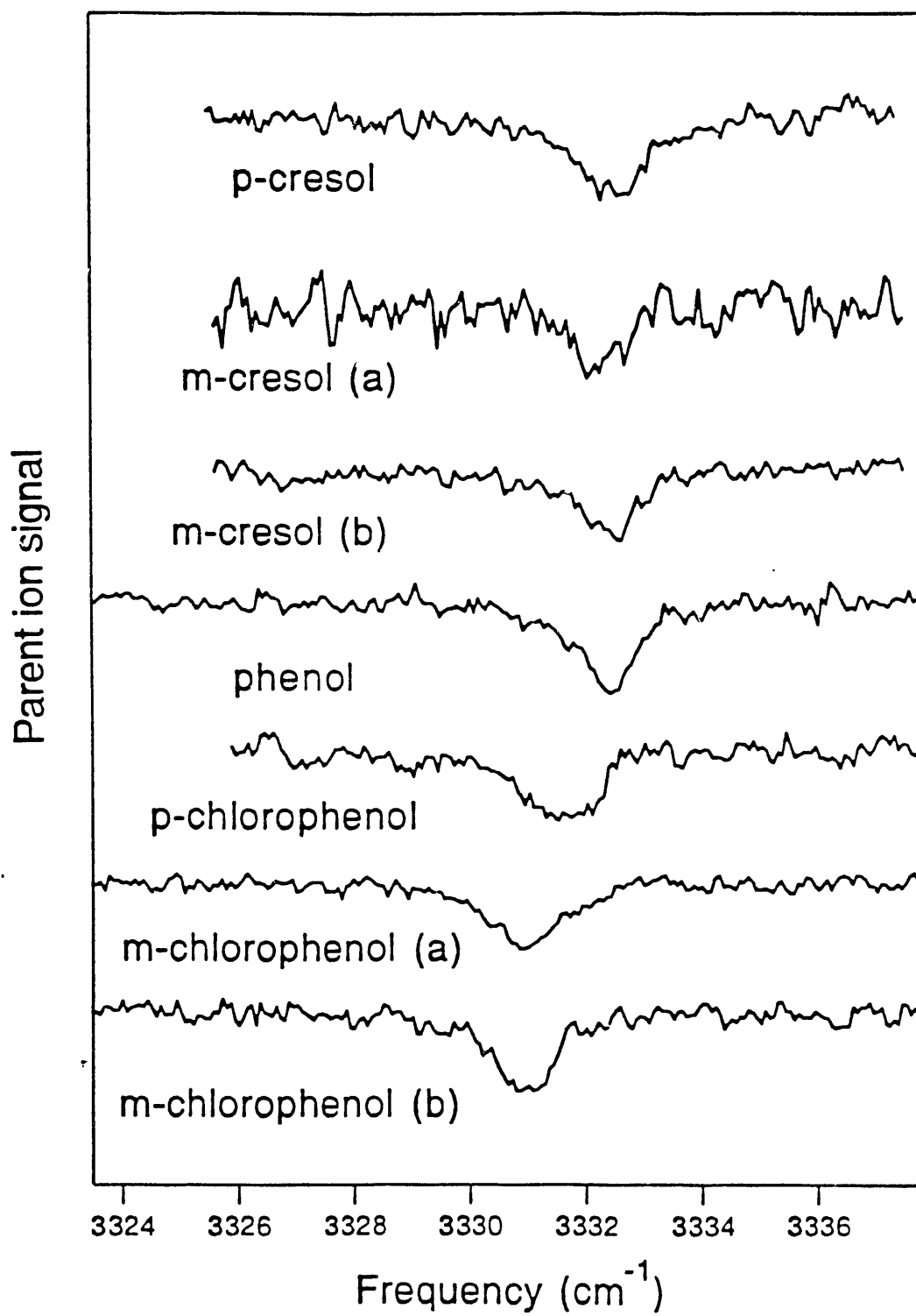


Figure 19. ILSRS spectra pertaining to the ammonia-localized N-H symmetric stretch in substituted phenol complexes. The pertinent substituted phenol for each spectrum is given in the figure.

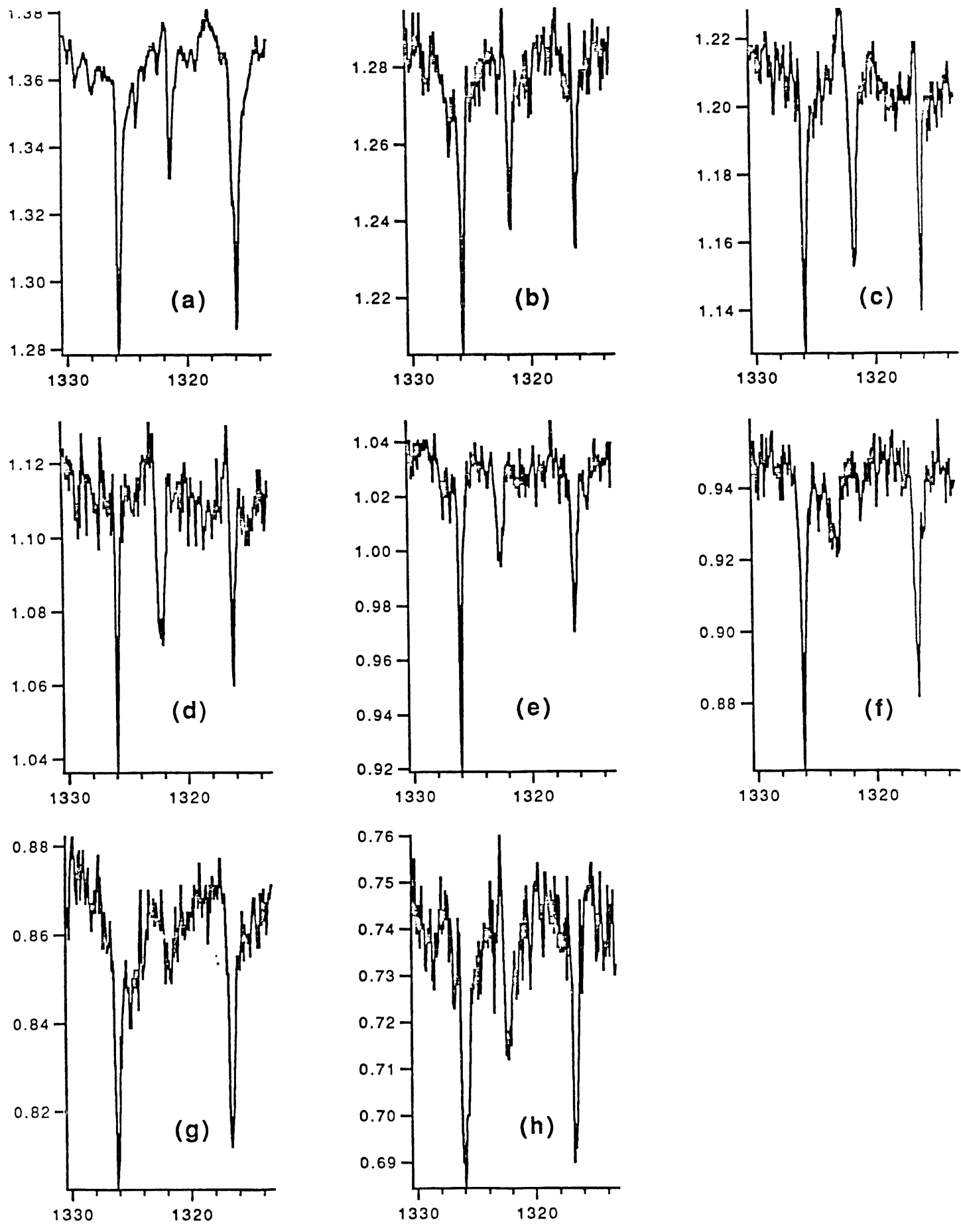


Figure 20. ILSRS spectra in the vicinity of 1320 cm^{-1} for carbazole-(Ar)_n clusters. Spectra (a) through (h) correspond to from one to eight argons, respectively.

right now. However, their existence implies that there are vibrational signatures which may be useful as probes of solvation in this system. Third, the linewidths of some of the resonances of the larger clusters are considerably narrower than one would have expected. For example, the linewidth of the 1326 cm^{-1} resonance in carbazole-(Ar)₅ is 0.3 cm^{-1} , implying a vibrational lifetime of greater than about 18 ps. Such a lifetime seems quite long given that carbazole is a fairly large molecule and that complexation with five argons should give rise to an enormous density of vibrational states in the cluster at 1320 cm^{-1} . Still, it is pertinent to point out that studies of the vibrational energy flow dynamics in large clusters are relatively few,³⁶ and one really does not yet know what typical behavior is. It is clear to us that the mass-selected ILSRS method and other IDSRS schemes (e.g., picosecond IGSRs) can contribute significantly to the characterization of such behavior. We plan to continue studies in this area.

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