PHYSICAL REVIEW B VOLUME 57, NUMBER 1 1 JANUARY 1998-I

High-pressure low-temperature phase transition in a doped *para*-terphenyl crystal: A spectral-hole-burning study

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(Received 5 June 1997)

The homogeneous width of zero-phonon lines in a chlorin-doped *para*-terphenyl crystal is determined by spectral hole burning at $T=4.2-14$ K under various hydrostatic pressures up to 7 kbar. A drastic broadening of spectral holes with pressure occurs on approaching the order-disorder (triclinic-to-monoclinic) phase transition which takes place under $P\approx 5.5$ kbar at $4.2\leqslant T\leqslant 14$ K. The thermal broadening of spectral holes at fixed pressures is an activated process with the activation energy depending on pressure and having a deep minimum at $P\approx 5.5$ kbar, i.e., in the phase-transition region. [S0163-1829(98)02801-X]

Structural phase transitions (PT's) have been one of the most challenging and intriguing topics of condensed matter research.[1] In general, the PT temperature T_{tr} depends on the pressure P and, conversely, the PT pressure P_{tr} depends on the temperature T, i.e., $T_{\mathrm{tr}}=T_{\mathrm{tr}}(P)$ and $P_{\mathrm{tr}}=P_{\mathrm{tr}}(T)$. Particularly, in the case of a monoclinic-to-triclinic PT in a *para*-terphenyl crystal observable at ambient pressure by cooling the sample below $T_{\mathrm{tr}}=193\,\mathrm{K}$,[2] application of hydrostatic pressure shifts the PT temperature strongly downwards, so that at around 5.5 kbar T_{tr} falls to $\sim 0\,\mathrm{K}$,[3] and at higher pressures the triclinic phase does not exist at all. Such a character of the phase boundary in *para*-terphenyl allows one to study this ''cold'' PT by the methods of high-resolution spectroscopy, including persistent spectral hole burning,[4,5] as well as by their time-domain counterparts, including photon echo.[6]

In this paper, we report on pressure and temperature dependences of hole widths in *para*-terphenyl (an aromatic molecular compound, $C_6H_5C_6H_4C_6H_5$) doped with free-base chlorin (a hydrogenated derivative of porphin, 7,8-dihydroporphin) at temperatures 4.2–14 K and pressures up to 7 kbar, including the critical region around 5.5 kbar.

The PT in a p-terphenyl crystal has been argued to be of an order-disorder type at normal pressure,[7] but acquiring displacive (soft mode) PT features with increasing pressure.[8] The order parameter involved is the torsional angle between the plane of the central and the plane of the coplanar outer phenyl rings in the p-terphenyl molecule.

The choice of chlorin as a dopant was motivated by the existence of an intramolecular phototransformation process (turning of the central proton pair by 90°) in a chlorin molecule,[9] providing an effective mechanism for burning persistent spectral holes into inhomogeneously broadened spectral lines of this impurity.

Beside a lot of normal-pressure data on the temperature dependence of the hole width (quasihomogeneous linewidth of zero-phonon lines) in various doped crystals and glasses[10,11] and also the recent results on the pressure dependence of the hole width at 4.2 K in isobaric-isothermal experiments (no pressure or temperature variations between the hole-burning and hole-recording acts),[12–15] this study is to our knowledge the first observation of *simultaneous* temperature and pressure dependences of the isobaric-isothermal hole width in a polymorphic solid over the PT region at low temperatures. (In an interesting study,[16] the temperature dependence of the hole width at 1.2–4.2 K for bacteriochlorophyll-*a* in triethylamine was measured only at a single high-pressure value, 30 kbar.)

The polycrystalline samples were prepared by dissolving chlorin (Chl) at 490 K in molten p-terphenyl (p-Tph) of purity $>99\%$ (Fluka) followed by slow cooling to room temperature. The Chl concentration was about 10^{-4} mol/mol. The same sample was used in all measurements under hydrostatic pressure. Our high-pressure low-temperature setup, consisting of a 15-kbar helium gas compressor, an optical high-pressure cell with three sapphire windows, and a liquid-helium cryostat, as well as further experimental details, has been described earlier.[12–15] The standard procedure involved the application of a helium-gas prepressure of about 5 kbar at room temperature, pressure adjustment at liquid-nitrogen temperature (P_{tr} for p-Tph is around 3.8 kbar at 77 K), and the subsequent cooling down to 4.2–14 K. Any temperature within that range could be stabilized with an accuracy of $\pm 0.1\,\mathrm{K}$. The final pressure value was determined to $\pm 0.15\,\mathrm{kbar}$ by measuring the pressure-induced shift of the R_1 emission line of a small chip of ruby placed in the high-pressure cell.

Spectral holes were burnt and recorded with a Coherent CR-699-29 single-frequency tunable ring dye laser of $\leqslant 2$ MHz linewidth by using DCM dye. Rather low burning intensities of $\sim 3\,\mu\mathrm{W/mm^2}$ and different burning times of 10–100 s were used. Holes were scanned in the fluorescence excitation spectrum of the zero-phonon line (ZPL) under study by measuring the fluorescence intensity of the sample at $\lambda > 650$ nm through proper cutoff glass filters, using excitation intensity of $\sim 0.03\,\mu\mathrm{W/mm^2}$. All the hole widths measured were extrapolated to the zero burning dose limit.[13,14] Ordinary fluorescence emission spectra of the sample and of

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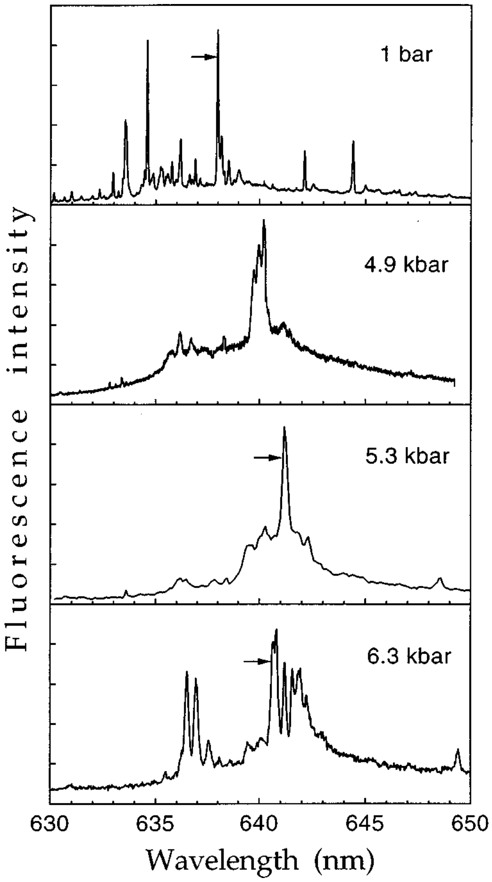

FIG. 1. Fluorescence emission spectra of p-Tph:Chl at $T=4.2$ K and various pressures. The arrows indicate the line chosen for spectral-hole-burning experiments at the pressures shown.

a ruby chip were detected with a LOMO DFS-24 double-grating spectrometer of a 0.5 cm^{-1} spectral resolution.

Figure 1 shows the inhomogeneous (nonselectively excited) fluorescence emission spectra of p-Tph:Chl at 4.2 K under various pressures. The spectrum measured at normal pressure contains a number of rather narrow [$\sim 1\ \mathrm{cm}^{-1}$ full width at half maximum (FWHM)] inhomogeneously broadened purely electronic ZPL's. Note that all these lines belong to Chl molecules occupying different, crystallographically inequivalent sites in the p-Tph host lattice. The whole inhomogeneous multiplet of the ZPL's seen in Fig. 1 reflects a local disorder, i.e., variations in local (site) geometry. The relative intensities of the recorded lines (especially of weaker ones) vary to some extent from sample to sample. However, these variations are much weaker than those induced by pressure.

As seen in Fig. 1, the spectrum taken at 5.3 kbar, i.e., close to P_{tr}, is drastically changed: The intensities of all but the 641.1-nm line are strongly reduced and a broad ($\sim 75\ \mathrm{cm}^{-1}$ FWHM) background structure appears. In such a pressure-induced evolution, the spectrum at 4.9 kbar displays an intermediate stage. The 6.3-kbar spectrum reveals a number of partially overlapping narrow ZPL's again, and it does not differ much from the spectrum recorded at still higher pressure of 7.2 kbar (not shown here). In both triclinic and monoclinic phases (below and above 5.5 kbar), all the ZPL's exhibit red pressure shifts with the mean pressure coefficient of about $-15\ \mathrm{cm}^{-1}$/kbar as averaged over all measured lines.

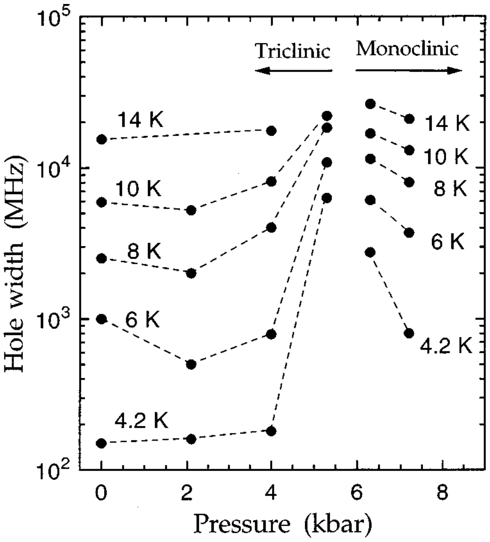

FIG. 2. Isobaric-isothermal hole widths (see the text) as a function of pressure for p-Tph:Chl at several fixed temperatures (4.2, 6, 8, 10, and 14 K). The lines traced between the data points serve only as guides for the eye.

Figures 2 and 3 show, respectively, the pressure and temperature dependences of the isobaric-isothermal hole widths (when $\Delta P=0$ and $\Delta T=0$ between burning and recording the holes). Under low pressures ($\leqslant 2$ kbar) the hole widths (FWHM) at all but the lowest (4.2 K) and the highest (14 K) temperatures decrease with increasing pressure (Fig. 2). Such a hole narrowing was earlier observed for chlorin molecules in frozen n-octane[13–15] and ascribed to the pressure-induced increase of the frequency of a quasilocal vibration active in the thermal broadening of the impurity transition. A similar effect—the pressure-induced increase of the dephasing time—was also observed in photon echo experiments for pentacene molecules in naphthalene[17] and for pentacene in the monoclinic phase of p-terphenyl at pressures of 8–18 kbar.[18]

An unlike behavior, the pressure broadening of holes in p-Tph:Chl at 4.2 K below ~ 2 kbar (see Fig. 2), may be explained by a contribution of spectral diffusion, directly observable in single-molecule spectroscopic studies.[19,20] In the ordered triclinic phase of a p-terphenyl crystal, almost all molecules freeze-in into fixed conformations. In real crystals this leads to the formation of two types of ordered domains separated by narrow (solitonic) domain walls.[2] The dynamics responsible for the spectral diffusion may then be related to the conformational ''jumps'' of the host molecules located in the domain wall region (an analog of the dynamics governed by two-level systems in glasses). In our experiments the spectral diffusion reveals itself as a temporal broadening of spectral holes on the time scale from 10 to 1000 s. No hole broadening in this time interval was observable at higher temperatures, above 4.2 K.

On approaching the PT point, the pressure dependence of the hole width changes qualitatively: In the pressure region from about 2 to 5.5 kbar, a large increase of the hole width with pressure takes place at all temperatures. Thus, for $T \leqslant 10$ K, the hole width grows about 4–40 times, as can be

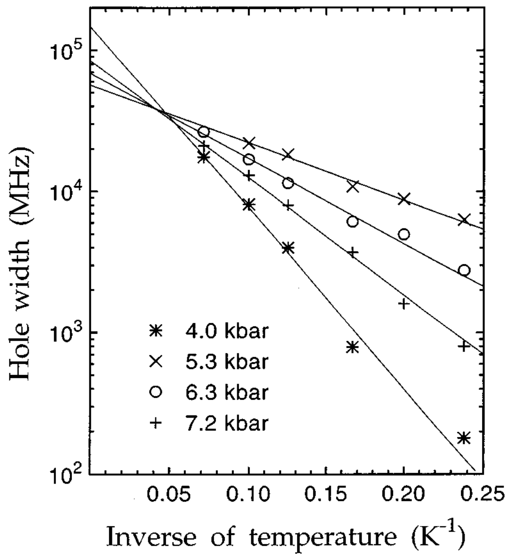

FIG. 3. Plots of isobaric-isothermal hole widths (see the text) vs reciprocal temperature for p-Tph:Chl at various fixed pressures near P_{tr} (4.0, 5.3, 6.3, and 7.2 kbar). The straight lines are least-squares fits to the data points.

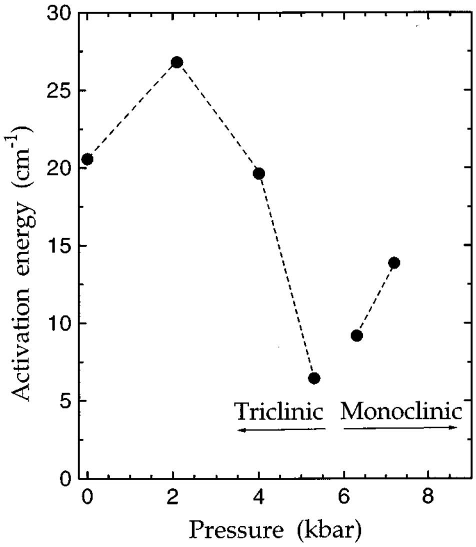

FIG. 4. Activation energy E for thermal broadening of spectral holes in p-Tph:Chl calculated from the plots of the hole width logarithm ln δ vs $1/T$ at various fixed pressures. The lines between obtained values of E are merely guides for the eye.

seen from Fig. 2. At pressures higher than P_{tr}, a decrease of the hole width with increasing pressure is observed again.

Close to the PT the thermal broadening of spectral holes has a thermally activated nature, as is evidenced by linear dependences of the logarithm of the hole width on the reciprocal temperature at several pressures near P_{tr} (Fig. 3). The following three observations—(i) the intersection of all extrapolated least-squares-fitted straight lines at about 20 K in Fig. 3, (ii) the smallest (nearest to zero) slope of the 5.3-kbar line in Fig. 3, and (iii) the pressure behavior of all the curves in Fig. 2 (their estimated peaking near 5.5 kbar)—allow us to suppose that close to $T^* = 20$ K and $P^* = 5.5$ kbar the dependence of the hole width δ (Ref. 21) on both pressure and temperature is rather weak. Then all the straight lines in Fig. 3 obtained at various fixed pressures can be represented with a reasonable accuracy as

$$\ln\delta(T) - \ln\delta(T^*) = -E\left[\frac{1}{kT} - \frac{1}{kT^*}\right], \tag{1}$$

where E is the activation energy for thermal broadening of a spectral hole at a fixed pressure. From this equation of a bundle of straight lines passing through the given point $[T^*,\delta(T^*)]$ in Fig. 3, by using an exponential form and taking into account the pressure dependence of δ at fixed temperatures through the variation of E with P, we get

$$\delta(T,P) = \delta(T^*,P^*)\exp\left\{-E(P)\left[\frac{1}{kT} - \frac{1}{kT^*}\right]\right\}, \tag{2}$$

where $\delta(T^*,P^*)$, i.e., the hole width at ~ 20 K and ~ 5.5 kbar, is equal to $\sim 3.6 \times 10^4$ MHz or $\sim 1.2\ \mathrm{cm}^{-1}$ (see Fig. 3).

The activation energy E, which according to the so-called exchange model[18,22] is associated with the energy of a low-frequency quasilocal vibrational mode interacting with an impurity electronic transition, has a rather strong and nonmonotonous pressure dependence, as shown in Fig. 4. The values of E in Fig. 4 were calculated as the slopes of the least-squares-fitted straight lines through the data points in the plots of $\ln\delta$ versus $1/T$ at several fixed pressures (0, 2.1, 4.0, 5.3, 6.3, and 7.2 kbar). Figure 4 illustrates that at pressures above ~ 2 kbar E decreases rapidly, attains a minimum value in the vicinity of P^*, and then increases at nearly the same rate.

We have not enough experimental data to determine the exact functional form of the pressure dependence of E. However, the $E \sim |P - P^*|^{1/2}$ behavior, similar to the pressure dependence of soft optical phonon modes in ferroelectrics,[23] seems to be compatible with our data. If this is the case, then $E(P^*) = 0$, and according to Eq. (2), we have $\delta(T,P^*) = \delta(T^*,P^*)$ and also $\delta(T^*,P) = \delta(T^*,P^*)$; i.e., the hole width δ as well as the homogeneous width Γ of the respective ZPL, $\Gamma = \delta/2$,[20] becomes temperature independent at $P = P^*$ and pressure independent at $T = T^*$.

There are only a few papers where the influence of pressure-induced polymorphic PT's on the electronic (vibronic) spectra of impurities or other defects in solids has been considered. In early room-temperature studies, mainly those on the alkali-halide crystals doped with s^2 ions (Tl^+, In^+, Pb^{2+}, and Bi^{3+} absorption bands[24] and KCl:Tl^+ emission and absorption bands[25]) and also on color centers in alkali halides (F and F-aggregate centers giving rise to F, M, N, and R_2 absorption bands[26]), only broad vibronic bands without any ZPL's were examined under high pressure. Abrupt changes in spectral positions and intensities of these bands as well as the emergence of new bands due to the change of crystal structure were reported there. Lately, the influence of the PT on ZPL's in the low-temperature absorption and fluorescence spectra of pentacene molecules doped into a p-terphenyl crystal has been studied.[3,27,28] Especially interesting for us are the recent results[18] on the pressure and temperature dependence of the photon echo decay in pentacene-doped p-terphenyl at $T=4.3-10\,\mathrm{K}$ under $P=0-18\,\mathrm{kbar}$, demonstrating essential impact of PT’s upon vibronic dephasing.

It is of interest to point at a particular difference between the results of Ref. 18 for pentacene-doped p-Tph and ours: In Ref. 18 only a minor (about 20%) decrease of the activation energy E with pressure in the triclinic phase of p-Tph has been observed, whereas in our case a decrease by a factor of about 4 occurs within the same pressure range. Apart from the obvious difference caused by different dopants, a possible explanation may also stem from the huge difference in the experimental time scales involved—down to a few tens of nanoseconds in the photon echo experiments contrasted to 10–1000 s in our spectral-hole-burning (SHB) measurements. While in the photon echo studies the results reflect only the vibrational dephasing, in our case a contribution to the hole width from the ‘‘slow’’ (yet fast as compared to our experimental time domain) spectral diffusion may become dominant when approaching the PT.

In conclusion, we have demonstrated the suitability of the SHB technique in the study of a structural phase transition. Besides, two general remarks concerning the SHB method should be made.

(i) Molecular probes as defects in a pure crystal can, of course, influence its phase transition,[29] particularly by nucleation of a new phase. Such effects may be of interest in themselves. However, narrowness of persistent spectral holes makes them sensitive to distant events (PT’s in bulk) as well. Therefore the results obtained by SHB may be applicable also to pure, undoped systems.

(ii) Other kinds of SHB measurements, performed by using hydrostatic pressures, e.g., pressure tuning[30,31] and pressure cycling[31] experiments (see also Ref. 14 for both cases), can be applied to tackle different problems (‘‘genetic’’ correspondence of dopant sites in different phases, ‘‘survival’’ of defects in a PT, etc.).

The authors are indebted to V. Hizhnyakov, N. Kristoffel, P. Konsin, and T. Örd for valuable discussions and to E. L. Chronister for sending the manuscript of Ref. 18 on photon echo studies prior to publication. This work was supported in part by the Estonian Science Foundation under Grant No. 345 and also Grant No. 2268.

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[1] *Structural Phase Transitions I*, edited by K. A. Müller and H. Thomas, Topics in Current Physics, Vol. 23 (Springer-Verlag, Berlin, 1981); *Structural Phase Transitions II*, edited by K. A. Müller and H. Thomas, Topics in Current Physics, Vol. 45 (Springer-Verlag, Berlin, 1991).

[2] J. L. Baudour, Y. Délugeard, and H. Cailleau, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **32**, 150 (1976).

[3] B. J. Baer and E. L. Chronister, J. Chem. Phys. **99**, 3137 (1993).

[4] A. A. Gorokhovskii, R. K. Kaarli, and L. A. Rebane, Pis’ma Zh. Éksp. Teor. Fiz. **20**, 474 (1974) [JETP Lett. **20**, 216 (1974)].

[5] B. M. Kharlamov, R. I. Personov, and L. A. Bykovskaya, Opt. Commun. **12**, 191 (1974).

[6] N. A. Kurnit, I. D. Abella, and S. R. Hartmann, Phys. Rev. Lett. **13**, 567 (1964).

[7] J. L. Baudour, H. Cailleau, and W. B. Yelon, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **33**, 1773 (1977).

[8] A. Girard, Y. Délugeard, and H. Cailleau, J. Phys. (Paris) **48**, 1751 (1987).

[9] K. N. Solov’ev, I. E. Zaleskii, V. N. Kotlo, and S. F. Shkirman, Pis’ma Zh. Éksp. Teor. Fiz. **17**, 463 (1973) [JETP Lett. **17**, 332 (1973)].

[10] K. K. Rebane and A. A. Gorokhovskii, J. Lumin. **36**, 237 (1987).

[11] S. Voelker, J. Lumin. **36**, 251 (1987).

[12] A. Ellervee, R. Jaaniso, J. Kikas, A. Laisaar, A. Suisalu, and V. Shcherbakov, Chem. Phys. Lett. **176**, 472 (1991).

[13] A. Ellervee, V. V. Hizhnyakov, J. Kikas, A. Laisaar, and A. Suisalu, J. Lumin. **53**, 223 (1992).

[14] A. Ellervee, J. Kikas, A. Laisaar, V. Shcherbakov, and A. Suisalu, J. Opt. Soc. Am. B **9**, 972 (1992).

[15] A. Ellervee, J. Kikas, A. Laisaar, and A. Suisalu, J. Lumin. **56**, 151 (1993).

[16] F. T. H. den Hartog, M. P. Bakker, J. M. A. Koedijk, T. M. H. Creemers, and S. Völker, J. Lumin. **66&67**, 1 (1996).

[17] R. A. Crowell and E. L. Chronister, Chem. Phys. Lett. **216**, 293 (1993).

[18] B. J. Baer and E. L. Chronister, J. Phys. Chem. **99**, 7324 (1995).

[19] M. Orrit and J. Bernard, Phys. Rev. Lett. **65**, 2716 (1990).

[20] W. P. Ambrose, T. Bashe, and W. E. Moerner, J. Chem. Phys. **95**, 7150 (1991).

[21] Note that a measured hole width δ (its zero-dose limit) is related to the homogeneous linewidth Γ of the respective ZPL by a simple expression $\delta=2\Gamma$. See, e.g., L. A. Rebane, A. A. Gorokhovskii, and J. V. Kikas, Appl. Phys. B: Photophys. Laser Chem. **29**, 235 (1982).

[22] R. M. Shelby, C. B. Harris, and P. A. Cornelius, J. Chem. Phys. **70**, 34 (1979).

[23] P. S. Peercy, Phys. Rev. Lett. **35**, 1581 (1975).

[24] R. A. Eppler and H. G. Drickamer, J. Phys. Chem. Solids **6**, 180 (1958); **15**, 112 (1960).

[25] P. B. Alers and P. E. V. Shannon, J. Chem. Phys. **41**, 1675 (1964).

[26] H. G. Drickamer, in *Solid State Physics: Advances in Research and Applications*, edited by F. Seitz and D. Turnbull (Academic, New York, 1965), Vol. 17, Chap. II, points 1a and 1c.

[27] E. L. Chronister and B. J. Baer, in *High-Pressure Science and Technology—1993*, edited by S. C. Schmidt, J. W. Shaner, G. A. Samara, and M. Ross, AIP Conf. Proc. No. 309 (AIP, New York, 1994), Pt. 2, p. 1507.

[28] B. J. Baer and E. L. Chronister, J. Chem. Phys. **100**, 23 (1994); Chem. Phys. **185**, 385 (1994); High Press. Res. **12**, 101 (1994).

[29] A. P. Levanyuk and A. S. Sigov, *Defects and Structural Phase Transitions*, Ferroelectricity and Related Phenomena, Vol. 6 (Gordon and Breach, New York, 1988).

[30] Th. Sesselmann, W. Richter, D. Haarer, and H. Morawitz, Phys. Rev. B **36**, 7601 (1987).

[31] G. Gradl, A. Feis, and J. Friedrich, J. Chem. Phys. **97**, 5403 (1992).