Microsolvation of porphine molecules in superfluid helium nanodroplets as revealed by optical line shape at the electronic origin

J. Fischer, S. Fuchs, A. Slenczka, M. Karra, and B. Friedrich

ARTICLES YOU MAY BE INTERESTED IN

Microsolvation of phthalocyanine molecules in superfluid helium nanodroplets as revealed by the optical line shape at electronic origin
The Journal of Chemical Physics 148, 144301 (2018); https://doi.org/10.1063/1.5022006

A computational quantum-mechanical model of a molecular magnetic trap
The Journal of Chemical Physics 149, 244112 (2018); https://doi.org/10.1063/1.5055767

Total cross section measurements for electron scattering from dichloromethane
The Journal of Chemical Physics 149, 244304 (2018); https://doi.org/10.1063/1.5080636
Microsolvation of porphine molecules in superfluid helium nanodroplets as revealed by optical line shape at the electronic origin

J. Fischer,¹ S. Fuchs,¹ A. Slenczka,¹,a) M. Karra,² and B. Friedrich²,a)
¹Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93053 Regensburg, Germany
²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

(Received 20 August 2018; accepted 4 December 2018; published online 27 December 2018)

We investigate the line shape at the electronic origin of single porphine molecules doped into superfluid helium droplets as a function of the droplet size. Helium droplets comprised of less than 10⁵ atoms are generated from an expansion of gaseous helium, while droplets with more than 10¹⁰ atoms originate from liquid helium. In contrast to our recent study on phthalocyanine, porphine is found to exhibit a solvent shift to the blue with respect to the gas-phase resonance frequency as well as a multiplet splitting. A comparison of the helium-induced features of phthalocyanine and porphine with those obtained in similar studies on tetracene and pentacene reveals that these occur chiefly as two kinds of excitations distinguished by their linewidths and their dependence on the droplet size. Moreover, at quasi-bulk conditions achieved with droplets in excess of 10⁶ helium atoms, none of these four dopant species yields an optical spectrum that can be assigned to a plausible rotational band structure.

Motivated by early studies of line shapes in electronic spectra of organic molecules doped into helium droplets, one of the authors (Slenczka) had investigated the line shape at the electronic origin of phthalocyanine in helium droplets. The asymmetry of the line shape and its dependence on the size of the helium droplets could be simulated quantitatively by adapting the well known excluded-volume model to molecules doped into helium droplets. Inhomogeneous line broadening could be readily explained as due to the size distribution of the helium droplets enclosing the dopant species. Consequently, beyond a certain droplet size and, ultimately, for bulk superfluid helium, this contribution to the inhomogeneous line broadening was expected to vanish and the band structure of a freely rotating solvated dopant molecule to dominate the spectrum. As described in Ref. 24, for phthalocyanine doped into He droplets with the number, N, of He atoms in excess of 10⁶, the asymmetry of the line shape did indeed disappear. Instead, a double peak was resolved which could be well fitted by the envelope of the rotational band structure of freely rotating He-solvated phthalocyanine.

However, contrary to the above, our recent spectroscopic investigation of the same system revealed that the spectral profile of phthalocyanine in large He droplets was in fact size-dependent. Instead of two peaks, we even found three for some droplet sizes, each peak with its individual intensity profile as a function of the droplet size. Under the assumption of a constant droplet temperature of 0.38 K for the range of droplet sizes produced, i.e., for 10⁴ ≤ N ≤ 10⁹, the intensity profile of a rotational band structure of a dopant should not vary once quasi-bulk conditions are reached. But the experiment showed otherwise. Moreover, the spectral width of each of the three peaks is about a half of the width expected for a freely

I. INTRODUCTION

Superfluid helium droplets amount to a cryogenic bath with unique properties for the investigation of structure and dynamics of molecular systems. Properties such as low temperature (0.38 K) and a vanishing viscosity have proved to be a boon for molecular spectroscopy. Molecular systems investigated in or on superfluid helium droplets range in size from diatomic linear rotors to polyatomic and large aromatic compounds to biomolecules such as proteins. The spectra of molecules in helium nanodroplets reflect purely molecular characteristics, helium-mediated attributes, and purely helium-induced features. In numerous cases, the details of the helium-attibuted features are either not resolved or rendered insignificant compared with the dominant molecular features that manifest within the zero-phonon line (ZPL). However, it is the helium-induced spectral features that provide valuable information on helium microsolvation, i.e., the interaction of the quantum fluid with a foreign species (impurity) on a molecular scale. Besides the well known phonon wing (PW), helium-induced features reveal themselves via spectral line shapes, including line splitting. Currently, there is no comprehensive, versatile model available for a quantitative prediction of helium-induced spectral features. The workings of microsolvation in superfluid helium droplets are governed by many-body dispersion interactions involving a quantum fluid and are the subject of current theoretical research.

¹Authors to whom correspondence should be addressed: alkwin.slenczka@chemie.uni-regensburg.de and brich@fhi-berlin.mpg.de

https://doi.org/10.1063/1.5052615
rotating solvation complex of phthalocyanine in helium droplets (at 0.38 K).

In order to shed light on the above conundrum, we carried out a series of spectroscopic experiments similar to those described above, but with porphine (C_{20}H_{14}N_{4}) instead of phthalocyanine. Our choice fell on porphine as a dopant because of its structural similarity with phthalocyanine in both its ground and excited states employed for its detection and because of previous work on its spectroscopy in helium droplets.\textsuperscript{12,20,26–29}

Herein, we present new experimental data on porphine, accompanied by model calculations of the inhomogeneous line broadening. While the inhomogeneous line broadening is found to be similar to that of phthalocyanine, albeit with an inverted solvent shift, the appearance of a fine structure in the form of additional peaks far below the bulk limit for solvation was accomplished by optimizing the spectral resolution mainly by avoiding saturation broadening. The spectra recorded under quasi-bulk conditions are compared to the rotational band systems of various empirical rotor models of the solvated dopant. Finally, we ponder upon the origin of two different kinds of helium induced fine structures distinguished by their respective half-widths in dependence on the droplet size. All the experimental spectra discussed in this paper show exclusively signals from singly doped droplets. This is possible because multiply doped droplets carry clusters of the dopant species. This solvent shift scales with the size/diameter of the helium environment. Beyond a certain droplet size, the solvent shift converges to a maximum value which corresponds to that of bulk helium. Thus, a given droplet size distribution is imprinted on the line shape of the molecular resonances as an inhomogeneous broadening, provided it includes a significant contribution from droplet sizes below the bulk limit. This effect can be expected to be ubiquitous with gradual variations from dopant to dopant. In particular, structurally similar molecules should exhibit qualitative or even nearly quantitative similarity of their spectral behavior. Despite its structural similarity with phthalocyanine, porphine in He droplets exhibits a line shape asymmetry at the electronic origin that is inverted with respect to that of phthalocyanine. As shown in Fig. 1, the slowly receding edge of the most intense peak is to the red/low frequency side, while the blue edge drops off more rapidly. Moreover, this most intense peak is accompanied by additional, much weaker peaks that are absent in the case of phthalocyanine. The gap between these peaks is about 0.35 cm\textsuperscript{-1}. We note that the fine structure shown in Fig. 1 remains unresolved at moderate resolution.\textsuperscript{12,13}

One of our goals was to determine whether the asymmetry of the peaks recorded for porphine in helium droplets generated under subcritical expansion conditions was of the same origin as that seen for phthalocyanine, while keeping in mind that the solvent shifts are mutually opposite for these two dopants. And indeed, controlled by varying the helium

II. EXPERIMENTAL

The experimental setup consists of a vacuum machine with two differentially pumped vacuum chambers. The first chamber contains the helium droplet source which was built according to the design developed in Göttingen.\textsuperscript{1,20} Highly purified helium (He 6.0) expands through a platinum orifice of 5 μm in diameter. The nozzle is attached to the second stage of a Sumitomo cold head RDK-408S2 and compressor unit F-50Hw which cools the nozzle down to almost 7.0 K. Resistive heating is used to increase the nozzle temperature. Droplets are either formed by the condensation from of a gas (subcritical expansion conditions) or by the fragmentation of a liquid (supercritical expansion conditions). At the given helium stagnation pressure of 30 bars, the temperature separating these two regimes is about 11 K. The transition from subcritical to supercritical expansion is accompanied by a discontinuous increase of the droplet sizes.\textsuperscript{1}

A second vacuum chamber contains the pickup unit for doping of the helium droplets as well as the fluorescence detection unit. The helium droplet beam enters via a conically shaped skimmer of a 1.4 mm diameter. Measured from the nozzle, the distance to the skimmer is about 20 mm and to the pickup unit about 120 mm. The pickup unit consists of a stainless steel cylinder wrapped in a heating wire. It is about 30 mm in diameter and 20 mm high. The heating wire is shielded by a stainless steel cover and a copper tube connected to a liquid nitrogen Dewar. 80 mm downstream from the pickup unit, a laser beam intersects the helium droplet beam at right angles. A condenser lens (f# = 2) orthogonal to both beams collects the laser induced fluorescence, which is imaged onto the photocathode of a photo multiplier tube (PMT) (Hamamatsu R943-02). The PMT is shielded by an appropriate edge filter in order to eliminate laser stray light and its signal is amplified [Stanford Research Systems SRS445] and fed into a photon counter (SRS 400).

The fluorescence is induced by an actively stabilized continuously tunable single mode ring dye laser (Coherent 899-29 autoscan) with a bandwidth of less than 1 MHz. It is pumped by a 10 W @ 532 nm semiconductor laser (Coherent Verdi G10) and operated with the Rh6G dye. The output power of the dye laser operated in single mode peaks at about 1 W.

Frequency stepping of the laser and photon counting is synchronized by hardware hand-shaking between the laser and the photon counter. The data reading and storing is controlled by a computer run under homemade software.

Simulations of the rotational band structure shown in Fig. 7 and in the supplementary material have been calculated by means of pgopher.\textsuperscript{20} Quantum chemical computations for the ground state of porphine were performed by density functional theory (DFT) using the B3LYP a commonly used hyper function:\textsuperscript{43} and a split-valence type basis set, 6-311+G(d,p), with the help of the Gaussian 09 software package.\textsuperscript{31}

III. RESULTS AND DISCUSSION

The line shape analysis at the electronic origin of phthalocyanine in superfluid helium droplets\textsuperscript{21,22} revealed helium-induced features. In short, the helium environment causes a shift of the resonance frequencies which is due to state-specific energetic stabilization of the electronic levels of the dopant species. This solvent shift scales with the size/diameter of the helium environment. Beyond a certain droplet size, the solvent shift converges to a maximum value which corresponds to that of bulk helium. Thus, a given droplet size distribution is imprinted on the line shape of the molecular resonances as an inhomogeneous broadening, provided it includes a significant contribution from droplet sizes below the bulk limit. This effect can be expected to be ubiquitous with gradual variations from dopant to dopant. In particular, structurally similar molecules should exhibit qualitative or even nearly quantitative similarity of their spectral behavior. Despite its structural similarity with phthalocyanine, porphine in He droplets exhibits a line shape asymmetry at the electronic origin that is inverted with respect to that of phthalocyanine. As shown in Fig. 1, the slowly receding edge of the most intense peak is to the red/low frequency side, while the blue edge drops off more rapidly. Moreover, this most intense peak is accompanied by additional, much weaker peaks that are absent in the case of phthalocyanine. The gap between these peaks is about 0.35 cm\textsuperscript{-1}. We note that the fine structure shown in Fig. 1 remains unresolved at moderate resolution.\textsuperscript{12,13}
nozzle temperature at the stagnation pressure fixed at 30 bars, the blue shift of porphine was found to increase with increasing droplet size. A series of ten spectra recorded for different droplet source temperatures is shown in Fig. 2(a). From top to bottom, the decreasing nozzle temperature (indicated in each panel) shifts the log-normal droplet size distribution to smaller ranges, whereby the peak positions shift to the red, cf. Fig. 2(b) red line. At the same time, the linewidth is found to increase as shown by the red line in panel (c) of Fig. 2. The similarity with the corresponding spectra of phthalocyanine provides strong evidence for a helium solvent shift of porphine to the blue. For heliophilic dopant species, the blue shift reveals a solvent-induced stabilization that is stronger for the ground state than for the electronically excited state involved in the optical transition. For phthalocyanine, this is the other way around, resulting in a red solvent shift. We note that at nozzle temperatures above 15 K, a remarkable change in the line shape is observed, see panel (a) of Fig. 2, which will be discussed further below. Panel (d) of Fig. 2 shows the signal intensity as determined from the peak area of the leading intense peak (red) which decreases monotonously with increasing nozzle temperature.

We also investigated the origin of the inhomogeneous line broadening of porphine in helium droplets by invoking the phenomenological line shape model that was previously successfully applied to phthalocyanine.\textsuperscript{21,22} The results for the most intense peak of the ZPL of porphine are summarized in Fig. 3. The black curves represent the experimental data, identical to those shown in Fig. 2, while the simulated line shapes are overlaid in red. The model simulation is based on the following four ingredients: (i) a log-normal droplet size distribution, whose parameters are all related to the average number, $N$, of He atoms per droplet as outlined in Ref. 32; (ii) Poisson distribution of the probability of single-porphine molecule capture/doping.\textsuperscript{33} Here, the pickup cross section scaling as $\propto N^{2/3}$ relates to the droplet size $N$, while all other parameters concerning the pickup oven are set by the geometry and heating power of the pickup unit. (iii) a transformation of the droplet size as expressed by the number $N$ of helium atoms into a shift of the transition frequency based on the excluded volume model.\textsuperscript{23} It was calculated from a (6,12) Lennard-Jones potential as outlined in Ref. 22. (iv) convolution by a Gaussian line shape in order to account for homogeneous and Doppler line broadening.

While the top five spectra in Fig. 3 agree with the simulation fairly well (average droplet size above 11 000 He atoms),
the five bottom spectra shown in panel (a) of Fig. 2 (average droplet size below $10^4$ atoms) exhibit notable deviations from the fit: An additional peak appears, shown in blue in Fig. 2(a), which was obtained by subtracting the simulated spectrum from the corresponding experimental one. The extra peak is shown in Fig. 4 by scattered dots and labeled by the corresponding average droplet size. Also shown is a Lorentzian fit to the extra peak (red curve). In agreement with the experimental data shown by the blue line in panel (b) of Fig. 2, the position of the extra peak, at 16 312.336(5) cm$^{-1}$, remains constant for all four spectra as does its width of only 0.024(2) cm$^{-1}$. Only the intensity varies, i.e., decreases with decreasing average droplet size, as shown by the blue line in panel (d) of Fig. 2.

Figure 5 shows additional high-resolution spectra of porphine that were measured in He droplets prepared by a supercritical expansion of He. The spectra are labeled by the nozzle temperature and the heating power applied to the pickup cell, the latter determining the vapour pressure of the dopant (porphine). For the given source stagnation pressure of 30 bars, the range of the nozzle temperature from 11.9 K to 10.15 K corresponds to average droplet sizes in the range of $2 \times 10^4$ to $2 \times 10^6$. The spectra (displayed in the left-hand part of Fig. 5) are shown in three columns, each column pertaining to a constant heating power/vapour pressure of porphine in the pickup cell, and ordered from top to bottom according to the nozzle temperature (average droplet size increases from top to bottom and the vapour pressure of porphine decreases from left to right). Within a given droplet size distribution (as determined by the nozzle temperature), the fraction of singly doped helium droplets shifts to larger droplets upon reducing the partial pressure (reducing the heating power) of porphine in the pickup cell. In the spectra shown in Fig. 5, the average size of singly doped droplets increases from top to bottom and from left to right. All three series of the spectra (shown in red, blue, and black) reveal an increasing solvent shift to the blue with increasing droplet size. This is shown in panel (a) of the right-hand part of Fig. 5 (with the same color-coding as in the left-hand part of the figure). Panel (b) shows that the half width of the resonance remains almost constant. Remarkably, within each of the three series (red, blue, and black), the blue edge of the resonance becomes steeper with increasing droplet size which comes through as more conspicuous for the bottom spectra corresponding to the largest droplets, apparently in line with the fact that the droplet size distribution is exponential in contrast to log-normal. We note that, within the spectral width of the signal, no fine structure was resolved for the given signal-to-noise ratio. Panel (c) of Fig. 5 shows that
the peak intensity, as obtained from the peak area, decreases with increasing average droplet size, as expected.

As noted above, the spectra of porphine in helium droplets exhibit two additional smaller peaks; see Fig. 1. Upon optimizing the signal-to-noise conditions, as was done for the spectrum shown in Fig. 1, the line shape of the two smaller peaks matches perfectly with that of the leading intense peak. As can be seen in panel (a) of Fig. 2, upon varying the droplet size distribution, the smaller peaks exhibit a shift identical to that of the leading peak. As long as the signal-to-noise ratio remains high enough, the observed change in the linewidth follows that of the leading peak. However, for an average droplet size below $10^4$ atoms (corresponding to nozzle temperatures above 15 K), the smaller peaks at the ZPL do not develop the sharp superimposed peak like that shown in Fig. 4 for the leading peak. This made us revisit phthalocyanine and take a closer look at the zero-phonon line and the phonon wing at its electronic origin. As shown in Fig. 6, the most intense leading peak is accompanied by a series of small extra peaks that appear way before the phonon wing. These exhibit a line shape almost identical to that of the leading peak. This kind of fine structure for both porphine and phthalocyanine is readily explained by the empirical model of a dopant species surrounded by a non-superfluid helium solvation layer exhibiting either its own quantized excitations or structural variants.\(^{14}\) Such resonances are of course highly affected by the inhomogeneous line broadening in a manner similar to that of the leading peak. Unfortunately, a line shape analysis similar to the one for the leading peak\(^ {25}\) is beyond what our signal-to-noise ratio affords.

Finally, we briefly discuss the simulated rotational substructure of a free rotor resembling the porphine-helium complex and compare it to the spectra recorded for supercritical expansion conditions (as shown in Fig. 5). Much like phthalocyanine,\(^ {25}\) we simulated the rotational spectra of seven free rotor models. This provided a systematic way of assessing the assignment to a rotational band structure (cf. Table I). The gas-phase rotational constants of porphine in the electronic ground state have been determined from DFT calculations. These were found to be essentially in agreement with previous calculations which, in addition, revealed an in-plane orientation of the transition dipole moment at the electronic origin (like

---

**FIG. 5.** Left-hand part: High-resolution optical spectra at the electronic origin ($S_0-S_1$) of porphine in superfluid helium droplets taken at a droplet source stagnation pressure of 30 bars and at different values of the droplet source temperature and the heating power at the pickup cell, as indicated. Right-hand part: (a) frequency of the leading peak as a function of the droplet source temperature; (b) half-widths of the resonance; (c) peak areas. Note that the color-coding used in the left- and right-hand part of the figure is the same.

---

**FIG. 6.** Fluorescence excitation spectrum showing the electronic origin of phthalocyanine in superfluid helium droplets. The helium droplet source was operated at a stagnation pressure of 20 bars and at a temperature of 10.2 K resulting in an average droplet size of roughly 20 000 He atoms. The leading peak of the zero-phonon line (ZPL) is accompanied by numerous smaller resonances, the most intense of which are marked by the red comb. For the sake of clarity, the spectrum is plotted for two intensity scalings. The phonon wing (PW) sets in beyond 2.5 cm$^{-1}$ on the abscissa.
phthalocyanine\(^{34}\). The gas-phase rotational constants of porphine are about three times larger than those of phthalocyanine. All the calculated stick-spectra (as a function of temperature) were convoluted with a Gaussian of appropriate half-width on the order of or somewhat less than the Gaussian width used for the line shape simulations in Fig. 4. The value of the half-width of the convoluting Gaussian was chosen so as to obtain a “smooth” rotational envelope for all models without masking the double or triple peaked rotational band structure. The calculated rotational band shapes together with the corresponding stick-spectra are provided as the supplementary material to this paper. The spectral widths of the resulting rotational band envelopes as determined at approximately half the corresponding peak intensities were subsequently extracted and plotted in Fig. 7 as a function of the rotational temperature. These calculated widths [full width at half maximum (FWHM)] represent the width that the rotational fine structure may impart to the experimental spectrum for the corresponding rotor type. We hence conclude that, at 0.38 K, all models yielding half widths above the zone demarcated by the grey dashed lines, namely, the two gas-phase models, are inconsistent with the experiment.

The first two models whose rotational constants are listed in Table I pertain to the gas phase conditions, either without (GaPh1) or with a minor change (GaPh2) in the moments of inertia upon electronic excitation and are not expected to yield a similarity with the experimental spectra measured in helium droplets. On the other hand, according to an empirical understanding of microsolvation in helium droplets, the two models RoTh1 and RoTh2 come closest to capturing the expected rotor properties, namely, a quasi-oblate symmetric top whose moments of inertia (as a rule of thumb, cf. Ref. 35) are three times larger than those in the gas phase. The rotational band system of a porphine solvation complex with such ground-state moments of inertia is calculated either without a change, upon excitation, of the moments of inertia about the secondary axes and an increase of the moment of inertia about the principal rotation axis of the symmetric top (RoTh1) or with decreased moments of inertia about the secondary axes and an increase about the principal rotation axis (RoTh2). However, both models lead to a double peaked rotational band system which was not observed in the experiment. The models labeled ModelA, ModelB, and ModelC all represent the same quasi-oblate symmetric top as ground state that, upon electronic excitation, becomes a spherical rotor with the same moment of inertia that the ground-state rotor had either about the secondary axis (ModelA) or the principal rotation axis (ModelC). ModelB maintains the quasi-oblate symmetric top moments of inertia upon excitation, but with a decreased moment of inertia about the rotation axis. Neither of the three models provides a realistic scenario for the excitation of the porphine solvation complex. However, the models represent reference points within the parameter space of the rotor. ModelA and ModelB give rise to spectral shapes that are inverted with respect to the experimental spectra (after neglecting the multiple peaked band structure). Only ModelC is capable of reproducing the typical asymmetry found in the spectra shown in the left part of Fig. 5. Although this model yields a half-width that comes close, at 0.38 K, to the experimental one, the corresponding rotational band extends over a much larger spectral range than found in the experiment.

In light of the convincing account of microsolvation of phthalocyanine in helium droplets rooted in previous investigations of the line shape of the corresponding electronic origin,\(^{20–22}\) recent additional results on phthalocyanine\(^{25}\) came as a surprise. While these results are in line with the effect of the droplet size distribution on the inhomogeneous line broadening, they also revealed that a substructure resolved under quasi-bulk conditions (i.e., in large droplets) cannot be assigned to a rotational fine structure.\(^{25}\) Instead of a rotational band system comprised of two peaks assigned to a P and an R branch congested by a Q branch, the observed fine structure consists of three peaks, each of which exhibits its own individual intensity profile upon variation of the droplet size distribution within the quasi-bulk regime. If a rotational band were present, it should fit into each of the three peaks. However, as shown already in Ref. 24 and confirmed by our recent study,\(^{25}\) the spectral width of the rotational band system expected for solvated phthalocyanine in helium droplets should be roughly twice as broad as each of the three individual peaks. Since an explanation of the counterintuitive experimental spectra is not at hand, seeking additional experimental data

<table>
<thead>
<tr>
<th>System</th>
<th>(A'')</th>
<th>(B'')</th>
<th>(C'')</th>
<th>(A')</th>
<th>(B')</th>
<th>(C')</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaPh1</td>
<td>8.81</td>
<td>8.81</td>
<td>4.41</td>
<td>8.81</td>
<td>8.81</td>
<td>4.41</td>
</tr>
<tr>
<td>GaPh2</td>
<td>8.81</td>
<td>8.81</td>
<td>4.41</td>
<td>8.46</td>
<td>8.46</td>
<td>4.59</td>
</tr>
<tr>
<td>RoTh1</td>
<td>2.94</td>
<td>2.94</td>
<td>1.47</td>
<td>2.94</td>
<td>2.94</td>
<td>1.43</td>
</tr>
<tr>
<td>RoTh2</td>
<td>2.94</td>
<td>2.94</td>
<td>1.47</td>
<td>2.82</td>
<td>2.82</td>
<td>1.53</td>
</tr>
<tr>
<td>ModelA</td>
<td>2.94</td>
<td>2.94</td>
<td>1.47</td>
<td>2.94</td>
<td>2.94</td>
<td>2.94</td>
</tr>
<tr>
<td>ModelB</td>
<td>2.94</td>
<td>2.94</td>
<td>1.47</td>
<td>2.94</td>
<td>2.94</td>
<td>2.21</td>
</tr>
<tr>
<td>ModelC</td>
<td>2.94</td>
<td>2.94</td>
<td>1.47</td>
<td>1.47</td>
<td>1.47</td>
<td>1.47</td>
</tr>
</tbody>
</table>

**FIG. 7.** Spectral half widths (FWHM) of simulated rotational fine-structure convoluted by a Gaussian line shape for seven rotor models as a function of temperature. The dashed horizontal lines show the lower and upper limits of the observed experimental half widths; see panel (c) of Fig. 2. The dotted vertical line marks the droplet temperature of 0.38 K.
on similar dopants such as porphine is a way to elucidate the problem. Below we discuss separately, the line shapes pertaining to droplet size distributions generated under subcritical and supercritical helium expansion conditions. In the former case, the inhomogeneous line broadening is due to a log-normal droplet size distribution, whereas in the latter case the effect of the droplet size is expected to be absent.

(a) Line shape at the electronic origin of porphine recorded in helium droplets generated under subcritical expansion conditions: The electronic spectra of porphine, taken at limited resolution, both in He droplets and in the gas phase\textsuperscript{13} suggested that the solvent shift was to the red, with a single-peaked ZPL. However, under appropriate spectral resolution, the experiment revealed that porphine in He droplets in fact exhibits a blue shift, with a multiply peaked ZPL. As illustrated in Fig. 3, the model of inhomogeneous line broadening introduced in Refs. 21 and 22 is capable of simulating both the phthalocyanine and porphine spectra for small droplets, despite the inverted helium solvent shift, cf. Fig. 2. With increasing nozzle temperature, the droplet size distribution shifts to smaller droplets as does the size distribution for singly doped droplets. With decreasing droplet size, the dispersion of the resonance frequency increases, while the solvent shift decreases. This is reflected in the experimental spectra by an increasing inhomogeneous line broadening and a shift of the signal towards the gas-phase frequency, which in the case of porphine is to the red. On the other hand, with increased droplet size, the signal is expected to converge to a linewidth and peak position pertaining to a bulk helium environment. The bulk regime is approached under supercritical expansion conditions that are accompanied by a marked discontinuity in the increase of the average droplet size, as summarized in Ref. 1. Even under supercritical expansion conditions, see Fig. 5, the signal continues to shift to the blue. In the case of phthalocyanine, the transition from subcritical to supercritical expansion conditions is accompanied by a reversal of the solvent shift from the red to the blue. This can be interpreted as a consequence of a steeper dependence of the solvent shift on the number of He atoms for the electronically excited state ($S_1$) than for the ground state ($S_0$), with the bulk limit reached at a smaller number of He atoms for $S_1$ than for $S_0$. In contrast, for porphine, no reversal of the solvent shift is observed, cf. Figs. 2–5, which we interpret as a consequence of a greater gradient of the dependence of the solvent shift for $S_0$ than for $S_1$ combined with a likely earlier onset of the bulk limit for $S_1$ than for $S_0$ as a function of the number of He atoms that makeup the droplet. These observations are in line with the “regular” behavior of a classic system consisting of a molecule embedded in a polarizable environment of finite size.

Apart from the above “regular” behavior, we also found a single sharp peak superimposed on the inhomogeneous line shape, cf. Fig. 4. Within the signal-to-noise ratio, a Lorentzian line, shown in red, centered at 16 312.336(1) cm\textsuperscript{-1}, with a half-width of only 0.025(1) cm\textsuperscript{-1}, could be fitted to this feature. Neither the frequency position of the feature nor its linewidth undergoes significant changes upon further reduction of the droplet size distribution. An assignment to intramolecular excitation can be safely excluded at frequencies below a wavenumber. Moreover, under the given droplet conditions, an intramolecular resonance should suffer inhomogeneous line broadening and peak shift upon variation of the droplet size distribution, which would also be the case for complexes of porphine with impurities. Since impurities as such can also be excluded (the corresponding signal should not disappear for droplets larger than 10\textsuperscript{4} helium atoms), the signal is most likely helium-induced. If so, the fixed frequency position of the feature as a function of the droplet size is indicative of a resonance linked to a particular droplet size. The feature’s linewidth, well matched by the Lorentzian fit, points to a transition to a well-defined quantum state with a lifetime on the order of 0.1 ns. Since the spectrum of internal excitations of bulk superfluid helium does not exhibit sharp isolated peaks at such low frequencies,\textsuperscript{37,38} the resonance may originate from specific modes of a finite-size droplet.

At the given experimental conditions, the sharp feature appears above a nozzle temperature of about 15 K, which corresponds to a threshold average droplet size of about 10\textsuperscript{4} helium atoms. Since the density of states of vibrational modes in the volume or at the surface of a droplet decreases with decreasing droplet size, the droplet size threshold as an upper limit for the onset of an isolated resonance appears plausible. The available experimental data make it possible to infer an upper bound on the energy of the droplet mode. The resonance frequency of 16 312.336(1) cm\textsuperscript{-1} represents the frequency of the droplet mode excitation added to the electronic excitation frequency of the dopant molecule. The lower limit of the resonance frequency of the corresponding ZPL is to the red of the asymmetric line shape in the spectrum in which the sharp feature first appears. According to the spectrum recorded for a nozzle temperature of 15.96 K, see panel (a) of Fig. 2, the intensity reaches a significant value at about 16 312 cm\textsuperscript{-1}, which is about 0.336 cm\textsuperscript{-1} below the peak frequency of the sharp signal. This shift equals the upper limit of the specific droplet mode frequency.

We note that the sharp resonance is definitely absent in the two smaller peaks located to the blue from the leading peak of the ZPL, which otherwise exhibit the same solvent shift dependence on the droplet size distribution as the leading peak, cf. panel (a) of Fig. 2. Hence, whatever be the origin of these additional peaks, they do not couple to the particular droplet mode like the leading one does.

The above assignment of the sharp feature in Fig. 4 is not unequivocal. The small linewidth and fixed frequency position of a droplet mode requires a selectivity for one particular mode of one particular droplet size, a rather unlikely precondition. Since similar spectral features have not been observed for phthalocyanine, their appearance must also depend on the dopant species. The selectivity for both a droplet excitation and an electronic excitation of a particular dopant species ought to be encoded in a corresponding coupling constant. If so, the electronic excitation of porphine and phthalocyanine must involve a fundamental difference, which may also account for the opposite helium solvent shifts observed for these dopants.

(b) Line shape at the electronic origin of porphine recorded in helium droplets generated under supercritical expansion conditions (yielding quasi-bulk conditions within...
the droplets): Under quasi-bulk conditions, the droplet size distribution does not account for inhomogeneous line broadening. Consequently, for superfluid helium droplets as host systems, the rotational band structure should become resolvable. In this respect, the results of our recent study on phthalocyanine went contrary to expectations. Despite limitations dictated by the signal-to-noise ratio (and a spectral width of the simulated rotational spectra that comes close to that of the experimental spectra, cf. Fig. 7), a collapse of the inhomogeneous line shape into a fine structure can be essentially excluded for porphine. In the case of porphine, the spectral width of the leading peak shown in Fig. 5 does not vary dramatically even at the transition from the subcritical to the supercritical source conditions. Most notably, the blue edge of the peak exhibits an increasing gradient with increasing average droplet size. However, a signature of what could be interpreted as rotational fine structure or a substructure similar to the triple-peak feature resolved for phthalocyanine (cf. Ref. 25) is absent. The model calculations covering a range of possible rotor models, listed in Table I, do not fit the experimental line shapes. Nevertheless, it was not impossible to find particular molecular rotors that fit the experiment (cf. supplementary material). However, neither these rotor types nor the fitted temperature fell within the acceptable range expected for porphine in large superfluid helium droplets.

### IV. Conclusions

The key results of the present study on porphine in He droplets are the extra peak (sharp feature) found for average droplet sizes below 10^4 helium atoms and the absence of the rotational band structure expected for a freely rotating porphine solvation complex under quasi bulk conditions.

Similar line shape studies at the electronic origin of two polycyclic aromatic hydrocarbons, tetracene, pentacene as dopant species reveal a kindred behaviour. Within the doubly peaked ZPL of tetracene, the leading peak is free of any substructure, like in the case of phthalocyanine under subcritical source conditions. Under such conditions, the second peak of tetracene and the singly peaked ZPL of pentacene are superimposed by spectrally sharp peaks which do not shift under variation of the droplets size distribution. Only their intensity varies as a function of the droplets size distribution—a behaviour similar to that of the sharp superimposed peak found in the spectrum of porphine (cf. Fig. 3). Under supercritical source conditions, neither tetracene nor pentacene exhibit a spectral feature that is related to a rotational band system.

A dopant that stands out is glyoxal, whose rotational band system could be fully resolved at an average droplet size of only 2800 helium atoms. Upon increasing the droplet size distribution to an average value of 20 000, the linewidth in the spectrum of glyoxal was found to increase to about 0.2 cm^-1, cf. Refs. 40–42, about twice that of phthalocyanine under similar conditions, cf. Fig. 6.

In view of the “diverging” experimental results provided by line shape studies of just a few systems, we concentrate in our future work on exploring more systems with additional techniques. In particular, we study polar complexes of phthalocyanine and porphine with small molecules via Stark spectroscopy—both in He droplets and in the gas phase.

### Supplementary Material

See supplementary material for the half-widths of the rotational fine structure for the seven models listed in Table I which were inferred from the convolution of the stick spectra with an appropriate line shape function as explained in the main text and a figure showing seven panels each with the stick spectrum and the convolution for one of the models as indicated in each panel. These have all been simulated for the droplet temperature of 0.38 K. Two additional figures show an almost perfect fit of the experiment (black line) by an asymmetric rotor with parameters and rotational constants as indicated in each panel. The set of rotational constants is far off the expected numbers for the dopant solvation complex, and in one case, the temperature does not match the well known droplet temperature.

### Acknowledgments

Financial support by the Schwerpunktprogramm 1807 “Control of London dispersion interactions in molecular chemistry” of the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

---

27 A. Slenczka, Molecules 22, 1244 (2017).
32 B. Schilling, MPI für Strömungsforschung, Göttingen, Germany, Bericht No. 7, 1993.
42 N. Pörtner, MPI für Strömungsforschung, Göttingen, Germany, Bericht No. 1, 2001.