

Small He clusters with aromatic molecules

U. Even,^{a)} I. Al-Hroub, and Joshua Jortner

School of Chemistry, Sackler Faculty of Exact Sciences, Tel Aviv University, 69978 Tel Aviv, Israel

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Excitation spectra of ultracold ($T=0.4$ K) large aromatic molecules (naphthalene, anthracene, and tetracene) solvated by a few (1–16) He atoms are reported. Measured spectral shifts and vibronic excitations for a series of mass selected He clusters are presented. Clusters on aromatic molecules with an increasing number of rings show unexpected, and size-dependent, spectral effects. We suggest that the novel spectroscopic features are due to the anisotropic delocalization of the He atoms on the surface of the aromatic molecule. © 2001 American Institute of Physics.

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I. INTRODUCTION

The use of large helium He clusters (nanodroplets, containing thousands of He atoms) as a solvent for atoms or molecules is of current interest. Several review articles^{1–3} analyze the spectroscopy of molecules imbedded in large He clusters containing 3000–10 000 He atoms. Evidence for superfluid behavior of the He solvent was found for several molecules^{4–6} embedded in the nanodroplets. The minimum size for the appearance of macroscopic properties (like superfluidity) is still an open question, though upper bounds were calculated^{7–9} or estimated from experiments.⁶ Analysis of the rotational constants of a molecule imbedded in He nanodroplets leads to the conclusion that only the first He solvation layer rotates with the molecule.⁹ Not much is known about the properties of small He clusters containing a chromophore molecule ($M\cdot He_n$; $n>2$). Blueshifts of the electronic origin and some vibrations associated with the He atom were reported for van der Waals complexes containing one or two He atoms.^{2,9–17} It has been suggested¹⁵ that due to the small mass of the He atom (and its weak interaction with the molecule), large amplitude motion, leading to complete delocalization, can occur in these systems at higher vibrations. This microscopic delocalization (in small He clusters) can be the precursor to the macroscopic superfluidity (and associated complete surface wetting) in the larger He clusters. In this paper we report on the spectroscopic evidence of the spectral shifts and vibronic structure supporting these ideas. These measurements can serve as a base from which larger cluster properties can be evaluated. Several aromatic molecules (naphthalene, anthracene, and tetracene), which are similar in structure (containing two, three, or four aromatic rings in a linear chain), were used. The molecules were cooled to less than 1 K in a high-pressure supersonic jet. The temperature was determined from the rotational envelope of the 0–0 electronic transitions in the bare chromophore and from the results shown in the following we deduce that the rotational temperature is ~ 0.4 K.¹⁸ Mass selective (two-

photon two-color) threshold ionization was used to obtain the excitation spectra of the $M\cdot He_n$ van der Waals complexes formed in the beam ($n=1-16$).

II. EXPERIMENT

The experimental system was described previously¹⁸ and will be briefly explained here. The molecules are heated (with He carrier gas) in a high temperature (300–550 K), high pressure (up to 120 bars), fast acting (10 μ s) pulsed valve with a 0.2 mm conical nozzle. The intense supersonic expansion cools the molecules down to ~ 0.4 K, which is measured by monitoring the rotational contour of their 0–0 transition. Helium condensed on the cold molecules to form van der Waals clusters (as much as 15% of the bare molecules were dressed with He atoms). The excitation spectra were obtained by two-color, two-photon spectroscopy. One photon was scanned to resonantly excite the S1 transitions. The second photon was held at (5 cm^{-1} above) the ionization threshold of each cluster. YAG pumped dye lasers (“continuum”) were used with a spectral resolution of 0.2 cm^{-1} and a pulse energy of 0.2 mJ to avoid power broadening. The softly ionized clusters were mass analyzed by a high resolution time-of-flight mass spectrometer.¹⁹ Extraction of the ions was delayed by 0.5 μ s (after the laser excitation) to avoid external field effects. The fast acting valve allowed us to use small pumps (200 l/s turbomolecular pumps) to maintain a low background pressure (10^{-7} Torr) in the two-chamber, skimmed, vacuum system. This method of soft ionization allowed us to probe the excitation of mass-resolved clusters with up to 20 He atoms with no evidence of extensive fragmentation.

III. RESULTS

Excitation spectra for naphthalene appear in Fig. 1 and the resulting 0–0 shifts are plotted as a function of the number of He atoms in Fig. 2. Corresponding results for Anthracene are shown in Figs. 3–5 and those for tetracene in Figs. 6 and 7. We draw attention to the following aspects.

^{a)} Author to whom all correspondence should be addressed. Electronic mail: even@chemsg1.tau.ac.il

Spectra of He on Naphthalene near the 0-0 Transition

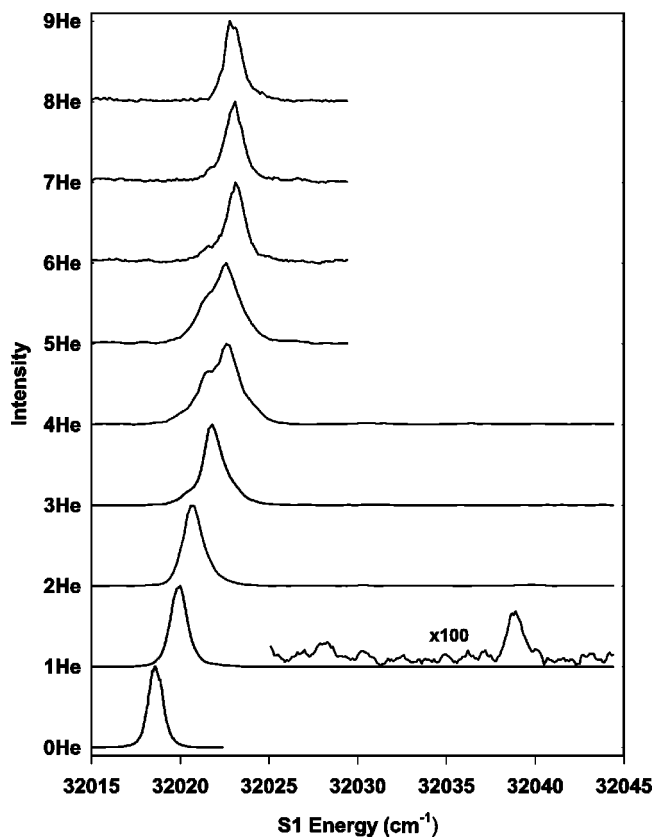


FIG. 1. Mass selected excitation spectra of He on naphthalene. Only a very weak vibration is detected at 20 cm^{-1} .

A. Naphthalene

The spectra show a smoothly increasing blueshift of the electronic origin. The blueshift approaches saturation at about 5 cm^{-1} for ~ 8 He atoms. A very weak vibration is found at $\sim 20\text{ cm}^{-1}$ above the origin for the 1 He complex. There may be two isomers (deduced from the doubled peak) for 4 and 5 He clusters.

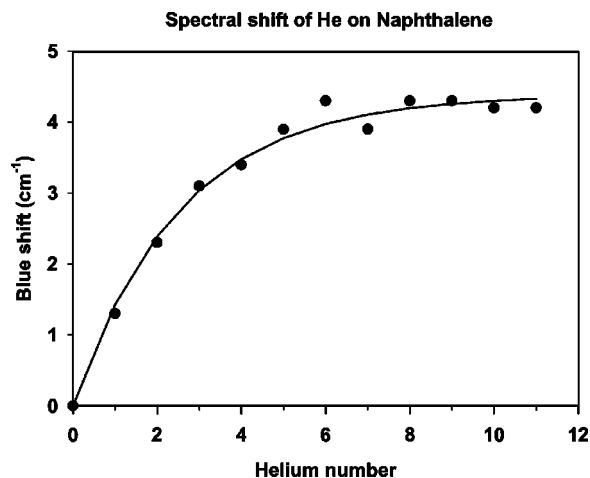


FIG. 2. Spectral shift of the origin of the 0-0 transition in naphthalene as a function of the number of attached He atoms. The smooth line is a fit to a rising exponential function in the number of atoms.

S1 Spectra of He clusters on Anthracene

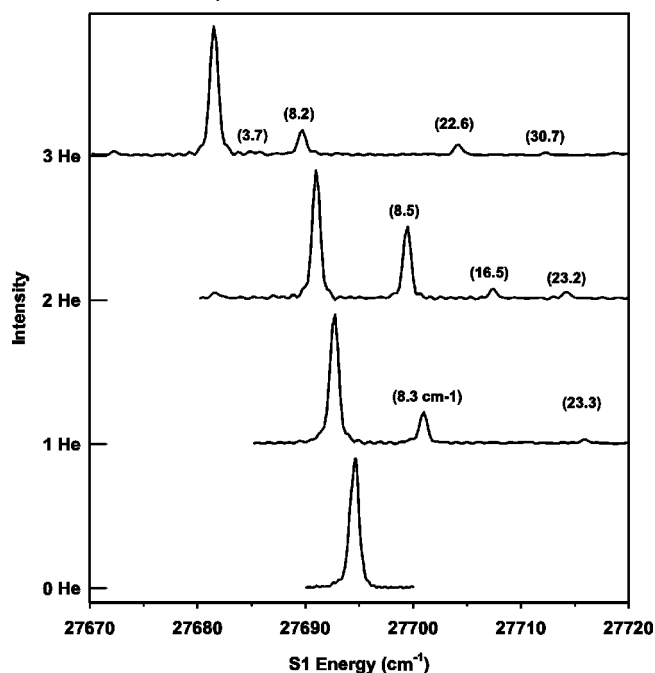


FIG. 3. Mass selected spectra of 0-3 He clusters on anthracene. Notice the progressive increase in the number of observed vibrations.

B. Anthracene

The spectral shifts are to the red, approaching saturation of the shift, at $\sim -38\text{ cm}^{-1}$, for 12 He atoms. There is a marked jump of the redshift for clusters of 3 and 4 He atoms.

S1 spectra of He clusters on Anthracene

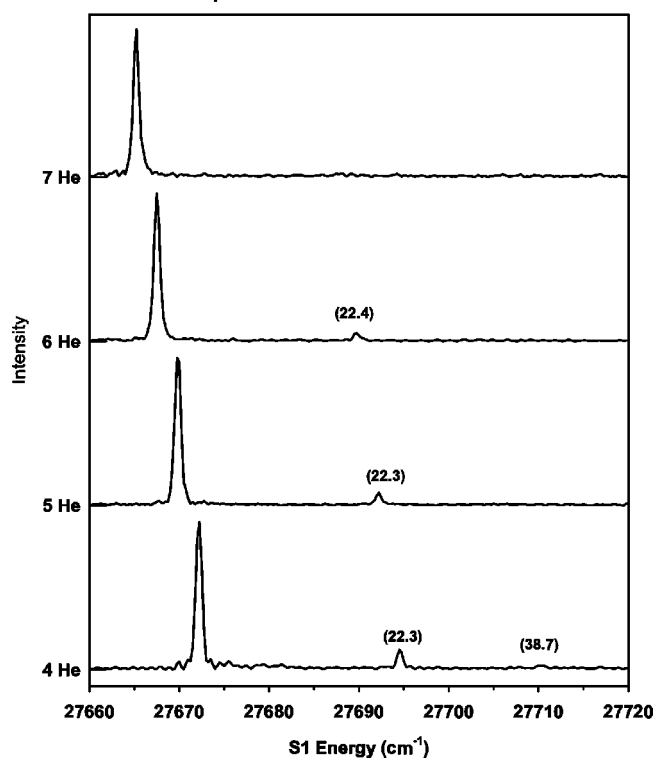


FIG. 4. Mass selected spectra of 4-7 He clusters on anthracene. Notice the disappearance of the vibronic transitions.

Spectral shifts of He on Anthracene

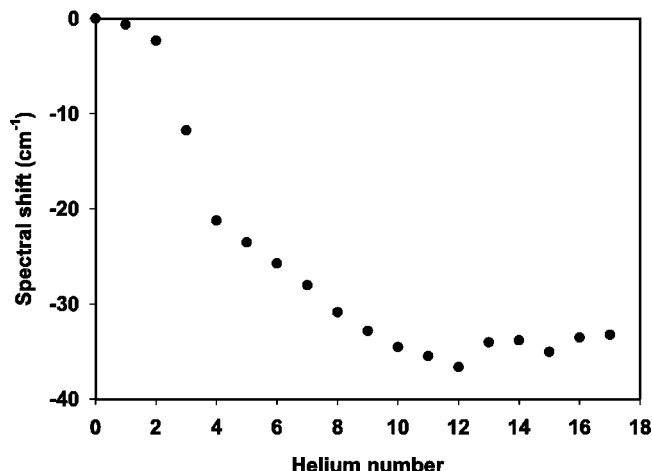


FIG. 5. Spectral shift of the origin of the 0–0 transition in anthracene. Compare to Fig. 2. Here the shift is larger and in the opposite direction. Note the significantly larger increments in the shift upon coverage by the third and fourth He atom.

Vibration lines appear with growing complexity for clusters with 1 He (8.3, 23.2, 37.3 cm^{-1}) and 2 He (8.5, 16.5, 23.2, 31.5, 37.2, 47 cm^{-1}) atoms, but gradually disappear for larger clusters. The 3 He clusters show weak vibronic bands at 3.7 cm^{-1} , and stronger bands at 8.2, 22.6, and 30.7 cm^{-1} . The 4 He clusters show very weak low energy bands at 2.0, 3.6 and 7.0 cm^{-1} and stronger bands at 22.3 and 38.7 cm^{-1} .

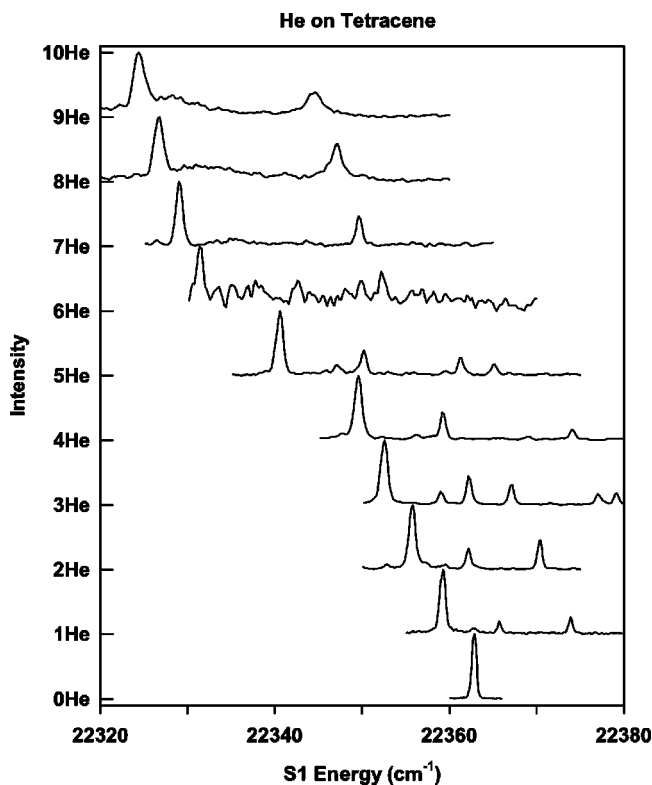


FIG. 6. Mass selected spectra of He clusters on tetracene. Note the simplification of the vibronic structure for larger clusters.

Spectral shifts of He on Tetracene

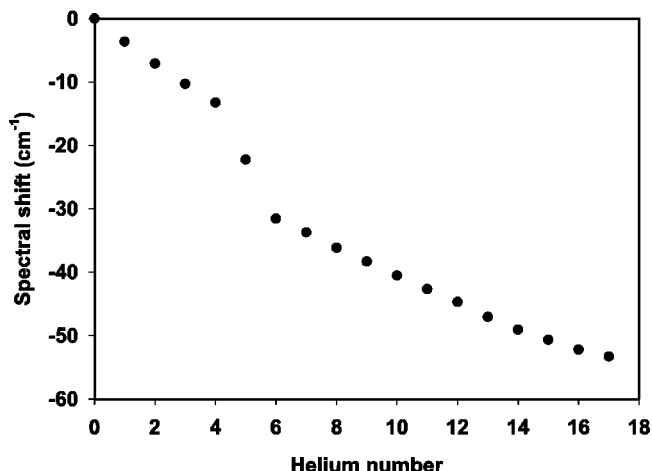


FIG. 7. The spectral shifts of He clusters on tetracene. Note the jump in spectral shift at the 5 and 6 He clusters.

The vibrations at 8 and 16 cm^{-1} disappeared. Clusters of anthracene with 5 or 6 He atoms exhibit only one strong vibration, at 22.4 cm^{-1} .

C. Tetracene

The spectral shifts are to the red. Saturation of the shift, at $\sim -60 \text{ cm}^{-1}$, is reached for ~ 20 He atoms. There is a marked jump of the redshift for 5 and 6 He atom clusters. Vibration lines appear with growing complexity for clusters with 1 and 2 He atoms (6.4, 14.6 cm^{-1}), reaching its most complex structure for 4 and 5 atoms (6.5, 9.6, 15.5, 20.7, 24.6, 30.1 cm^{-1}), but diminishing in complexity for larger clusters. By the time we reach 7 He atoms, only the vibration at 20 cm^{-1} remains.

IV. DISCUSSION

Spectral shifts of the chromophore electronic transition upon solvation (by rare gas atoms) are an important diagnostic tool for the nature of the interaction.^{13,20,21} In the series of aromatic-He clusters a small blue spectral shift was observed in benzene·He_n ($n=1,2$)^{22,23} and in naphthalene·He_n ($n=1-12$) reported herein. The limiting shift for large He droplets was reported to be +15 cm^{-1} for naphthalene.¹ Significantly larger spectral shifts to the red were measured for anthracene and tetracene. The limiting shift for large He droplets was reported to be -103 cm^{-1} for tetracene.¹ Three features of the spectral shift of the lowest spin-allowed electronic excitation of aromatic·He_n clusters will be addressed.

- (i) The qualitative difference between the blue spectral shifts of benzene·He_n ($n=1,2$)^{10,23} and of naphthalene·He_n ($n=1-12$), and the red spectral shifts of anthracene·He_n ($n=1-16$) and of tetracene·He_n ($n=1-17$).
- (ii) The size dependence of the spectral shifts $\delta\nu$ vs n for a family of M·He_n clusters.

- (iii) The limiting spectral shifts of M in large He droplets¹ and its relation to $\delta\nu$ for the smaller clusters studied herein.

Regarding point (i), we note that the spectral shifts of $M \cdot He_n$ clusters originate from a balance between the contributions of short-range repulsive interactions and dispersive interactions.²⁴ While for clusters of aromatic molecules with heavy rare gases, i.e., Ar, Kr, and Xe, the dispersive contribution to the spectral shift dominates,^{25,26} for $M \cdot He_n$ clusters both dispersive and repulsive contributions have to be incorporated in view of the relatively low dispersive term, which is proportional to the polarizability of the rare-gas atom.²⁵ The dispersive contributions are determined by the nature of the electronic excitation of the aromatic molecule.^{25,27} For the lowest spin-allowed, weak, ${}^1L_b(\alpha)$ transition of naphthalene, the dispersive contribution to the spectral shift is low, due to cancellation effects between the contributions of the lowest electronic.²⁷ Accordingly, we expect that for the ${}^1L_b(\alpha)$ transition of naphthalene, as well as for the weak vibronically induced ${}^1A_g - {}^1B_{2u}$ transition of benzene in He clusters, the dispersive contribution to the spectral shift is small, with $\delta\nu$ being dominated by the repulsive contributions, which result in an overall blue spectral shift for benzene $\cdot He_n$ and naphthalene $\cdot He_n$ clusters. In contrast, for the intense ${}^1L_a(p)$ transition of anthracene and tetracene in He clusters, the dispersive contribution dominates over the repulsive term and the overall spectral shifts are to the red. These considerations are borne out by calculations of spectral shifts of anthracene $\cdot He_n$ ($n=1-4$) clusters.²⁴ The size dependence of the spectral shifts $\delta\nu$ ($n=1-16$) [point (ii)] qualitatively differs between the blue $\delta\nu$ values for naphthalene $\cdot He_n$ (dominated by the repulsive contributions), which exhibit a monotonous, smooth increase with increasing n (Fig. 2), and the red $\delta\nu_n$ values for anthracene $\cdot He_n$ (Fig. 5) and for tetracene $\cdot He_n$ (Fig. 7) (involving a balance between dispersive and repulsive contributions), which reveal an abrupt jump in $\delta\nu_n$ vs n for anthracene $\cdot He_3$ and for tetracene $\cdot He_5$. The irregular pattern of the size-dependent red spectral shifts for anthracene $\cdot He_n$ with low values for $n=1$ (structure (1/0)) and for $n=2$ [structure (1/1)] and a jump for $n=3$ [structure (2/1)], implies a large difference in $\delta\nu_n$ for the two-sided (1/1) and the one-sided (2/0) He configurations. This pattern for the He clusters is in a marked contrast with the size dependence of $\delta\nu_n$ for aromatic molecules with heavy rare gases,^{25,27} where isomer specificity is minor. The large difference between the spectral shifts of the (1/1) and the (2/0) configurations of anthracene $\cdot He_2$ is due to the large increase of the delocalization of the He atoms along the long molecular axis in the (2/0) isomer, which is induced by He–He repulsion.²⁸ Anisotropic spatial delocalization, in conjunction with confinement within the nuclear framework of the aromatic molecule, drives the two He atoms toward the exterior regions of the anthracene molecule, where the dispersive contribution to the spectral shift is large. Accordingly, the red spectral shift for the (2/0) isomer is considerably larger than for the (1/1) isomer, in accord with detailed calculations of the spectral shifts for anthracene $\cdot He_n$ ($n=1,2$).²⁴ Similarly, a dramatic enhancement of the dispersive

contribution to the spectral shift, due to a large-amplitude long-axis motion of three He atoms induced by He–He repulsion, is manifested in the jump of $\delta\nu_n$ for tetracene $\cdot He_5$ [configuration (3/2)]. The addition of a third He atom to the microsurface of the four-ring tetracene pushes the He atoms density toward outer regions where the dispersive contribution is large. The irregular pattern of the red spectral shifts of $M \cdot He_n$ clusters manifests the unique features of He–He repulsion, driving anisotropic delocalization and confinement in nuclear quantum systems. Finally, we turn to the relation between the spectral shifts of finite $M \cdot He_n$ clusters ($n=20$) and those of M in large He droplets¹ [point (iii)]. It is interesting to note that only half of the asymptotic shift (reported for large He droplets) is obtained by adding about 20 He atoms. This occurs in the range of sizes where both short-range, as well as long-range interactions play a role. With increasing the cluster size around M, beyond $n=20$ or so, the exterior He regions contribute only to the dispersive spectral shift. Thus for tetracene $\cdot He_n$ clusters this dispersive contribution of exterior layers decreases the spectral shift from $\delta\nu_{17} = -55 \text{ cm}^{-1}$ to $\delta\nu_D = -103 \text{ cm}^{-1}$ for the large droplet.¹ These dispersive contributions can be quantified in terms of a cluster size equation,²⁹ with $\delta\nu_D = \delta\nu_I - A(r_1^{-3} - R_D^{-3})$, where $\delta\nu_I$ is the (dispersive+repulsive) contribution from the first layer of He atoms with a radius R_I , $A = 4\pi\rho\beta/3$, where r is the number density, β is a single atom dispersive parameter, and R_D is the droplet radius. Experimental scrutiny of this cluster size equation will be of interest.

The vibrational level structure exhibited in the spectra of moderately small anthracene $\cdot He_n$ ($n=1-4$) and tetracene $\cdot He_n$ ($n=1-6$) clusters, corresponds to nuclear excitations in the S_1 electronically excited state. Bach *et al.*¹⁵ have reported delocalization and side crossing of a single He atom in high vibrational excitations on the microsurface of dimethylnaphthalene. The large-amplitude local modes of the (1/0) and (1/1) configurations for anthracene–He clusters will be analyzed in a subsequent work.²⁴ A key experimental observation is that at the same He coverage, when large changes in the spectral shift occur, there is also an onset of a simplification in the vibrational level structure of the clusters. The vibronic structure simplification can occur if the clusters become vibrationally hot as more He atoms are added (releasing their condensation energy of $\sim 100 \text{ cm}^{-1}$ per atom). We cannot rule out this explanation, but argue against it. The rotational contour of the electronic origin of smaller He complexes $M \cdot He_n$ ($n=1-6$) is narrow (similar to the bare molecule width), indicating that our high-pressure jet has enough cooling capacity for these clusters. A possible interpretation of the “vibrational collapse” may rest on the change in the character of the nuclear excitations from local modes to collective modes. Such an interpretation will imply that the collective modes in $M \cdot He_n$ clusters are the precursors of collective modes in large He (IV) droplets.³⁰ This suggests that more quantum mechanical calculations of collective excitations in small doped He clusters would be useful.

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