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# Intermolecular vibrations of the phenol dimer revealed by spectral hole burning and dispersed fluorescence spectroscopy

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Inter- and intramolecular vibrations of the Phenol dimer have been examined using spectral hole burning and dispersed fluorescence spectroscopy. The dispersed fluorescence spectra have been recorded via excitation of the electronic donor origin and all intermolecular vibrational transitions. The Franck–Condon intensity pattern allowed a straightforward assignment of the ground state vibrational frequencies to the excited state frequencies, which were examined by hole-burning spectroscopy. The existence of another conformer that possibly absorbs in the region of interest was ruled out by hole-burning spectroscopy. For obtaining the hole-burning spectra, the electronic origin of the donor chromophore was analyzed, while the hole-burning laser was scanned over the region of interest. As both acceptor and donor part belong to one molecule the hole-burning signal could be analyzed via fluorescence from one of the chromophores. © 1995 American Institute of Physics.

## I. INTRODUCTION

Playing “cluster puzzle” is fascinating, but complicated. Generally a single experimental method is not sufficient to fit together all pieces of the mosaic. Supersonic jet expansion is the method of choice for isolating the molecular complexes and simplifying their spectra by adiabatic cooling. Cluster size distributions depend on expansion conditions like nozzle diameter and channel length, nozzle temperature, expansion distance, stagnation pressure, molecular concentrations, and point of analysis time of the gas pulse. While it is possible to optimize an expansion for small or large clusters, true cluster size selection is hopeless via variation of the expansion conditions. A convenient cluster size specific spectroscopic technique such as resonant two photon ionization (R2PI) with time of flight mass analysis can be used if part of the molecular complex is a (aromatic) chromophore.

Fragmentation of cluster ions, however, remains a problem even if soft two-color excitation just above the vertical ionization threshold is applied. Spectral hole burning (SHB) allows us to assign all burned vibronic transitions to the analyzed transition. Holes are only observed if burned and analyzed transition share a common ground state level. Hence this method can be used to distinguish between different cluster sizes, conformers, and hot vibrational states.<sup>1–3</sup>

SHB-R2PI may be the most powerful tool up to now for a first insight into the cluster puzzle. For investigation of the electronic ground state  $S_0$  of a cluster and its vibrational states, several double resonance techniques have been developed. The most efficient instrument for elucidation of the intermolecular vibrations of complexes with aromatic chromophores is still a simple dispersion of the cluster fluorescence (DF) obtained from excitation of different  $S_1$  vibrational states. A wealth of information about the  $S_0$  intermolecular potential can be obtained from the vibrational frequencies, the anharmonicities, and the Franck–Condon in-

tensity pattern of progressions and combination bands. High quality DF, even of weak transitions, is possible now using a monochromator of high dispersion and multichannel detection via an image intensified, gated charged couple device (CCD) camera. Use of different isotopomers facilitates the vibrational assignments by comparison of the vibrational shifts with results from good quality ab initio calculations and normal mode analysis as far as appropriate.<sup>4</sup> Ionization-detected stimulated emission (IDSEP)<sup>5</sup> can be used to measure  $S_0$  state vibrations of the cluster. Resonant stimulated pumping is, however, efficient only in case of fast intramolecular vibrational relaxation (IVR) in the terminating level (compared to the  $S_1$  lifetime). Therefore this method seems to be limited to ground state vibrational frequencies  $>500$   $\text{cm}^{-1}$  and hence was used to measure cluster-induced vibrational frequency shifts of intramolecular modes or combination bands of intra- and intermolecular modes. The low frequency intermolecular modes are not directly accessible by this method. These modes, however, are most susceptible to the intermolecular potential and to the quality of corresponding ab initio calculations. Nevertheless, valuable information about the Phenol( $\text{H}_2\text{O}$ )<sub>*n*</sub> ( $n=1-3$ ) ground state vibrations were obtained by Stanley and Castleman<sup>6</sup> and Ebata *et al.*<sup>7</sup> in the range of 500–1500  $\text{cm}^{-1}$  by using IDSEP. Hartland *et al.*<sup>8</sup> used ionization-detected stimulated Raman scattering (IDSRS) to investigate the nonfluorescing moiety of clusters with aromatic chromophores, e.g., the OH stretching region (3500–3700  $\text{cm}^{-1}$ ) in the Phenol dimer and in Phenol ( $\text{H}_2\text{O}$ )<sub>1</sub>.

Recently, Fourier transform microwave spectroscopy<sup>9</sup> and high-resolution laser-induced fluorescence (LIF)<sup>10</sup> have been used to obtain the rotational constants of Phenol ( $\text{H}_2\text{O}$ ) in the  $S_0$ - and  $S_1$ -state, respectively, and to investigate the tunnel splitting from internal rotation of the  $\text{H}_2\text{O}$  moiety around the H-bond axis.

The Phenol( $\text{H}_2\text{O}$ )<sub>1</sub>, Phenol( $\text{CH}_3\text{OH}$ )<sub>1</sub>, and Phenol( $\text{C}_2\text{H}_5\text{OH}$ )<sub>1</sub>, as well as the Phenol dimer cation radi-

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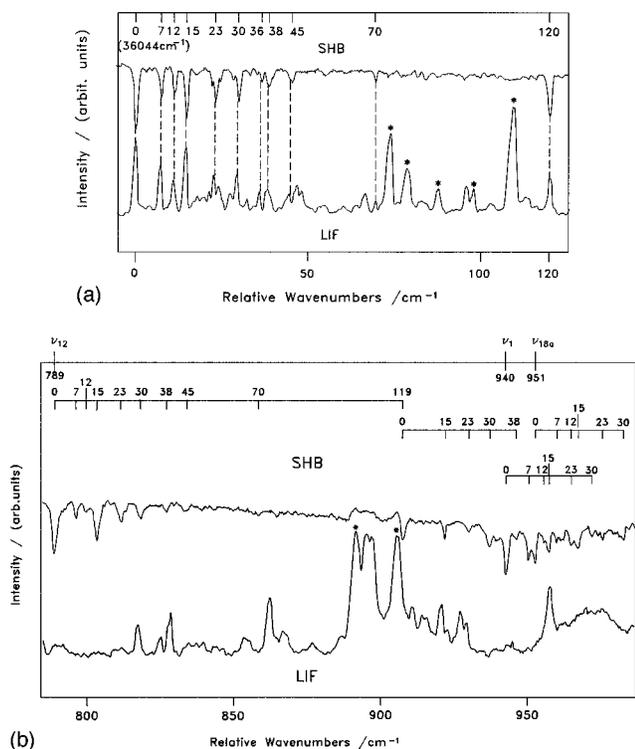


FIG. 1. (a) LIF and SHB of the Phenol dimer in the region of the donor origin. The spectral holes are analyzed via excitation of the donor origin. The bands marked with \* belong to Phenol ( $\text{H}_2\text{O}$ )<sub>1</sub>. Accuracy of band positions:  $\pm 1 \text{ cm}^{-1}$ . (b) LIF and SHB of the Phenol dimer in the range 780–1000  $\text{cm}^{-1}$  on the blue side of the donor origin. The bands marked with \* belong to Phenol ( $\text{H}_2\text{O}$ )<sub>1</sub>. Accuracy of band positions:  $\pm 1 \text{ cm}^{-1}$ .

icals, were investigated by Dopfer *et al.*<sup>11–16</sup> using zero-kinetic-energy photoelectron spectroscopy (ZEKE).

## II. EXPERIMENT

The apparatus used for spectral hole burning and dispersed fluorescence spectroscopy has been described elsewhere.<sup>17</sup> It consists of a high-vacuum chamber and a pulsed nozzle (general Valve Iota One 500  $\mu\text{m}$  nozzle hole). The fluorescence at a nozzle hole-laser distance  $X/D=30$  is collected with a two-lens system and detected by a peltier-cooled photomultiplier (Thorn EMI 9789). The vacuum is maintained by a 2000  $l\text{s}^{-1}$  oil diffusion pump (Edwards), backed by a rotatory pump (Leybold D65B). Pressures are  $1 \cdot 10^{-6}$  (beam off) and  $5 \cdot 10^{-4}$  mbar (beam on). The electronic origin of the cluster is probed by an excimer (Lambda Physik EMG 102) pumped, frequency doubled dye laser (Lambda Physik FL 2002). Another excimer (Lambda EMG 200) pumped, frequency doubled dye laser (Fl 3002) counterpropagates the probe laser for hole burning. The burn laser is slightly collimated by a  $f=1000$  mm lens to a similar size as the probe laser. The spatial distance between burn and probe laser focus is about 0.5 mm, to compensate for the time delay between both lasers. Both lasers and the pulsed nozzle are triggered by a four-channel digital delay generator (Stanford Research DG 535). The delay between burn and probe laser was adjusted to 400–800 ns, while the delay between nozzle-trigger and probe laser was 1.8 ms.

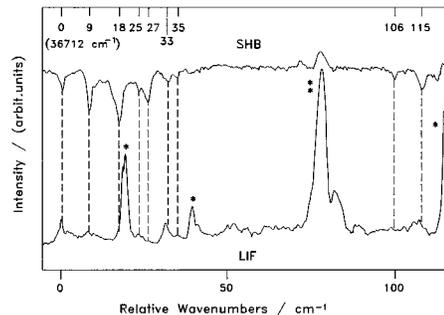


FIG. 2. LIF of the Phenol dimer in the region of the acceptor origin. The spectral holes are analyzed via excitation of the donor origin. The bands marked with \* and \*\* belong to Phenol ( $\text{H}_2\text{O}$ )<sub>1</sub> and Phenol, respectively. Accuracy of band positions:  $\pm 1 \text{ cm}^{-1}$ .

The spectra were taken with 0.5 mbar Phenol, seeded in 4000 mbar He. The photomultiplier signal is averaged with a boxcar integrator (Stanford Research SR250) and recorded by a chart recorder. The fluorescence signal caused by the burn laser is separated from the probe signal by positioning the boxcar gate to the scattered light of the probe laser.

The fluorescence emission spectra were taken in the same vacuum chamber. The emitted fluorescence was collected and focused by a two-lens system on the entrance slit of a 1 m Czerny–Turner monochromator with an aperture of  $f/8.4$  (Jobin Yvon THR 1000). We used a holographic grating (11  $\text{cm} \times 11 \text{ cm}$ ) with 2400 grooves/mm. The resulting linear dispersion  $d\lambda/dx$  at 280 nm is 7.2,  $\text{\AA}/\text{mm}$ . The fluorescence is imaged on the photocathode of the CCD camera, intensified and recorded on the CCD chip after 15:25 reduction of the image size in an optical fiber taper. With a CCD chip width of  $1/3''$  and a pixel size of 23  $\mu\text{m}$ , a range of 750  $\text{cm}^{-1}$  of the emission spectrum can be taken in one mirror position of the monochromator.

The dispersed fluorescence is recorded with 12 bit resolution in first grating order by the intensified slow scan gated CCD camera (LaVision, Flame Star) positioned in the image plane of the monochromator. The resulting two-dimensional array ( $x$ =height of the entrance slit:  $y$ =dispersion) is averaged over a curved  $x$  range, to compensate for errors due to the spherical aberration of the grating. A single dispersed fluorescence spectrum was obtained by summing the fluorescence of 200 laser pulses on the CCD chip and subtracting the background straylight (gas pulse off) after 200 laser pulses. Ten of these spectra were averaged to obtain the overall spectra shown in the Figs. 3–11.

## III. RESULTS AND DISCUSSION

### A. Hole-burning spectroscopy

In the hydrogen bridge bonded Phenol dimer, one Phenol moiety is the proton donor, while the other acts as proton acceptor.<sup>18</sup> The donor absorbs at longer, the acceptor at shorter wavelengths than the Phenol monomer.<sup>18,19</sup>

Figures 1(a) and 1(b) show the SHB spectrum of the Phenol dimer in the region of the donor origin and 780–1000  $\text{cm}^{-1}$  on the blue side of the donor origin (upper traces). The lower traces show the LIF spectra in the same spectral re-

TABLE I. Excited state ( $S_1$ ) intermolecular vibrational frequencies observed in the donor part of the hole-burning spectrum of the Phenol dimer.

Frequency <sup>a</sup> [cm <sup>-1</sup> ]	Assignment <sup>b</sup>
7	1
12	2
15	3 (1+1)
23	4 <sup>c</sup> (2+2) (3+1) (1+1+1)
30	5 <sup>c</sup> (3+3) (1+2+2)
36	2+4 (2+2+2)
38	3+4 <sup>c</sup>
45	3+5 (3+3+3)
70	5+5+2 <sup>c</sup> (3+4+5)
120	6 <sup>d</sup>

<sup>a</sup>Relative to the donor origin at 36044 cm<sup>-1</sup>.

<sup>b</sup>Assignments as described in Sec. III. The bands in brackets may be hidden by the main feature.

<sup>c</sup>Tentative assignments. The 38 and 70 cm<sup>-1</sup> features may be fundamental bands, while the 23 cm<sup>-1</sup> and 30 cm<sup>-1</sup> features could also belong to the indicated combination band(s).

<sup>d</sup>Intermolecular stretch vibration.

gions for comparison. The donor origin was measured at  $36044 \pm 1$  cm<sup>-1</sup> in good agreement with the value of Dopfer *et al.*<sup>15</sup> The spectral holes were analyzed by probing the  $S_1^{\text{donor}}$  origin. All bands in the SHB spectrum match with bands in the LIF spectrum (dashed lines in Fig. 1). The remaining LIF bands in Fig. 1 are Phenol (H<sub>2</sub>O)<sub>1</sub> transitions from water traces in the Phenol sample. Hence only *one conformer* of the Phenol dimer absorbs in the investigated spectral region. The SHB spectrum shows a number of low-frequency bands which will be analyzed later.

Figure 2 shows the SHB and LIF spectrum of the Phenol dimer in the region of the acceptor origin. The spectral holes

TABLE II. Excited state ( $S_1$ ) intermolecular vibrational frequencies observed in the acceptor part of the hole-burning spectrum of the Phenol dimer.

Frequency <sup>a</sup> [cm <sup>-1</sup> ]	Assignment <sup>b</sup>
9	1
18	2 (1+1)
25	3
27	4 (1+2) (1+1+1)
33	5 (1+3)
35	1+4
106	6
115	6+1

<sup>a</sup>Relative to the acceptor origin at 36703 cm<sup>-1</sup>; see text for details.

<sup>b</sup>Assignments as described in Sec. IV. The bands in brackets may be hidden by the main feature.

are analyzed via excitation of the *donor* origin. This is possible, because donor and acceptor part belong to the same  $S_0$  Phenol dimer and share a common set of ground state levels. Hence holes via  $S_1^{\text{acceptor}} \leftarrow S_0$  burning can be analyzed by a  $S_1^{\text{donor}} \leftarrow S_0$  transition. This is favorable because the excited donor Phenol fluoresces much more efficiently than the acceptor part. Measurements of Sur and Johnson support the finding of an effective donor fluorescence.<sup>20</sup> They measure a  $S_1^{\text{donor}}$  lifetime of 16 ns and an internal conversion yield of nearly zero compared to 2 ns and 0.54 for the Phenol monomer.<sup>20</sup> Due to this difference in fluorescence yield only donor transitions could be detected via LIF in early investigations of the similar *p*-cresol dimer.<sup>21</sup>

All bands in the LIF spectrum match with transitions in the SHB spectrum or can be traced back to Phenol (H<sub>2</sub>O) or Phenol. Hence again only one conformer of the Phenol dimer

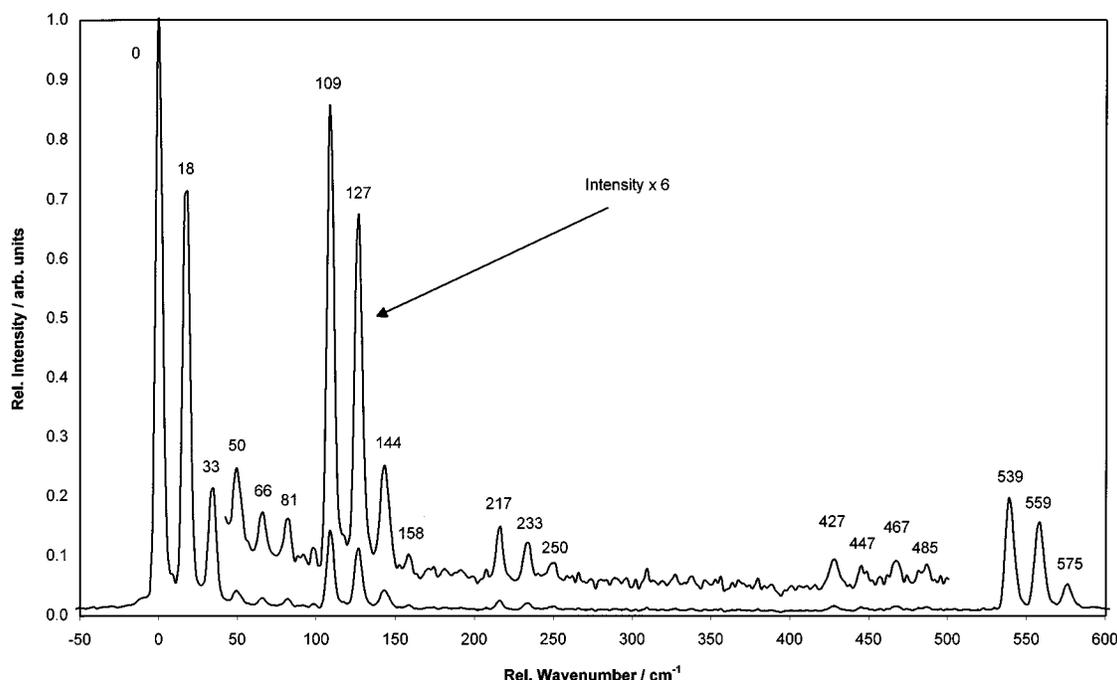


FIG. 3. Dispersed fluorescence spectrum of the Phenol dimer recorded via excitation of the donor origin  $0^0$ ; expanded view of the weak transitions. Spectral resolution is 3 cm<sup>-1</sup>, error in band positions  $\pm 2$  cm<sup>-1</sup>.

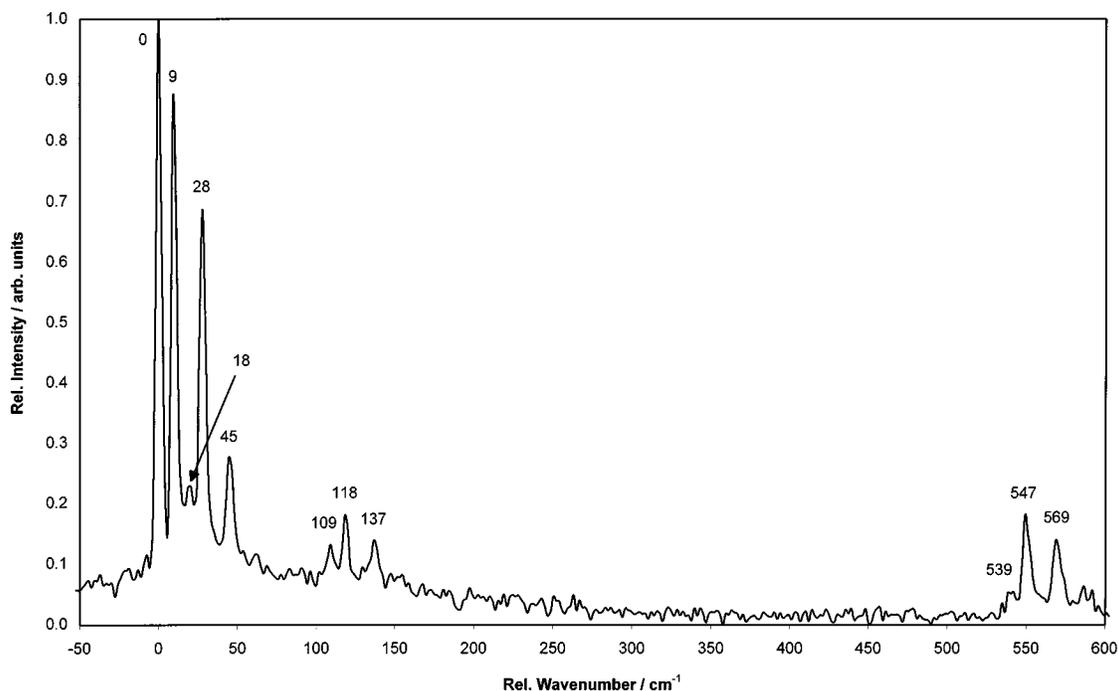


FIG. 4. Dispersed fluorescence spectrum of the Phenol dimer recorded via excitation of the donor  $S_1$  state at  $7\text{ cm}^{-1}$ . Spectral resolution is  $3\text{ cm}^{-1}$ , error in band positions  $\pm 2\text{ cm}^{-1}$ .

absorbs in the acceptor spectrum—the same conformer as in the donor region.

We observe eight low-frequency bands on the blue side ( $0\text{--}120\text{ cm}^{-1}$ ) of the acceptor origin. Contrary to results of Dopfer *et al.*,<sup>15</sup> the hole-burning spectra show unambiguously that the band at  $36703\text{ cm}^{-1}$  is not a “hot” band, but the electronic origin of the acceptor excited dimer. Variation of stagnation pressure showed no change of LIF intensity of this band relative to a monomer band used for normalization. Possibly a hot band hides the acceptor origin in their investigation, which was performed in a rather warm molecular beam. Indeed, as shown in Table IV and discussed later, the two first bands in the  $S_0$  state and  $S_1^{\text{acceptor}}$  state, respectively, have very nearly the same frequencies (9 and  $18\text{ cm}^{-1}$ ), so that the corresponding hot bands appear at the frequency of the electronic origin. Accordingly, our assignment of the low-frequency vibrations in the acceptor part is different from Ref. 15.

Altogether the hole burning spectra of the acceptor Phenol are of similar quality as the donor spectra. This is in striking contrast to the LIF spectra in Fig. 2, which show much poorer signal-to-noise ratios when the acceptor part is excited. Indeed, the intermolecular vibrations at  $106$  and  $115\text{ cm}^{-1}$  have not been observed by LIF and resonantly enhanced multiphoton ionization (REMPI) spectroscopy.<sup>15</sup> We attribute the smallness of the signals in the acceptor part to fast IVR to the lower-lying  $S_1^{\text{donor}}$  state. The IVR rate generally increases with increasing energy and competes more efficiently with spontaneous emission and ionization. To the contrary,  $S_1 \leftarrow S_0$  hole burning is not obstructed by short  $S_1$  lifetimes, which may even enlarge the hole depth. This is a major advantage of hole-burning spectroscopy compared to LIF and REMPI.

The weak fluorescence of the acceptor Phenol is due to the short lifetime of the  $S_1^{\text{acceptor}}$  state. Careful inspection of the linewidths in the SHB spectra in Figs. 1 and 2 shows a rather gradual increase from  $\sim 1.1\text{ cm}^{-1}$  [full width at half maximum (FWHM)] for the donor origin and its low-frequency vibrations to  $1.6\text{--}2.0\text{ cm}^{-1}$  in the region of its intramolecular vibrations at  $780\text{--}1000\text{ cm}^{-1}$ ; cf. Fig. 1(b). Interestingly enough, the linewidths of the intramolecular  $2_0^1$  and  $18 a_0^1$  transitions are  $2\text{ cm}^{-1}$  compared to  $1.8\text{ cm}^{-1}$  for the nearby  $1_0^1$  band. The intramolecular mode 1 corresponds to a very harmonic “ringbreathing” motion of benzene, whose vibronic coupling to other modes may be rather small.

Tables I and II show our tentative assignment of the low-frequency bands in the donor and acceptor spectrum to the six fundamentals as well as to combination bands and overtones. The assignment of the bands 1, 2, 3 and 6 in the donor spectrum to fundamentals seems to be unambiguous because there are no reasonable combinations of other fundamentals to explain their frequencies and intensities. Moreover, the dispersed fluorescence spectra support their assignment strongly as discussed in Sec. III B (below).

## B. Dispersed fluorescence spectroscopy

Figure 3 shows the DF spectrum of the Phenol dimer after excitation of the electronic origin of the donor in the range  $0\text{--}600\text{ cm}^{-1}$  to the red of the donor origin. We observe low-frequency modes at  $18, 33, 50, 66,$  and  $81\text{ cm}^{-1}$  and combination of some of these bands with an intense transition at  $109\text{ cm}^{-1}$  and transitions at  $217$  ( $2.109$ ),  $427$  ( $18b$ ), and  $539\text{ cm}^{-1}$  ( $6a$ ). Similarly, to the  $S_1^{\text{donor}} \leftarrow S_0$  spectrum we do not observe long progressions with substantial intensity of nondiagonal transitions. Also, the  $0_0^0$  transition is the most

TABLE III. Ground state ( $S_0$ ) intermolecular vibrational frequencies observed after excitation of all  $S_1$  intermolecular donor vibrations.

0	0,0+ 7 cm <sup>-1</sup>	0,0+ 12 cm <sup>-1</sup>	0,0+ 15 cm <sup>-1</sup>	0,0+ 23 cm <sup>-1</sup>	0,0+ 30 cm <sup>-1</sup>	0,0+ 36 cm <sup>-1</sup>	0,0+ 38 cm <sup>-1</sup>	0,0+ 45 cm <sup>-1</sup>	0,0+ 70 cm <sup>-1</sup>	0,0+ 120 cm <sup>-1</sup>	Assignment <sup>a</sup>
	9		9	9	9						1
18	18	18	18	18	18		18	18		18	2
	28	28				28					1+2
33		33	33	33	33			33		33	3
	45		45			45	45				4 (1+2+2)
50		50	50	50	50			50			5 (2+3)
			59			59	59				4+2
66			66		66			66	66		5+2 (3+3)
			74			74	74				4+3
81					81			81	81		5+3
								94			5+2+2
									98		5+3+2
109	109		109	109	109					109	6
	118		118	118							6+1
127		127		127	127			127	127	127	6+2
	137										6+2+1
144		144	144	144	144				144	144	6+3
158		158		158	158					158	6+5
						167					6+4+2
		175			175			175	175		6+5+2
								192	192		6+5+3
217										217	6+6
233										233	6+6+2
250		250								250	6+6+3
										316	6+6+6
										334	6+6+6+2
										348	6+6+6+1+2
427											$\nu_{18b}$ *
447											$\nu_{18b}+2$
467											$\nu_{18b}+3$
485											$\nu_{18b}+5$
539		539	539	539	539						$\nu_{6a}$ *
	547		547								$\nu_{6a}+1$
559		559			559						$\nu_{6a}+2$
	569										$\nu_{6a}+1+2$
575		575	575	581	575						$\nu_{6a}+3$
			593	593	593						$\nu_{6a}+5$

<sup>a</sup>Vibrational states in the electronic ground state  $S_0$ . Assignments as described in Sec. V.

\* Intramolecular vibrations.

intense one. From that we conclude that the  $S_0/S_1^{\text{donor}}$  potentials are only slightly shifted with respect to each other. This helps in assigning the following spectra, which were obtained from dispersion of vibrationally excited  $S_1^{\text{donor}}$  states.

### 1. $S_1^{\text{donor}}$ 1<sup>1</sup> intermediate state at 7 cm<sup>-1</sup>

Figure 4 shows the DF spectrum, which is obtained with one quantum of mode 1 (7 cm<sup>-1</sup>) excited in the  $S_1^{\text{donor}}$  state. Besides the resonance fluorescence from the pumped transition, the band at 9 cm<sup>-1</sup> is the most intense one. The intensity of the resonance fluorescence is somewhat uncertain in the spectra shown in Figs. 3–13 because the (small) amount of scattered laser light has to be subtracted. Figure 4 presents strong evidence for a 7 cm<sup>-1</sup> ( $S_1$ )/9 cm<sup>-1</sup> ( $S_0$ ) correlation, c.f. Table III. The band at 18 cm<sup>-1</sup> is also observed when exciting the electronic origin (Fig. 3) and is the first band with noticeable intensity there. It can be assigned to the second  $S_0$  fundamental; cf. Table III.

Most importantly, there is no obvious hint at the 9 cm<sup>-1</sup> vibration in the 0<sup>0</sup> DF spectrum due to very poor 1<sup>0</sup> Franck–

Condon factors. Hence it is *not* sufficient to merely disperse fluorescence from the 0<sup>0</sup> state to obtain *all* spectroscopically accessible  $S_0$  vibrational levels. Several or all  $S_1$  vibrational states have to be excited and their fluorescence dispersed to get a complete picture.

The band at 28 cm<sup>-1</sup> may be a fundamental, but is more probably a 1+2 combination band because it cannot be observed at all after 0<sup>0</sup> excitation and is not especially prominent in any of the other DF spectra. The band at 45 cm<sup>-1</sup> is very intense after excitation of the  $S_1^{\text{donor}}$  vibration at 23 cm<sup>-1</sup> in Fig. 7 and can be attributed to the corresponding fundamental in the  $S_0$  state. The characteristic 9 and 18 cm<sup>-1</sup> intensity pattern is again seen in combination with the 109 and 539 cm<sup>-1</sup> vibrations.

### 2. $S_1^{\text{donor}}$ 2<sup>1</sup> intermediate state at 12 cm<sup>-1</sup>

The DF spectrum obtained via excitation of the 2<sup>1</sup> state at 12 cm<sup>-1</sup> is shown in Fig. 5. The most intense transition is the one at 18 cm<sup>-1</sup>, which can be seen in many of the DF spectra; cf. Table III. It can be assigned to the 2<sub>1</sub> state of the

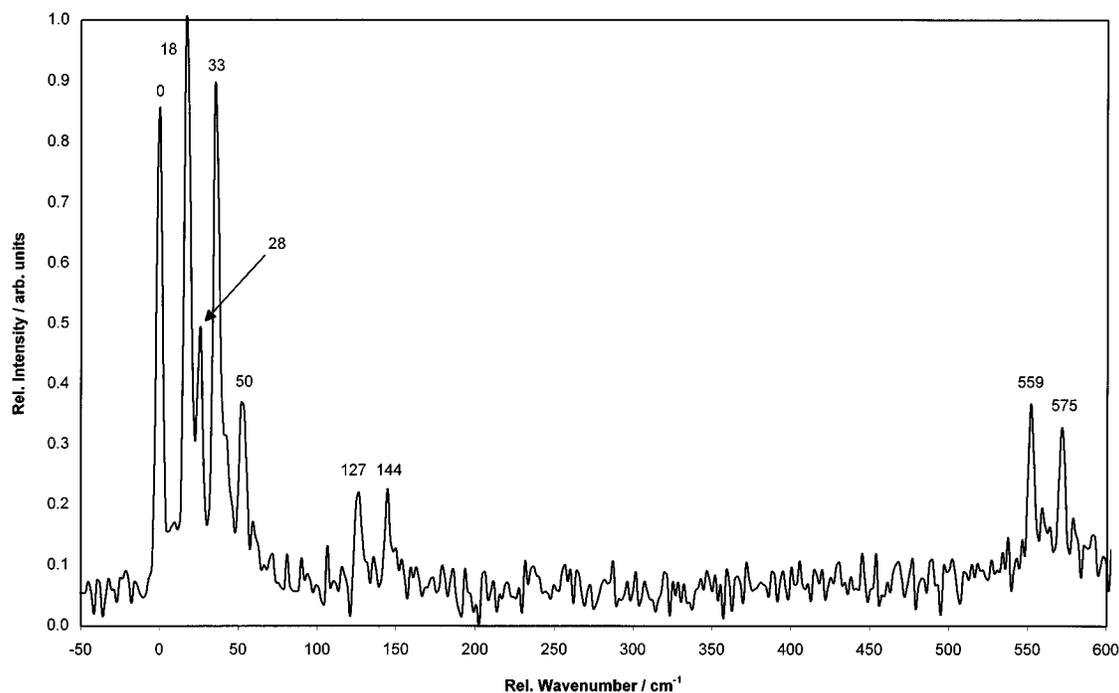


FIG. 5. Dispersed fluorescence spectrum of the Phenol dimer recorded via excitation of the donor  $2^1$  state at  $12\text{ cm}^{-1}$ . Spectral resolution is  $3\text{ cm}^{-1}$ , error in band positions  $\pm 2\text{ cm}^{-1}$ .

Phenol dimer. Again, the  $28\text{ cm}^{-1}$  band is quite prominent, which supports its assignment as 1+2 combination band. The intense band at  $33\text{ cm}^{-1}$  is observed in many other DF spectra as well and cannot be explained by reasonable combinations. Accordingly, it is assigned to a fundamental (Table

III), which shows up to be the most prominent band, when the  $S_1^{\text{donor}}$  fundamental at  $15\text{ cm}^{-1}$  is pumped; cf. Fig. 6.

The  $50\text{ cm}^{-1}$  band is the most intense transition when the  $S_1^{\text{donor}}$  fundamental state at  $30\text{ cm}^{-1}$  is pumped and can be assigned as the corresponding  $S_0$  fundamental; cf. Table III.

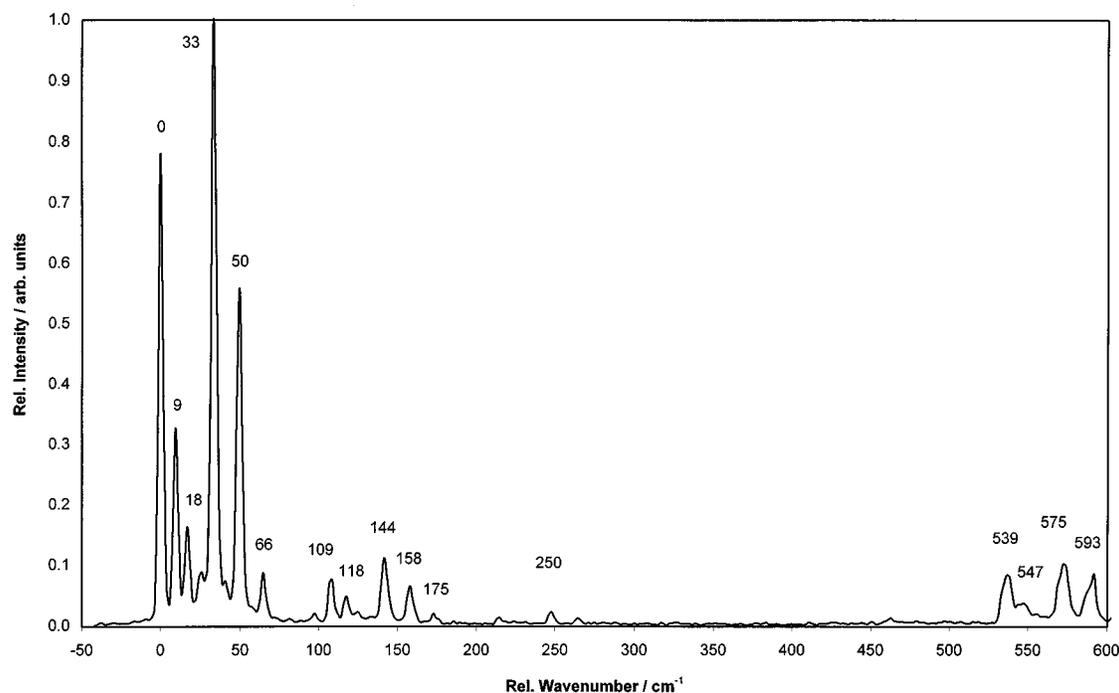


FIG. 6. Dispersed fluorescence spectrum of the Phenol dimer recorded via excitation of the donor  $3^1$  state at  $15\text{ cm}^{-1}$ . Spectral resolution is  $3\text{ cm}^{-1}$ , error in band positions  $\pm 2\text{ cm}^{-1}$ .

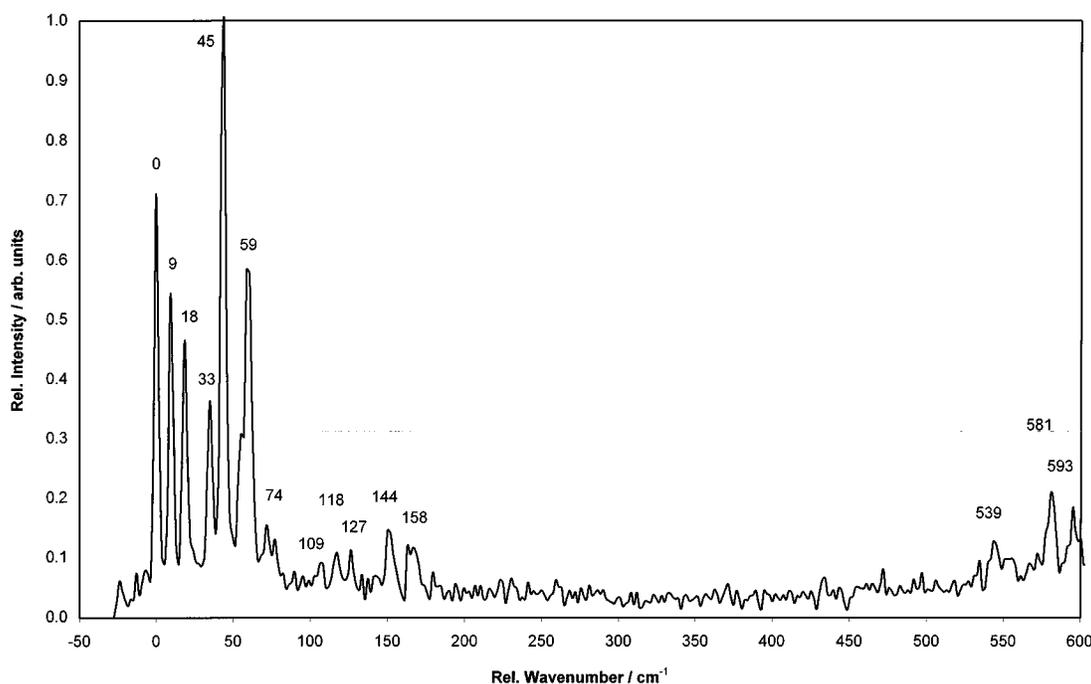


FIG. 7. Dispersed fluorescence spectrum of the Phenol dimer recorded via excitation of the donor state at  $23\text{ cm}^{-1}$  (tentative assignment). Spectral resolution is  $3\text{ cm}^{-1}$ , error in band positions  $\pm 2\text{ cm}^{-1}$ .

The  $18$  and  $28\text{ cm}^{-1}$  vibrations again combine with the  $109$  and  $539\text{ cm}^{-1}$  vibrations with a characteristic intensity pattern.

### 3. $S_1^{\text{donor}} 3^1$ intermediate state at $15\text{ cm}^{-1}$

Figure 6 shows the DF spectrum obtained via excitation of the donor state at  $15\text{ cm}^{-1}$ . The most prominent band is the one at  $33\text{ cm}^{-1}$ , which is assigned as  $3_1$  state. For the other assignments, see Table III.

### 4. $S_1^{\text{donor}}$ intermediate state at $23\text{ cm}^{-1}$

The DF spectrum obtained after excitation of the donor state at  $23\text{ cm}^{-1}$  is displayed in Fig. 7. The most intense transition is the one at  $45\text{ cm}^{-1}$ , which tempts us to assign it to a  $S_0$  fundamental.

As pointed out before, the assignment of the  $23\text{ cm}^{-1}$  vibration as  $S_1^{\text{donor}}$  fundamental is tentative, however; cf. Table I. The  $45\text{ cm}^{-1}$  band obviously matches a  $18+28\text{ cm}^{-1}$  combination, also. For the other assignments, see Table III.

### 5. $S_1^{\text{donor}}$ intermediate state at $30\text{ cm}^{-1}$

Excitation of the donor state at  $30\text{ cm}^{-1}$  leads to the DF spectrum shown in Fig. 8. The most prominent band here is the one at  $50\text{ cm}^{-1}$ , which is observed in a number of other DF spectra as well; cf. Table III.

As the assignment of the  $30\text{ cm}^{-1}$  band to a  $S_1^{\text{donor}}$  fundamental is not clear, the  $50\text{ cm}^{-1}$  band can be ascribed to a fundamental or to a combination band (e.g.,  $18+33\text{ cm}^{-1}$ ). For the other assignments, see Table III.

### 6. $S_1^{\text{donor}}$ intermediate state at $36\text{ cm}^{-1}$

Excitation of the donor state at  $36\text{ cm}^{-1}$  leads to the DF spectra shown in Fig. 9. The most prominent band at  $59\text{ cm}^{-1}$  can tentatively be assigned as a combination  $18+45\text{ cm}^{-1}$ . The corresponding  $S_1$  fundamental frequencies are  $12+23\text{ cm}^{-1}$  (cf. Table III), which indeed agree with the excited state frequency of  $36\text{ cm}^{-1}$ . This supports our assignment of the  $36\text{ cm}^{-1}$  band as  $2+4$  combination band in Table I. The band at  $74\text{ cm}^{-1}$  may be assigned as  $45+33\text{ cm}^{-1}$  combination corresponding to  $23$  and  $15\text{ cm}^{-1}$  in the  $S_1$  state. For the other assignments, see Table III.

### 7. $S_1^{\text{donor}}$ intermediate state at $38\text{ cm}^{-1}$

Figure 10 shows the DF spectrum obtained via excitation of the donor state at  $38\text{ cm}^{-1}$ . The band at  $74\text{ cm}^{-1}$  is the most prominent one because it belongs to the combination  $45+33\text{ cm}^{-1}$  corresponding to  $23+15\text{ cm}^{-1}$  in the  $S_1$  state. This supports our assignment of the  $38\text{ cm}^{-1}$  band as  $3+4$  combination band in Table I. For the other assignments, see Table III.

### 8. $S_1^{\text{donor}}$ intermediate state at $45\text{ cm}^{-1}$

The DF spectrum obtained via excitation of the  $S_1^{\text{donor}}$  band at  $45\text{ cm}^{-1}$  is displayed in Fig. 11. The  $45\text{ cm}^{-1}$  band probably stems from a combination transition; cf. Table I. We prefer the assignment  $3+5$  ( $15+30\text{ cm}^{-1}$ ) compared to  $3\times 3$  ( $3\times 15\text{ cm}^{-1}$ ) because the DF spectra obtained after excitation of the  $15$  and  $30\text{ cm}^{-1}$  transitions, respectively, “combine” better to the  $45\text{ cm}^{-1}$  DF spectrum.

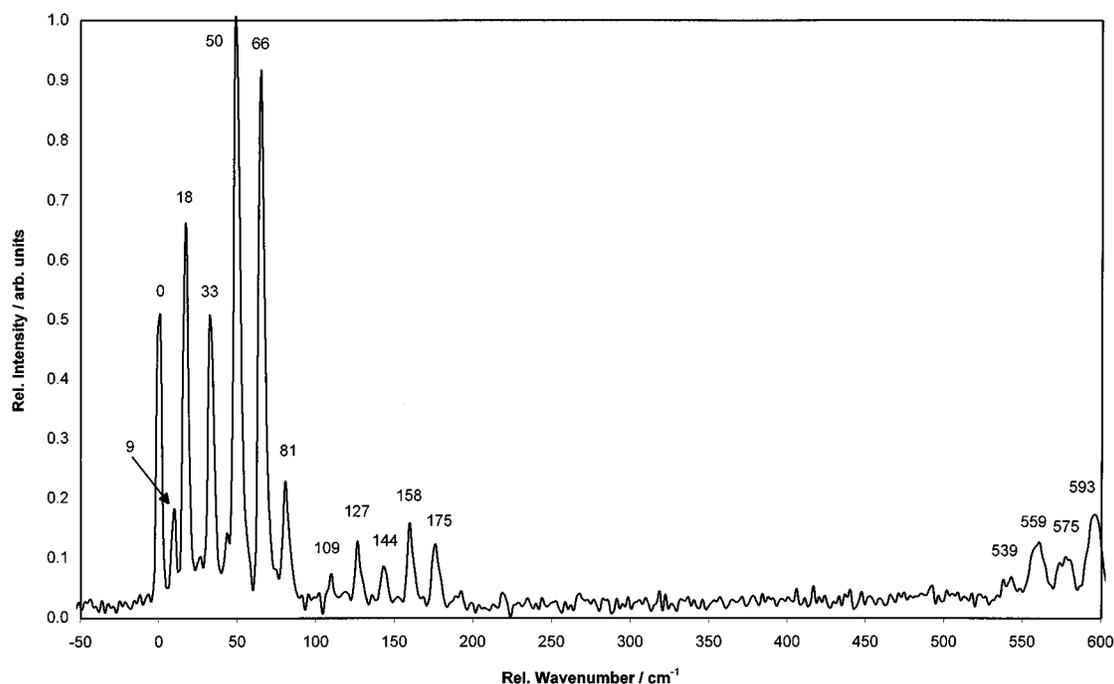


FIG. 8. Dispersed fluorescence spectrum of the Phenol dimer recorded via excitation of the donor state at  $30\text{ cm}^{-1}$ . Spectral resolution is  $3\text{ cm}^{-1}$ , error in band positions  $\pm 2\text{ cm}^{-1}$ .

### 9. $S_1^{\text{donor}}$ intermediate state at $70\text{ cm}^{-1}$

Figure 12 shows the DF spectrum obtained from excitation of the donor vibration at  $70\text{ cm}^{-1}$ . The most prominent bands are located at  $66$  and  $81\text{ cm}^{-1}$  and may be attributed to combination bands  $2+5$  ( $18+50\text{ cm}^{-1}$ ) and  $3+5$  ( $33+50\text{ cm}^{-1}$ ). On the other hand, there are no indications of bands

at  $18$ ,  $33$ , and  $50\text{ cm}^{-1}$  in the spectrum. For this reason it cannot be excluded that the  $70\text{ cm}^{-1}$  band belongs to a  $S_1^{\text{donor}}$  fundamental correlating with  $66\text{ cm}^{-1}$  in the  $S_0$  state. In this case, the  $81\text{ cm}^{-1}$  band should be assigned as  $66+18\text{ cm}^{-1}$  and the  $98\text{ cm}^{-1}$  band as a  $66+33\text{ cm}^{-1}$  combination. Indeed, theory and experiment of the Phenol( $\text{CH}_3\text{OH}$ ) cluster,

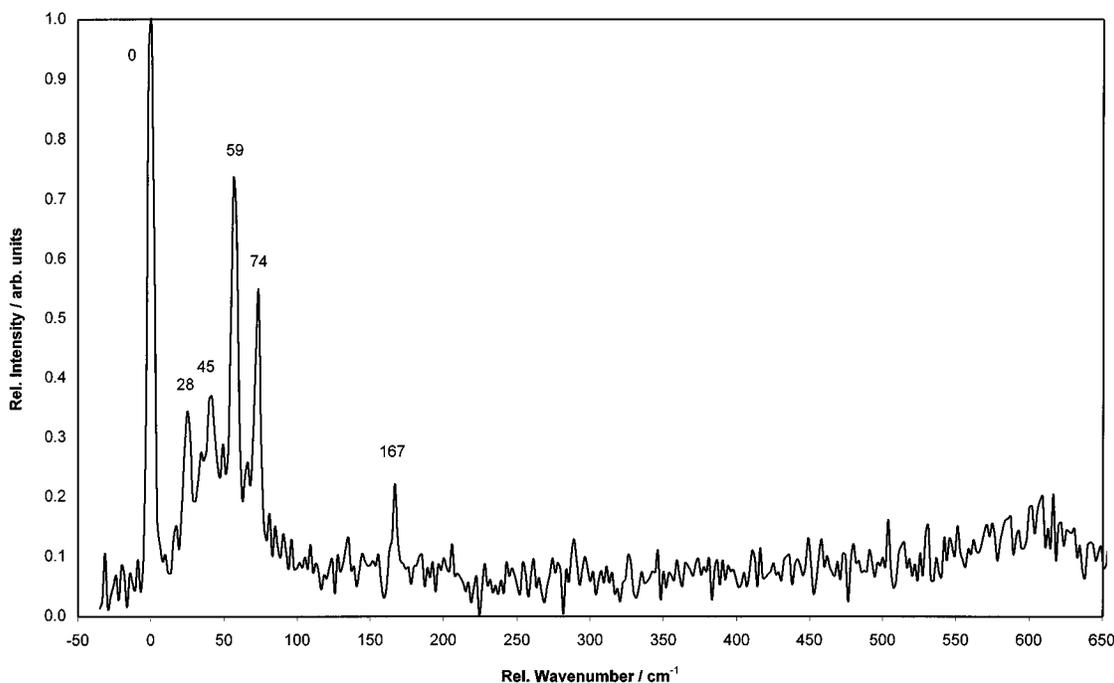


FIG. 9. Dispersed fluorescence spectrum of the Phenol dimer recorded via excitation of the donor  $S_1$  combination state at  $36\text{ cm}^{-1}$ . Spectral resolution is  $3\text{ cm}^{-1}$ , error in band positions  $\pm 2\text{ cm}^{-1}$ .

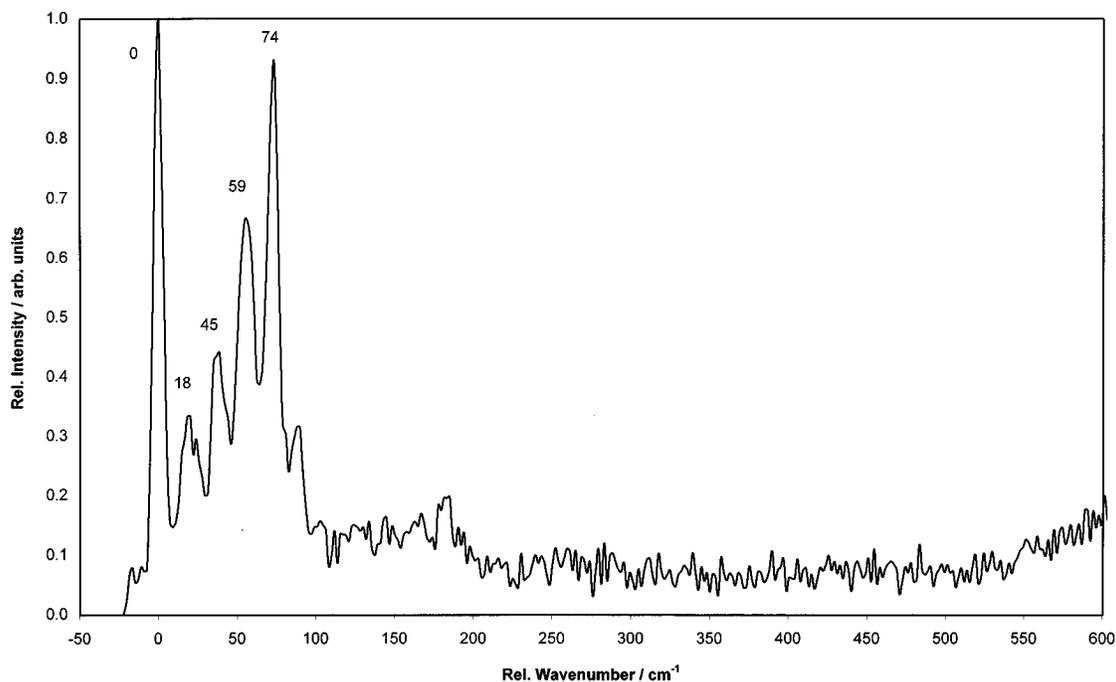


FIG. 10. Dispersed fluorescence spectrum of the Phenol dimer recorded via excitation of the donor  $S_1$  combination state at  $38\text{ cm}^{-1}$ . Spectral resolution is  $3\text{ cm}^{-1}$ , error in band positions  $\pm 2\text{ cm}^{-1}$ .

for example, demonstrate intermolecular vibrations in the “intermediate” energy range  $60\text{--}100\text{ cm}^{-1}$ .<sup>22</sup> It has to be left to a normal coordinate analysis of the Phenol dimer based on ab initio calculations to decide if there are dimer vibrations in this range.

#### 10. $S_1^{\text{donor}} 6^1$ intermediate state at $120\text{ cm}^{-1}$

Fluorescence from the  $6^1$  donor state at  $120\text{ cm}^{-1}$  gives rise to the spectrum shown in Fig. 13. The assignment of the bands is very clear here; cf. Table III. The most prominent

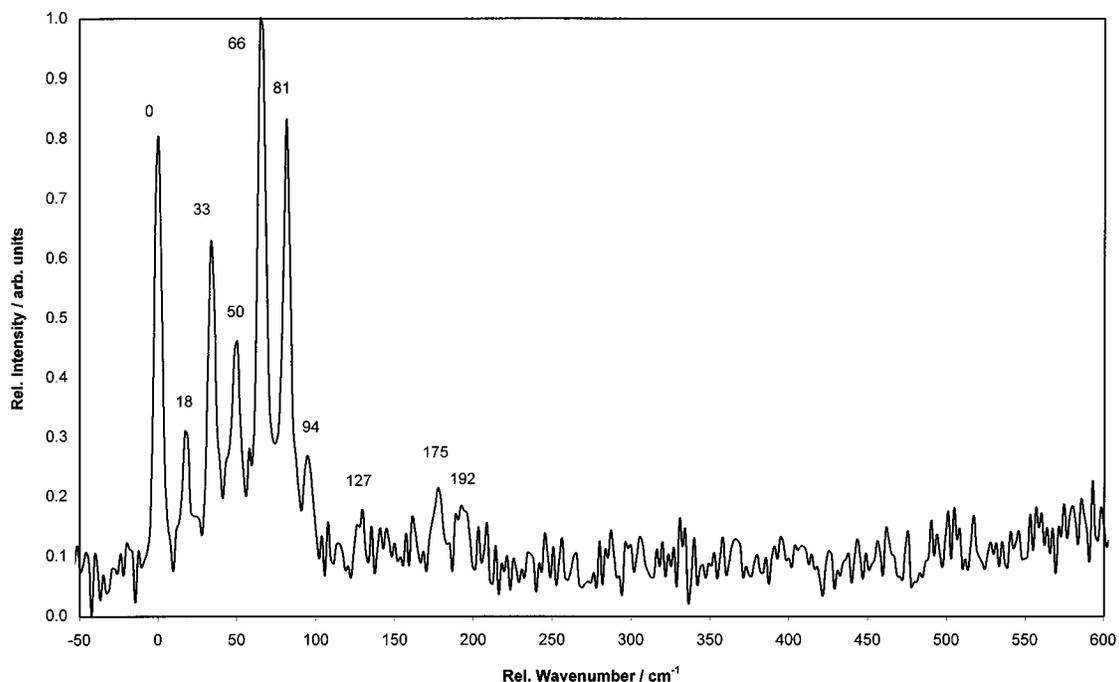


FIG. 11. Dispersed fluorescence spectrum of the Phenol dimer recorded via excitation of the donor  $S_1$  combination state at  $45\text{ cm}^{-1}$ . Spectral resolution is  $3\text{ cm}^{-1}$ , error in band positions  $\pm 2\text{ cm}^{-1}$ .

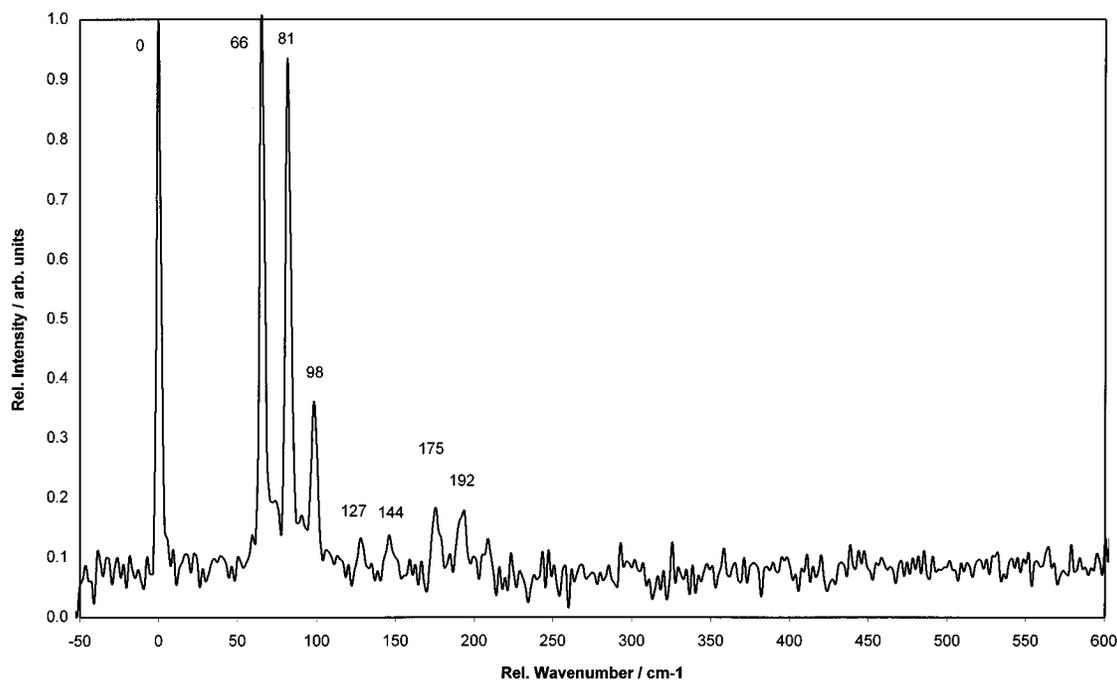


FIG. 12. Dispersed fluorescence spectrum of the Phenol dimer recorded via excitation of the donor  $S_1$  combination state at  $70\text{ cm}^{-1}$ . Spectral resolution is  $3\text{ cm}^{-1}$ , error in band positions  $\pm 2\text{ cm}^{-1}$ .

band is the one at  $109\text{ cm}^{-1}$ , which can be assigned to the  $6_1$  state. Similarly, to the DF spectrum obtained via excitation of the  $0^0$  donor state, combinations with the fundamentals 2 and 4 at 18 and  $33\text{ cm}^{-1}$  are observed. The same combinations are observed with the overtones  $6_2$  at  $212\text{ cm}^{-1}$  and  $6_3$

at  $316\text{ cm}^{-1}$ . Obviously, the fundamental 6 is quite harmonic. Fig. 13 shows a perfect example of an easily interpretable DF spectrum.

From its frequency and intensity, we assign the donor  $6^1$  vibration at  $120\text{ cm}^{-1}$  to the intermolecular stretch vibration

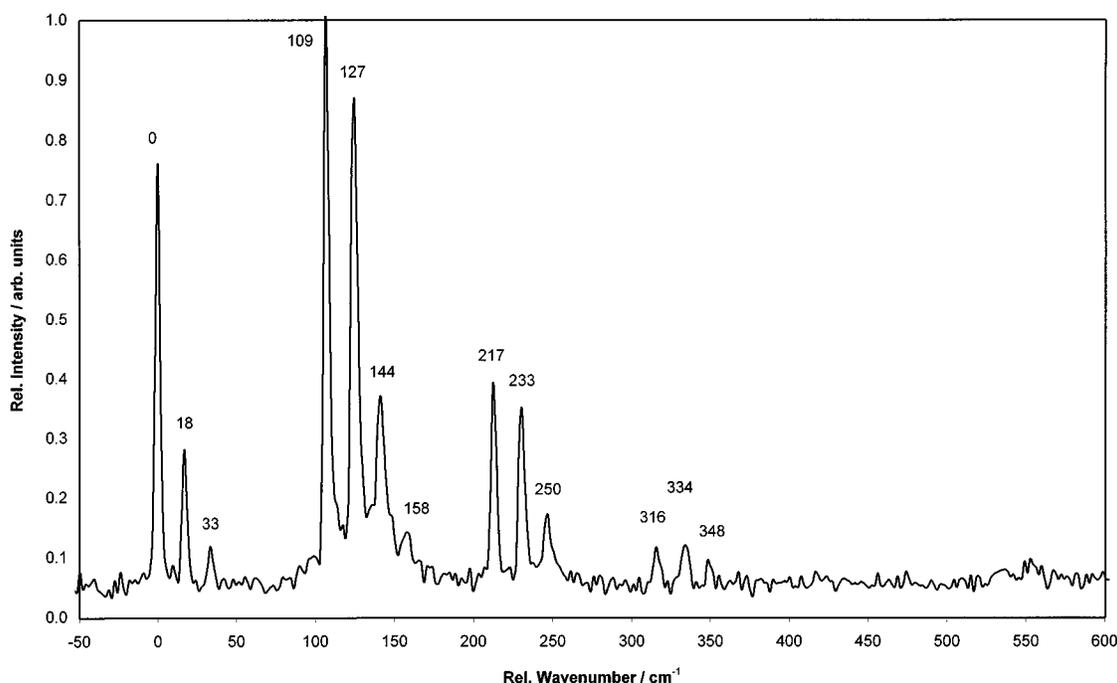


FIG. 13. Dispersed fluorescence spectrum of the Phenol dimer recorded via excitation of the donor  $6^1$  state at  $120\text{ cm}^{-1}$  (intermolecular stretch vibration in the  $S_1$  donor state of the Phenol dimer). Spectral resolution is  $3\text{ cm}^{-1}$ , error in band positions  $\pm 2\text{ cm}^{-1}$ .

TABLE IV. Correlation of the fundamental vibrations in the  $S_0$  and  $S_1$  electronic states.

$S_0$ [ $\text{cm}^{-1}$ ]	$S_1^{\text{donor}}$ [ $\text{cm}^{-1}$ ]	$S_1^{\text{acceptor}}$ [ $\text{cm}^{-1}$ ]
9	7	9
18	12	18
33	15	25
45	23	27
50	30	33
109	120	106

$\sigma$  of the hydrogen bonded dimer as was already done in Refs. 15 and 18.

Accordingly, the  $6_1$  state at  $109 \text{ cm}^{-1}$  belongs to  $\sigma$  in the  $S_0$  state, while the band at  $106 \text{ cm}^{-1}$  in Fig. 2 belongs to  $\sigma$  in the  $S_1^{\text{acceptor}}$  state; cf. Table IV.

The frequency difference between donor and acceptor stretch vibrations can be qualitatively explained by the change in electron density of the hydrogen bonded atoms upon  $S_1 \leftarrow S_0$  excitation.<sup>23</sup> Electronic excitation of Phenol leads to a shift of electron density from the oxygen atom of the hydroxyl group to the aromatic ring. Hence the electron density at the oxygen atom is decreased. If the acceptor moiety is excited, then the proton accepting capability of the O atom is lowered, the hydrogen bond is weakened (blue shift of the acceptor origin relative to the electronic origin of Phenol), and the stretch frequency decreases ( $106 \text{ cm}^{-1}$  relative to  $109 \text{ cm}^{-1}$  in the  $S_0$  state).

Electronic excitation in the donor part leads to a lower electron density at the H atom of the donor OH group, and hence to a stronger attraction of the acceptor O atom (whose electron density is not changed by the donor excitation), a stronger H-bond (red shift of the donor origin), and a higher stretch frequency ( $120 \text{ cm}^{-1}$  relative to  $109 \text{ cm}^{-1}$  in the  $S_0$  state).

#### IV. CONCLUSIONS

By spectral hole burning and dispersed fluorescence spectroscopy of all low frequency intermediate states we were able to unambiguously assign four of the possible six intermolecular vibrations in the  $S_0$ ,  $S_1^{\text{donor}}$ , and  $S_1^{\text{acceptor}}$  state of the Phenol dimer. We propose assignments for the remaining two fundamentals.

The full assignment and the correlation to specific rocking, torsion, and wagging motions have to be left to SHB-R2PI experiments with isotopomers of the Phenol dimer and to *ab initio* based normal mode calculations which are on the way in our laboratory.

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