Helium-Droplet-Assisted Preparation of Cold RbSr Molecules

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We present a combined experimental and theoretical study of the RbSr molecule. The experimental approach is based on the formation of RbSr molecules on helium nanodroplets. Utilizing two-photon ionization spectroscopy, an excitation spectrum ranging from 11 600 up to 23 000 cm^{-1} was recorded. High level *ab initio* calculations of potential energy curves and transition dipole moments accompany the experiment and facilitate an assignment of transitions. We show that RbSr molecules desorb from the helium droplets upon excitation, which enables dispersed fluorescence spectroscopy of free RbSr. These spectra elucidate $X^2\Sigma^+$ ground and excited state properties. Emission spectra originating from states corresponding to the $\mathrm{Rb}(5s\,{}^2S) + \mathrm{Sr}(5s5p\,{}^3P)$ asymptote were recorded; spin-orbit coupling was included for the simulation. The results should provide a good basis for achieving the formation of this molecule in cold collisions, thus offering intriguing prospects for ultracold molecular physics.

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The quest for ultralow temperatures in atomic and molecular physics enabled the discovery of many intriguing phenomena related to the quantum nature of ultracold gases [1]. The realization of atomic Bose-Einstein condensates [2,3] and Fermi gases [4] at the end of the past century has triggered a tremendous growth of interest in ultracold physics. Since that time, the family of quantum-degenerated gases has been continuously growing and the realm of ultracold physics has been extended from the atomic into the molecular regime [5,6]. Today, new upcoming experiments envisage the cooling and controlled manipulation of molecules that possess both magnetic and electric dipole moments. Proposed new applications for this type of ultracold molecules range from novel prospects in quantum computation [7,8] to tests of fundamental physical constants with unprecedented sensitivity [9,10]. The group of alkaline earth monohalides is a representative of this class of molecules with significant electric dipole moment in the ground state (see, e.g., SrF [11]) and a relatively simple electronic structure (see, e.g., CaF [12]). However, cooling these radicals to ultracold temperatures has proven to be difficult, but recent experimental efforts towards efficient cooling schemes look promising [13–15]. On the other hand, the mixed alkali-alkaline earth (Ak-Ake) diatomics also possess a $^2\Sigma$ ground state with a single unpaired electron, have similar electronic dipole moments, and can be formed in cold collisions from atoms in a magneto-optical trap [16].

The association of molecules and subsequent coherent population transfer into their ground state [17,18] is based on a profound knowledge of their electronic structure. Experimentally, the study of Ak-Ake molecules in molecular beams or heat pipe ovens is very challenging because of the large differences in the vapor pressure of the constituents. In addition, their spectroscopy suffers from a strong dimer background of the (singlet) alkali partner. Consequently, only a few Ak-Ake molecules (LiCa [19–21], LiBa [22–24], and LiMg [25]) have been characterized experimentally, despite the rising interest in these molecules.

In this Letter we use a new approach for the preparation and characterization of Ak-Ake molecules which have hitherto eluded from an experimental investigation and which is especially suitable for Ak-Ake molecules with heavier Ak partners. As a first application to an unknown system, we present a combined experimental and theoretical study of the RbSr molecule. The interest in this molecule is growing [26–28] and the recent formation of quantum degenerated mixtures of Rb and Sr [16] suggest that RbSr is the favored candidate for the preparation of ultracold Ak-Ake molecules. Note that another promising class for the preparation of ultracold $^2\Sigma$ ground state molecules is represented by the alkali-Yb diatomics [29–32], which exhibit a similar electronic structure as the Ak-Ake molecules. In our method we isolate the molecules on helium nanodroplets. This method has enabled fascinating experiments [33,34], which brought new insights into various phenomena in physics, e.g., the microscopic manifestation of superfluity [35–37], the observation of the superfluid phase in hydrogen [38], or the spectroscopic investigation of homo- and heteronuclear high-spin alkali dimers and trimers [39–43]. Some of these experiments have brought valuable contributions in the “alkali age” of ultracold molecular physics [42,43]. Our new approach combines parts of the previous methods in terms of molecule preparation and spectroscopic techniques to a more elaborate and universal approach. The method is not restricted to Ak-Ake molecules and may allow the formation of various molecules constituted from atoms for which quantum degeneracy has been achieved.

In a first step, we use a resonance enhanced two-photon ionization (R2PI) scheme to cover large spectral ranges

($> 10\,000$ cm^{-1}). The inherent mass sensitivity of the method guarantees an identification of RbSr transitions. In a second step we exploit the fact that molecules desorb from the helium nanodroplets upon laser excitation, giving access to free molecules in dispersed fluorescence (DF) spectroscopy studies. This reveals insight into the ground ($X^2\Sigma^+$) and excited states of free RbSr. Together with high-level *ab initio* calculations, utilizing a complete active space self-consistent field (CASSCF) approach and the multireference configuration interaction (MRCI) method, we can present a comprehensive study of the RbSr molecule from 11 600 up to 23 000 cm^{-1}. The reliability of our approach has been demonstrated in a previous study of LiCa [44], which allowed a comparison with other experimental methods.

The experimental setup has been described in more detail elsewhere [45–47]. In brief, helium droplets are produced in a supersonic jet expansion; helium gas under high pressure (60 bar) is expanded through a cold (15 K) nozzle (5 μm) into vacuum. At this condition, helium droplets with a maximum of the log-normal droplet size distribution at $\hat{N} = 6000$ are produced. The helium droplet beam traverses first through a pick-up cell loaded with Rb and subsequently through a second, loaded with Sr. The pickup probability is dictated by Poisson statistics [48] and the average number of Rb and Sr atoms on the droplet can be adjusted with the temperature of the pickup cells. While for R2PI experiments the cell temperatures are optimized for maximum RbSr signal, the temperature for laser induced florescence experiments is lowered in order to suppress the Rb and Sr dimer background signal. Note that Ak dimer singlet background is absent because on helium droplets, predominantly triplet dimers are formed [41].

R2PI spectroscopy is used to record the excitation spectrum. A XeCl laser pumped dye laser covers the examined spectral regime by using various laser dyes. Wave numbers below 11 600 cm^{-1} are not supported by the laser resonator optics and cannot be reached in our experiments. The dye laser is scanned across the entire spectral range from 11 600 to 23 000 cm^{-1} and the ion yield is recorded with a time-of-flight mass spectrometer with angular reflectron as a function of the laser wave number. During the R2PI process, the molecules detach from the helium nanodroplets and can be monitored with the TOF in the mass window corresponding to RbSr$^+$ ions.

The vibrationally resolved transition at 14 000 cm^{-1} was investigated by DF spectroscopy utilizing a continuous-wave ring dye laser operated with Pyridine 2 and a modified grating monochromator with an attached CCD camera. Laser induced fluorescence (LIF) spectroscopy studies of this spectral region will be presented separately [49].

In order to provide a comprehensive description of the RbSr molecule, we calculated potential energy curves and transition dipole moments for the experimentally investigated spectral region, up to the $\mathrm{Rb}(5s\,^2S) + \mathrm{Sr}(5s5p\,^1P)$ asymptote. Details of the theoretical methods and results will be presented separately. In short, we applied post-Hartree Fock molecular orbital theory using the MOLPRO 2012 package [50]. Rb and Sr were described by a combination of an effective core potential [51,52], a core polarization potential, and a moderately sized uncontracted basis set (Rb [$14s, 11p, 7d, 4f, 2g$], Sr [$15s, 12p, 8d, 5f, 2g$]). Initially a CASSCF calculation [50,53] was performed with an active space of three electrons in 27 orbitals. Subsequently, we applied the MRCI [50,54] method. Figure 1 shows a selection of the calculated potential energy curves. Doublet $^2\Sigma^+$ and $^2\Pi$ states, which can be reached from the $X^2\Sigma^+$ ground state, are shown as solid red and blue curves, respectively. Spin-orbit interaction was included in the calculation for states corresponding to the $\mathrm{Rb}(5s\,^2S) + \mathrm{Sr}(5s5p\,^3P_{0,1,2})$ asymptote. The calculations were accomplished by applying the Breit-Pauli Hamiltonian [55] to wave functions determined by the MRCI approach. A part of the results, which is relevant for the DF spectra, are shown as magenta ($\Omega = 1/2$) and cyan ($\Omega = 3/2$) potential energy curves in the inset in Fig. 1. While the ground state of RbSr has been addressed by several other calculations [26–28], a theoretical study of lower excited states has been presented only very recently [28] [up to the $\mathrm{Rb}(4d\,^2D) + \mathrm{Sr}(5s^2\,^1S)$ asymptote] to which our results can be compared.

Calculations of higher excited RbSr states are very challenging because of the close lying atomic energy levels of Rb and Sr. As can be seen from Fig. 1, this results in numerous avoided crossings and a strong mixing of states.

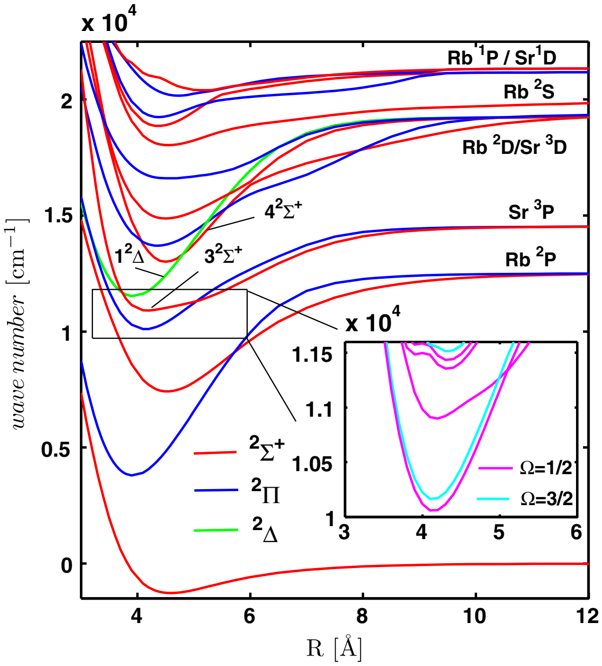

FIG. 1 (color online). Selection of calculated doublet state potential energy curves of the RbSr molecule obtained with a MRCI approach and the CASSCF method. The inset shows relativistic potential energy curves relevant for DF spectroscopy, calculated by applying a Breit-Pauli Hamiltonian to MRCI wave functions.

Consequently, results from different approaches differ strongly (up to > 1000 cm^{-1}). However, in combination with the experiment, the calculation enables an assignment of observed transitions and, conversely, the experimental spectra allows us to infer the actual electronic structure and a judgment on the reliability of the calculations.

A survey spectrum of RbSr on He$_N$ obtained with R2PI spectroscopy is shown in Fig. 2, ranging from 11 600 up to 23 000 cm^{-1}. The helium droplets provide a superfluid low temperature (0.37 K) environment for the RbSr molecules. This simplifies the assignment because all molecules are excited from the $X^2\Sigma^+$ ($\nu'' = 0$) vibronic ground state. The stick spectrum in Fig. 2 represents the calculated Frank-Condon factors times the square of the transition dipole moment (FCF $*$ TDM^2) for rotational quantum number $J = 0$, using the LEVEL8 program of Le Roy [56]. The experimental spectrum is well reproduced by the calculation below 16000 cm^{-1}. Above 16000 cm^{-1}, where the calculation of potential energy curves becomes increasingly challenging because of the proximity of atomic asymptotes, the calculated transitions differ from the experiment. By comparing experiment and theory, a reliable assignment up to 20 500 cm^{-1} becomes possible. Above 20 500 cm^{-1} the increasing density of molecular potential energy curves forbids an unambiguous assignment. Note that relative intensities of recorded transitions cannot be compared because of different ionization schemes and laser pulse energies.

The recorded transitions of the RbSr molecule on He$_N$ appear as structureless broadened features. The broadening is caused by a simultaneous excitation of the molecule and vibrations of the helium droplet (phonons) [57,58]. For vibrationally resolved levels this effect manifests itself in a lambda-shaped peak form, where the rising edge coincides with the transition of the free molecule. In general, the heavy RbSr molecules exhibit narrow vibrational spacings and vibrational bands overlap. The absence of zero-phonon lines in the spectrum in Fig. 2 suggests a strong coupling between RbSr and the droplet surface [41,57,58].

Among the recorded transitions, the $4^2\Sigma^+ \leftarrow X^2\Sigma^+$ transition is an exception because it is vibrationally resolved. This offers the opportunity for the selective excitation of vibrational levels and the determination of spectroscopic constants for the $4^2\Sigma^+$ state. The latter are deduced by determination of the onset of the rising edge of each vibrational level, which coincides typically within ~ 5 cm^{-1} with the free molecule level [44]. An analysis of the R2PI data reveals $T_e = 14\,006(4)$ cm^{-1}, $\omega_e = 86(3)$ cm^{-1} and $\omega_e x_e = 1.2(0.7)$ cm^{-1} for the $4^2\Sigma^+$ state.

A dispersed fluorescence spectrum recorded upon excitation of the $4^2\Sigma^+(\nu' = 0) \leftarrow X^2\Sigma^+(\nu'' = 0)$ transition is shown in Fig. 3. The spectrum reveals information (i) on the $X^2\Sigma^+$ ground state as well as the $4^2\Sigma^+$ state and (ii) about lower states which are involved in the relaxation dynamics of the molecule.

The right panel of Fig. 3 shows the part of the spectrum in the vicinity of the excitation laser which is set to the maximum of the blueshifted RbSr-He$_N$ 0-0 transition at 14 060 cm^{-1}. Upon excitation the molecule desorbs from the droplet, which becomes evident from the emerging sharp spectral lines slightly below the laser line. These lines correspond to transitions from the $\nu' = 0$ level into $\nu'' = 0$ and 1 levels of the ground state. Their spacing of (42 ± 5) cm^{-1} serves as an approximation for the harmonic constant ω_e of the ground state (valid within our resolution), which is in excellent agreement with our calculation ($\omega_e = 42.2$ cm^{-1}) and the values reported by Żuchowski, Guérout, and Dulieu [28] ($\omega_e = 39$ and 38.1 cm^{-1}, respectively). This result verifies that the current calculations for the ground state are of very good quality at short ranges.

From the left panel of Fig. 3 it becomes evident that the majority of the fluorescence originates from electronically lower states. Note that the emission in the region of 12 000 to 12 800 cm^{-1} originates from states that correspond to the

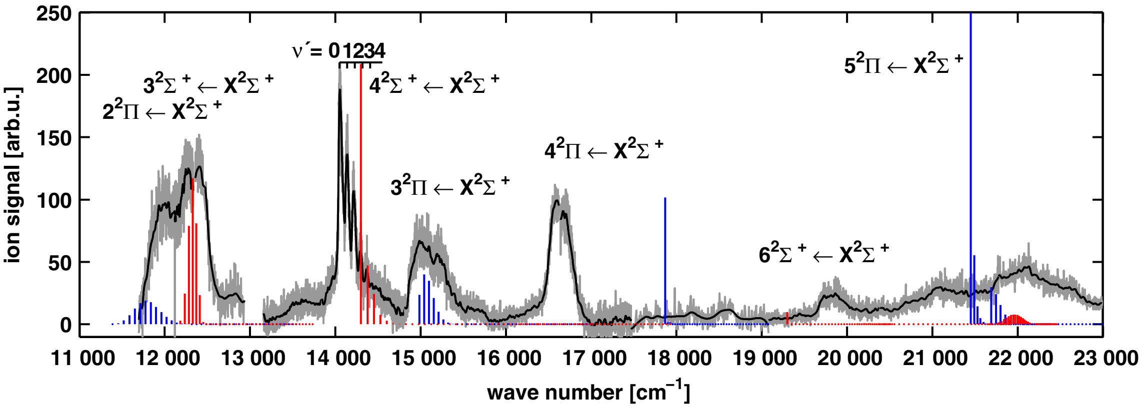

FIG. 2 (color online). Excitation spectrum of RbSr molecules on helium nanodroplets recorded by R2PI spectroscopy. The stick diagram represents the calculated Frank-Condon factors (FCF $*$ TDM^2) from the MRCI potential energy curves, transitions into $^2\Sigma^+$ and $^2\Pi$ states are shown as red and blue sticks, respectively. Note that beyond 16 000 cm^{-1} calculations become increasingly challenging because of the proximity of atomic asymptotes and the difference between the stick spectra and experimental spectra increases, e.g., the shift (calc-measured) of $4\,^2\Pi \leftarrow X^2\Sigma^+$ amounts to ~ 1250 cm^{-1}.

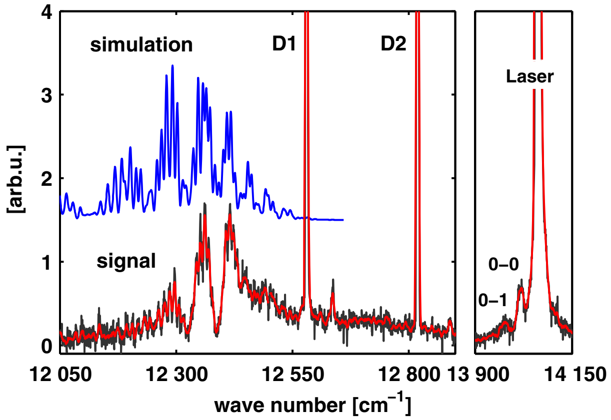

FIG. 3 (color online). Dispersed fluorescence spectrum of RbSr formed on helium nanodroplets upon excitation of the $4^2\Sigma^+(\nu' = 0) \leftarrow X^2\Sigma^+(\nu'' = 0)$ transition. The right panel shows the region in the vicinity of the excitation laser, the (ν'-ν'') 0-0 and 0-1 transitions are marked. The left panel shows fluorescence light originating from lower states, which are populated during the relaxation of the molecule. The simulated spectrum is shown as a blue line above the experimental spectrum (red).

$\mathrm{Rb}(5s\,^2S) + \mathrm{Sr}(5s5p\,^3P)$ asymptote, which is among the most interesting for ongoing ultracold molecule experiments [16,28]. In addition to molecular emission, the rubidium D1 and D2 lines can be seen in Fig. 3, which originate from fragmented RbSr molecules and a residual atomic and dimer background. For a proper description of the DF spectrum spin-orbit interaction ($A_{\mathrm{Sr}(^3P)} = 193.7\ \mathrm{cm}^{-1}$) cannot be neglected. Hence we calculated the relevant relativistic potential energy curves, shown in the inset in Fig. 1. The lowest three states (two $\Omega = 1/2$ and one $\Omega = 3/2$ state) were included in the simulation of the spectrum, which is shown in blue in Fig. 3. Transitions were calculated by using the LEVEL8 program [56], the linewidth was considered by a Gaussian function with an FWHM of 6 cm^{-1}, approximately the resolution of the monochromator. The main features of the spectrum are well reproduced by the lowest $\Omega = 1/2$ state that originates from the $^3P_1$ asymptote (second lowest $\Omega = 1/2$ state in Fig. 1), which is of $3^2\Sigma^+$ character at short range. According to our calculation, this state has the highest transition dipole moment. Minor contributions from the $\Omega = 1/2$ and 3/2 states below are taken into account. The simulation reproduces the large structures, spaced by ~60 cm^{-1} as well as the finer structures on the order of ~10 cm^{-1} only if a maximum of the populated states is assumed at 12 820 cm^{-1}, corresponding to a maximum population around the $\nu' \sim 14$ level of the dominant $\Omega = 1/2$ state. In addition, the simulated spectrum is shifted by 90 cm^{-1} to lower energies in order to match the measured band position. In the nonrelativistic MRCI picture, the maximum of the population lies exactly in the region where the $^2\Delta$ state has its potential minimum and exhibits a crossing with the $3^2\Sigma^+$ state. In the relativistic picture, the $^2\Delta$ state will mix with doublet and quartet states that belong to the Sr ^3P asymptote. The $^2\Delta$ state, which crosses the initially excited $4^2\Sigma^+$ state in the proximity of the potential minimum, provides a relaxation channel for the RbSr molecule. If it is assumed that the molecule is bound long enough to the droplet, the fact that the helium matrix can carry away energy will affect and enhance the relaxation process. The observation of sharp spectral lines implies that the molecules must have desorbed and that relaxation and desorption evolves on a shorter time scale than the spontaneous decay of the excited $4^2\Sigma^+$ state. Note that on the basis of our data, we can not exclude a population of the $2^2\Sigma^+$ and $1^2\Pi$ states, which would cause emission in the infrared regime. In summary, we have presented first results for a large energy range of electronic excitations of the RbSr molecule that may be a prime candidate for molecular physics in the ultracold regime. R2PI spectroscopy enabled the recording of an excitation spectrum from 11 600 up to 23 000 cm^{-1} and an assignment of transitions by comparison with high-level *ab initio* calculations. The experiment revealed that the molecules desorb from the droplet upon excitation, which provides access to free RbSr by dispersed fluorescence spectroscopy and which elucidates ground and excited state properties. Furthermore, relaxation of the molecule leads to a population of lower states which correspond to the $\mathrm{Rb}(5s\,^2S) + \mathrm{Sr}(5s5p\,^3P)$ asymptote. The resulting emission spectrum could be simulated on the basis of relativistic potential energy curves.

Beyond the RbSr molecule, our results suggest that the helium droplet isolation approach together with our spectroscopic recipe that combines R2PI with DF spectroscopy, provides a powerful tool for the characterization of molecules which may be produced in the ultracold regime. The exceptional doping possibilities provided by helium droplets will allow the formation of many new molecules that may also involve Yb [29–32] or Cr [59–61] as constituents.

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