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Spectroscopy of barium attached to superfluid helium clusters

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Abstract. To complement the data on absorption spectra of alkaline earth atoms attached to superfluid helium clusters we are reporting on barium atoms attached to $^4\mathrm{He}_N$. The absorption spectrum of the lowest singlet transition is blue-shifted and strongly broadened compared to the corresponding unperturbed Ba ($6s6p\ ^1\mathrm{P}_1^\mathrm{o} \longleftarrow 6s^2\ ^1\mathrm{S}_0$) transition in accord with the observations on Sr and Ca added to He_N [F. Stienkemeier, F. Meier, and H.O. Lutz: J. Chem. Phys. **107**(24), 10 816 (1997)]. Moreover, we compare the asymptotic values of shift and width of the excitation spectrum with increasing helium cluster size $\mathrm{He}_{\bar{N}}$ ($\bar{N} \approx 1000$ up to $\bar{N} \approx 10\,000$) to those found for barium atoms in bulk liquid helium.

PACS. 36.40.Mr Spectroscopy and geometrical structure of clusters

1 Introduction

Large helium clusters doped with atoms or molecules have recently become of great interest [1, 2]. These clusters are superfluid, having an internal temperature of 370 mK [3, 4]. Spectra of attached metal atoms as e.g. Ag [5], alkali (Li, Na, K) [6] and alkaline earth atoms (Ca, Sr) [7] display lineshifts and broadenings for absorption and emission due to effects of bubble formation in the superfluid. Up to now the binding of alkaline earth metals to the cluster is not fully understood and the question of solvation inside the cluster or surface location is not answered yet. In this paper, we present new data on barium atoms attached to helium clusters, and compare them to the behavior of barium atoms in bulk liquid helium. Furthermore a detailed description of the experimental setup will be given in this paper.

2 Experimental

A schematic diagram of the experimental setup is shown in Fig. 1. The He clusters are produced in a supersonic expansion from a cold nozzle. Helium (purity 99.9999%, stagnation pressure $P \leq 100$ bar) expands through a hole of $D = 5$ or 10 μm in diameter into a vacuum chamber at typically 10^{-4} mbar pressure. The cluster size can be varied by changing the expansion conditions. The gas load is pumped by an unbaffled diffusion pump (8000 l/s), backed by a roots pump (500 m^3/h) and a rotary pump (65 m^3/h). The nozzle is cooled by a two-stage, closed loop cooler (CTI, model 350 CP) with helium as refrigerant. The first stage of the cold head is used for both precooling the gas supply and to establish complete shielding at a temperature of about 65 K in order to screen the nozzle from thermal radiation. An extra outer water-cooled shield was necessary to reach the desired low nozzle temperature because of the heat which emerges from the unbaffled diffusion pump. The nozzle is connected to the second stage of the cold head by copper braids to decouple the mechanical noise from the cold head and allow adjustment of the cluster beam during operation. Depending on the gas load we reach terminal nozzle temperatures as low as $T \approx 12$ K. For thermal stabilization a temperature controller (Lakeshore, model 330) feeds a thermocoax heater coil around the nozzle. After a skimmer of 0.4 mm in diameter an oven provides the vapor for pick-up of the chromophores. The cylindrical oven with 3 mm entrance and exit orifices is heated via radiation from a cylindrical heater with tantalum coils. Two separate ovens at different temperatures up to 1300 K can be operated at the same time if attachment of two different chromophores is required. The oven vacuum chamber is evacuated to 2×10^{-7} mbar by a baffled diffusion pump (3000 l/s). After a further skimmer of 4 mm in diameter the doped cluster beam reaches the third vacuum chamber (pumped by a turbomolecular pump) where the laser excitation of the chromophores takes place. The barium is excited by the light from a cw dye laser system (Coherent 699) using Rhodamin 110 as laser dye. The laser beam is introduced into the vacuum chamber via a single-mode fiber and coupling optics, and crosses the cluster beam at right angles; perpendicular to the plane defined by both beams a photomultiplier collects the reemitted light with an acceptance of $\approx \pi$ solid angle. This laser-induced fluorescence (LIF) assembly is located about 80 cm and 40 cm away from the He nozzle and the pick-up oven, respectively. Further downstream a surface ionization detector is set up in a separate UHV chamber to detect the alkali and alkaline earth chromophores. Moreover, the ion current in this ion pump driven chamber is a reliable tool to control the

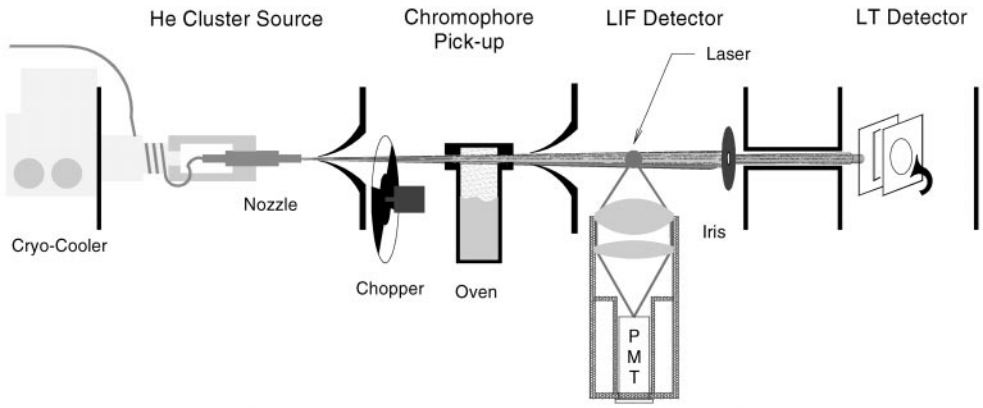

Fig. 1. Schematic diagram of the experimental setup.

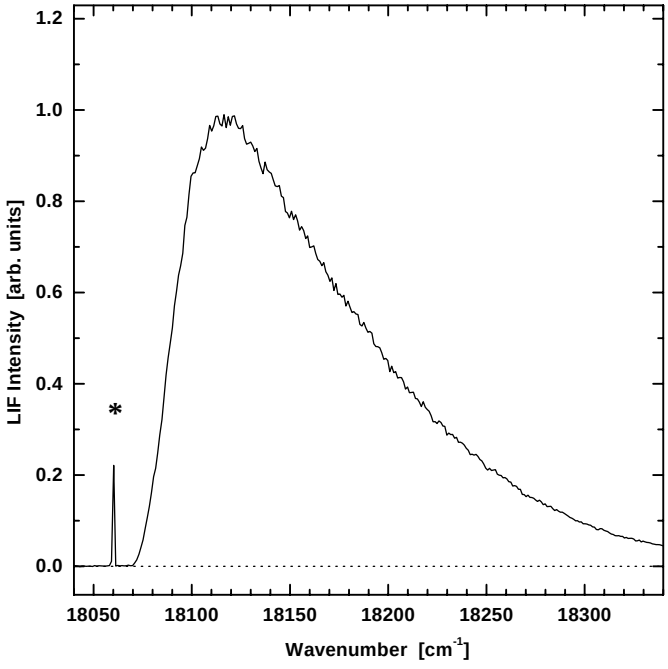

Fig. 2. Absorption spectrum of barium atoms attached to large helium clusters ($\bar{N} \approx 8000$). The spike marked with an asterisk is due to excitation of gas phase Ba atoms and indicates the unshifted $6s6p\ ^1\mathrm{P}_1^\mathrm{o} \longleftarrow 6s^2\ ^1\mathrm{S}_0$ transition.

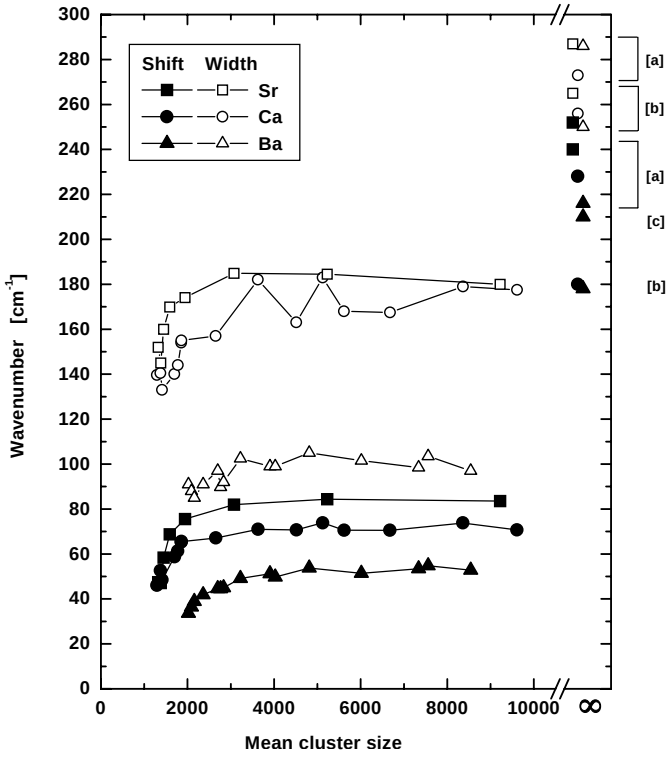

Fig. 3. Shift and width of the absorption spectra relative to the gas phase transition when varying the helium cluster size. Solid symbols correspond to the shift of the absorption peak, open symbols give the values of the width (FWHM); Ca, Sr and Ba are represented by circles, squares and triangles, respectively. The symbols to the right indicate the bulk values (a: [11], b: [13], c: [14]).

flow of helium gas/clusters from the nozzle throughout the apparatus.

3 Results and discussion

Figure 2 shows an absorption spectrum for excitation of the lowest singlet transition of barium detected by LIF for a helium cluster size of $\bar{N} \approx 8000$. The average cluster size $\bar{N}$ has been determined by the scaling relation $\bar{N} \sim P/T^{2.4}$ [8] with $\bar{N} = 7000$ at $P_0 = 60$ bar, $T_0 = 18$ K [9]. The reduction of the cluster size due to evaporation of roughly 100–200 He atoms after the pick-up of Ba was not taken into account. For large He clusters the maximum of the absorption is blue-shifted by about $50\,\mathrm{cm}^{-1}$ with respect to the atomic Ba transition ($6s6p\ ^1\mathrm{P}_1^\mathrm{o} \longleftarrow 6s^2\ ^1\mathrm{S}_0$) and the line is asymmetrically broadened by about $100\,\mathrm{cm}^{-1}$ (FWHM) due to the perturbation by the helium environment. A corresponding broadening and shift of the absorption profile is known from laser-induced fluorescence measurements of Ba atoms embedded in bulk liquid and solid helium by several groups [10, 12–14]. The mechanism for this effect is well understood from bubble formation, although quantitative calculations are not satisfactory to date; the reason lies in the sensitivity to pair interaction

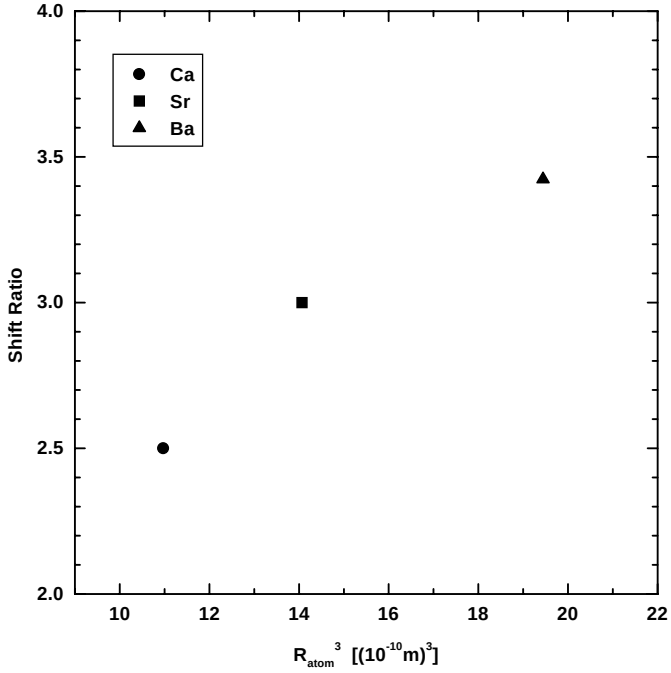

Fig. 4. Ratio of bulk [13] and cluster line shift vs. chromophore atomic size R^3_{atom}; R_{atom} is the radial expectation value of the valence electrons [15]. Ca, Sr and Ba are represented by circles, squares and triangles, respectively.

potentials which are not known with a sufficient accuracy yet. Figure 3 displays the dependence of shift and width on the $\mathrm{He}_{\bar{N}}$ cluster size ($\bar{N} \approx 1000 \ldots 10\,000$) for Ba as well as for Ca and Sr [7], including the results from bulk helium [10, 13, 14]. In our measurements, an increase in cluster size leads to rapid saturation; the line shifts and widths for all probed alkaline earth atoms are basically constant for $\bar{N} \approx 4000$ and larger. Interestingly the asymptotic values for Ba amount to only 30% and 40% of the shift and width found in bulk liquid He [13], respectively. Apparently, the alkaline earth atoms Ca, Sr and Ba attached to He clusters display quite similar behavior concerning the characteristics of the spectra as well as the saturation with cluster size; a quantitative comparison shows that the ratio of line shifts for bulk liquid He as compared to those for He clusters increases with increasing chromophore size R_{atom} (Fig. 4). The similar appearance of the Ba and Ca/Sr spectra suggests also the barium to reside in a dimple on the He cluster's surface rather than being solvated inside. This conclusion follows the argumentation presented earlier for Ca and Sr [7]: A blue shift of the absorption line indicates a solvated bubble state in case of alkaline atoms in bulk liquid He [16]; nevertheless we only find a blue shift of about 50 cm^{-1} for Ba attached to large He clusters which is much less than in the case of bulk liquid He, indicating that a fully developed bubble is not formed. Since there is no further information, e.g. from Ba-He pair interaction potentials or emission spectra, no arguments contradicting a surface location have occurred from the barium data presented here. Providing a surface location of the alkaline earth atoms, the increasing ratio of the line shifts plotted in Fig. 4 might indicate a less pronounced dimple for larger chromophores.

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References

1. J.P. Toennies, A.F. Vilesov: Annu. Rev. Phys. Chem. **49**, 1 (1998)
2. K.K. Lehmann, G. Scoles: Science **279**, 2065 (1998)
3. M. Hartmann, R.E. Miller, J.P. Toennies, A. Vilesov: Phys. Rev. Lett. **75**(8), 1566 (1995)
4. M. Hartmann, F. Mielke, J.P. Toennies, A.F. Vilesov, G. Benedek: Phys. Rev. Lett. **76**(24), 4560 (1996)
5. A. Bartelt, J.D. Close, F. Federmann, N. Quaas, J.P. Toennies: Phys. Rev. Lett. **77**(17), 3525 (1996)
6. F. Stienkemeier, J. Higgins, C. Callegari, S.I. Kanorsky, W.E. Ernst, G. Scoles: Z. Phys. D **38**, 253 (1996)
7. F. Stienkemeier, F. Meier, H.O. Lutz: J. Chem. Phys. **107**(24), 10 816 (1997)
8. H. Haberland: in *Clusters of Atoms and Molecules*, ed. by H. Haberland, Springer Series in Chemical Physics, vol. 52, p. 221
9. J. Harms, J.P. Toennies: unpublished results
10. H. Bauer, M. Beau, B. Friedl, C. Marchand, K. Miltner, H.J. Reyher: Phys. Lett. A **146**(3), 134 (1990)
11. H. Bauer, M. Beau, B. Friedl, C. Marchand, K. Miltner, H.J. Reyher: Phys. Lett. A **146**(3), 134 (1990). To compare this data with our data, we obtained the shift of the absorption maximum from the shift of the leading slope given by Bauer *et al.*, assuming the ratio of both quantities to be the same as for Sr for all quoted elements
12. J.H. M Beijersbergen, Q. Hui, M. Takami: Phys. Lett. A **181**, 393 (1993)
13. Qin Hui: Ph.D. thesis, Saitama University (1997)
14. S.I. Kanorsky, M. Arndt, R. Dziewior, A. Weis, T.W. Hänsch: Phys. Rev. B **50**(9), 6296 (1994)
15. J.P. Desclaux: At. Data Nucl. Data Tables **12**(4), 311 (1973)
16. Y. Takahashi, K. Sano, T. Kinoshita, T. Yabuzaki: Phys. Rev. Lett. **71**, 1035 (1993)