Discovery of dumbbell-shaped Cs*Heₙ exciplexes in solid ^4He

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We have observed several new spectral features in the fluorescence of cesium atoms implanted in the hcp phase of solid helium following laser excitation to the 6^2P states. Based on calculations of the emission spectra using semiempirical Cs-He pair potentials the newly discovered lines can be assigned to the decay of specific Cs*Heₙ exciplexes: an apple-shaped Cs(AΠ₁/₂)He₂ and a dumbbell-shaped Cs(AΠ₁/₂)Heₙ exciplex with a well defined number n of bound helium atoms. While the former has been observed in other environments, it was commonly believed that exciplexes with n > 2 might not exist. The calculations suggest Cs(AΠ₁/₂)Heₙ to be the most probable candidate for that exciplex, in which the helium atoms are arranged on a ring around the waist of the dumbbell shaped electronic density distribution of the cesium atom.

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Alkali atoms and helium atoms in their ground states strongly repel each other by virtue of the Pauli principle. However, an alkali atom excited to one of its P states can exert an attractive potential on a helium atom that can lead to bound states, known as exciplexes. The formation of alkali-helium exciplexes was considered for the first time by Dupont-Roc and Karnorsky et al. as an explanation for the observed quenching of atomic fluorescence from light alkali atoms (Na, Li) embedded in liquid or solid ^4He. In the meantime such molecules have been observed in different environments, such as liquid helium and cold helium gas, as well as on the surface of helium nanodroplets. Here we present the first observations of such exciplexes in a solid helium matrix.

In earlier experiments we have studied the excitation and fluorescence spectra of atomic cesium implanted into the bcc and hcp phases of solid helium. It was found that the excitation at the D₃ transition (6S₁/₂-6P₃/₂) results in atomic fluorescence at the same transition, blue shifted (with respect to the free Cs atom) by the interaction with the helium matrix. At the same time, excitation on the D₂ transition (6S₁/₂-6P₃/₂) produced merely a weak fluorescence on the D₁ emission line, which indicates that the 6P₃/₂ atoms are partly quenched into the 6P₁/₂ state, while the main relaxation channel remained unknown. Recently, the extension of the spectral range of our detection system allowed us to discover several new emission lines, red shifted with respect to the atomic fluorescence line. We attribute those lines to the formation and decay of Cs*Heₙ molecules.

The maximal number of helium atoms for different alkali-helium exciplexes was found previously to be n_max = 4 for K*Heₙ, n_max = 6 for Rb*Heₙ, n_max = 2 for Cs*Heₙ. Hirano et al. discussed on the basis of Cs*He₂-He potential energy surfaces that there should be no stable Cs*He₃ configuration. They therefore conclude that exciplexes with more than n_max = 2 do not exist, since they regard the exciplex formation as a sequential process (Cs* → Cs*He₁ → ... → Cs*Heₙ). However, our experimental results demonstrate unambiguously that in the hcp phase of solid helium Cs(AΠ₁/₂)Heₙ exciplexes with n > 2 are formed, when the cesium atoms are excited to the 6P₃/₂ state. From the relative integrated observed line intensities we conclude that the formation of those exciplexes is the most probable deexcitation channel of the 6P₃/₂ state.

In the present experiment a ^4He matrix doped with Cs atoms was produced by the technique described in our earlier papers. Data were taken in the hcp phase of solid ^4He at a temperature of 1.5 K and a pressure of 31.6 bar. For the excitation of the embedded atoms we used a single mode cw Ti:Al₂O₃-laser, pumped by a Nd:YVO₃ laser. The laser wavelength was tuned to the D₂ absorption line of cesium, whose resonance wavelength is shifted to 800 nm due to the influence of the surrounding helium matrix. The atomic fluorescence light from the sample volume (~ 3 mm³) is detected by a fiber coupled optical spectrum analyzer (Ando Co. Ltd., AQ-6315A) which has a detection range of 350-1750 nm. The spectral resolution was limited to about 5 nm.

Fig. shows a typical recorded emission spectrum, as well as calculated spectra of several Cs*Heₙ exciplexes. The smallest peak at 11400 cm⁻¹ corresponds to fluorescence on the D₁ transition, indicating the existence of a transfer channel between 6P₃/₂ and 6P₁/₂ states. That process was studied before, in experiments with superfluid helium. Another emission line appears at 10520 cm⁻¹. We attribute this broad and asymmetric peak to the emission of Cs(AΠ₃/₂)He₂ exciplexes, which had previously been observed in liquid helium and in cold helium gas. The peak presented here is blue-shifted with respect to the one reported in by approximately 500 cm⁻¹. The shift is due to the influence of the helium...
and can be expressed by the operator $V_{6P}^{\text{Cs}-\text{He}}(r) = \sum_{i=1}^{n} V_{6P}^{\text{i}}(r_{i})$, with $r_{i} = r(r, \theta = \pi/2, \varphi_{i} = i2\pi/n)$ and $n = 1, 2, \ldots$. In addition we include He-He interactions by summing over the corresponding $V_{\text{He-He}}(R)$ potentials between neighboring helium atoms using the semi-empirical potential given by Beck [4]. The distance $R$ between two neighboring helium atoms is a function of the cesium–helium separation $r$ and the number $n$ of helium atoms: $R = |r_{i} - r_{i+1}| = 2r\sin(\pi/n)$. After including the spin-orbit interaction in Cs the total interaction potential of the Cs*He$_{n}$ system reads

$$V_{\text{Cs*He}_{n}}(r) = V_{6P}^{\text{Cs}-\text{He}}(r) + nV_{\text{He-He}}(R) + 2/3\Delta L \cdot S,$$

where $\Delta = 554.0$ cm$^{-1}$ is the fine-structure splitting of the free cesium 6P state and $S$ the electronic spin operator. $V_{\text{Cs*He}_{n}}(r)$ is diagonalized algebraically. In Figs. 2 and 3 the resulting $r$-dependencies of the eigenvalues are shown for Cs*He$_2$ and Cs*He$_3$ respectively. The same plots also show the ground state potentials given by $nV_{6S}^{\text{i}}(r) + nV_{\text{He-He}}(R)$. The potentials are labelled according to their electronic configurations as $X^{2}\Sigma_{1/2}$, $A^{2}\Pi_{1/2}$, $A^{2}\Pi_{3/2}$ and $B^{2}\Sigma_{1/2}$. The quantization axis is defined by the symmetry axis of the exciplexes, which is the internuclear axis of the cesium atom and the two helium atoms in the case of Cs*He$_{n=1,2}$, whereas for Cs*He$_{n\geq 3}$ it is the axis of the helium ring. Pictographs next to the curves show the variation of the cesium electronic density as the $n$ helium atoms, indicated by two filled circles, approach the cesium atom.

From the adiabatic potentials of Figs. 2 and 3 one sees that the helium atoms, due to the Pauli principle, are repelled by the cesium valence electron. However, in cases where the atoms approach along a nodal line or in a nodal plane of the electron distribution they experience an attractive van der Waals force until they are repelled by the cesium core. This definitely holds for the Cs(AII$_{1/2}$)He$_2$ exciplex. For Cs(AII$_{1/2}$)He$_2$ the situation is more complicated. When the two helium atoms are far away the electronic configuration is the one of the 6P$_{1/2}$ state of the free cesium atom, which has a spherical symmetry and is hence, as the 6S$_{1/2}$ ground state, repulsive for the helium atoms. However, when the helium atoms approach the cesium atom the electronic wave function of the latter is deformed and becomes apple-shaped. This new configuration now offers a binding potential minimum. The formation of this second configuration has a potential barrier of 79 cm$^{-1}$, which is much higher than the thermal energy of 1.0 cm$^{-1}$. If, on the other hand, the two atoms do not approach simultaneously, but one after the other, only the first atom has to overcome the potential barrier thereby forming the apple-like electronic configuration of a Cs*He$_1$ structure, which then becomes attractive for a second helium atom approaching from the opposite side. A third helium atom approaching the Cs(AII$_{1/2}$)He$_2$ exciplex will again be repelled. However, if it comes sufficiently close, the electronic configuration changes to a dumbbell shape, which has a binding minimum for the three helium atoms. Here too, a potential
FIG. 2: Adiabatic potentials of the Cs$^+$He$_2$ system, including the spin-orbit interaction. The two helium atoms are located at $r$ and $-r$ on the quantization (rotationally symmetry) axis, indicated in the pictographs by a solid line. The shape of the electronic density distribution of the cesium atom changes significantly as helium atoms (filled circles) approach.

FIG. 3: Adiabatic potentials of the Cs$^+$He$_n$ system. The six helium atoms are located on a ring of radius $r$ concentric with the symmetry axis. Only the $A^2\Pi_{1/2}$ potential has a binding attractive well.

We calculated the adiabatic potentials and the vibrational zero-point energies for all Cs$^+$He$_n$ systems up to $n = 9$. The treatment of the molecular vibrations is approximate and will be described elsewhere. Higher vibrational states are not populated at the temperature of the experiments and can be neglected, as well as the contributions from rotations.

The $n$ dependence of the zero-point energies for Cs($\Pi_{1/2}$)He$_n$ exciplexes is represented in Fig. 3 by filled circles. Also shown are the heights of the potential barriers (open squares) and the depths of the potential minima (open circles). All energies are given with respect to the dissociation limit, i.e., the electronic energy of the 6P$_{1/2}$ state. The significant increase of the potential barrier when going from $n = 2$ to $n = 3$ reflects the discussion given above. The configuration with $n = 8$ has the deepest attractive potential, while its zero-point energy due to the stronger localization of helium atoms exceeds the barrier energy, which makes that complex unstable. Cs($\Pi_{1/2}$)He$_7$ seems to be the largest possible quasi-bound exciplex. Only the molecule with $n = 6$ has an energy below the dissociation limit and is hence predicted to be stable. Note that for rubidium several configurations are predicted to be stable and Rb($\Pi_{1/2}$)He$_n$ exciplexes with $n = 1…6$ have been observed recently [4].

In a last step we calculated the shape of the emission.
sion lines by using the Franck-Condon approximation in a similar way as the authors of [8]. Among all exciplexes considered, the best agreement of the calculated spectra with the experimental ones is provided by those shown in Fig. 1 by solid curves. The shape and width of the line at 10520 cm$^{-1}$ agrees well with the calculated emission line of Cs(A$\Pi_{1/2}$)He$_2$. However, the apparently excellent agreement between the positions of these lines is accidental as the pressure shift, i.e., the influence of the surrounding helium matrix was not taken into account. In fact, K. Enomoto et al. [8] measured the emission line of Cs(A$\Pi_{3/2}$)He$_2$ exciplexes in cold helium vapor environment to lie at about 10000 cm$^{-1}$. We like to mention that that we have also observed fluorescence from Cs(A$\Pi_{1/2}$)He$_2$ exciplexes, not discussed here, following D$_1$ excitation [12,13].

![Figure 4](image)

**FIG. 4:** Energy dependencies of the Cs(A$^2\Pi_{1/2}$)He$_n$ exciplexes as a function of the number $n$ of helium atoms. Shown are the minimal energies (open circles) of the potential wells, the barrier heights (open squares) and the total zero-point energies (filled circles). All energies are given with respect to the dissociation limit, i.e., the electronic energy of the 6$P^{3/2}$ state. Corresponding points are joined by lines to guide the eye. The temperature of the helium matrix corresponds to $kT = 1.0$ cm$^{-1}$.

The correct assignment of the strongest measured peak at 7130 cm$^{-1}$ in Fig. 1 is a more subtle task. It is clear that the line originates from a Cs(A$\Pi_{1/2}$)He$_n$ exciplex, in which the helium atoms form a ring in the nodal plane of the Cs atom. It is very likely that this line also shifts with helium pressure. Moreover, as the ring-shaped exciplexes contain a larger number of helium atoms any imprecision of the initial pair potentials will be amplified. As a consequence the line positions of the higher order Cs*He$_n$ systems cannot be predicted with sufficient accuracy to allow an unambiguous assignment of the observed line. The overall good agreement between calculated and measured lineshapes indicates that the line at 7130 cm$^{-1}$ originates from the decay of an exciplex with a specific number $n$ of bound helium atoms and that it is not a superposition of lines from exciplexes with different values of $n$. Such superpositions were observed in the case of Rb*He$_n$ exciplexes in cold $^4$He vapor [4]. The theoretical considerations suggest, as a best guess, that the observed peak at 7130 cm$^{-1}$ originates from decaying Cs*He$_6$ complexes, as those exciplexes have minimal energy and are the only ones predicted to be stable.

In summary, we have performed a study of laser induced fluorescence of cesium atoms trapped in the hcp phase of a helium crystal. We have reported the observation of new spectral features, which are broader and more intense than the pure atomic lines. We believe that those lines are formed by the emission from two types of specific Cs*He$_n$ exciplex structures, viz., an apple-shaped complex with two helium atoms bound to the Cs atom and a dumbbell-shaped complex, in which a ring of helium atoms is bound to the nodal plane of the Cs wave function. These assignments are supported by model calculations, which allow us to obtain the corresponding emission spectra. In the case of the ring structure the calculations suggest $n = 6$ as the most likely number of bound atoms.

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