Alkali–helium exciplex formation on the surface of helium nanodroplets. I. Dispersed emission spectroscopy

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Dispersed emission spectra collected upon the $4{^2}P_{3/2,1/2} \rightarrow 4{^2}S_{1/2}$ optical excitation of K atoms attached to helium nanodroplets include broad, structured, red-shifted features which are shown to be due to K*He exciplex formation, paralleling our former observation of Na*He [J. Reho, C. Callegari, J. Higgins, W. E. Ernst, K. K. Lehmann, and G. Scoles, Discuss. Faraday Soc. 108, 161 (1997)]. The exciplex formation is demonstrated by the agreement obtained in comparing the K*He $A(1){^2}II \rightarrow X(1){^2}Σ$ emission spectra with the predictions derived from available ab initio potential energy surfaces. Recent analysis of both exciplex emissions also points to the possibility of triatomic (Na*He$_2$ and K*He$_2$) exciplex formation for a small fraction of the alkali atoms. The lack of fluorescence quenching, which is present when the spectra are taken in bulk liquid helium, is due to the surface location of the alkali atoms on the helium droplets that allows the nascent Na*He and K*He exciplexes to desorb from the droplet and emit as isolated molecules. © 2000 American Institute of Physics. [S0021-9606(00)01145-4]

I. INTRODUCTION

The study of atom-doped or molecule-doped helium nanodroplets has recently attracted widespread attention both because of their highly quantum nature and because they provide an ultracold matrix in which rotational resolution can be obtained. 1–4 While a variety of atoms, molecules, and ions have been attached to helium droplets, 5–10 or implanted into bulk liquid, 11–14 and solid helium, 15,16 the use of alkali atoms has found a central place among these studies due to the simple, hydrogen-like valence character of the alkali atoms (thus similar to H atoms studied on He surface) 17 and to the optical accessibility of the alkali atomic transitions.

While the $D_1$ line ($n^2P_{3/2} \rightarrow n^2S_{1/2}$ transition) of Cs and Rb can be simulated within the framework of the bubble model 18 in which the alkali atom resides in a spherical cavity produced by the Pauli repulsion between the helium bath and the alkali valence electron, the doubly-peaked profile of the $D_2$ ($6^2P_{3/2} \rightarrow 6^2S_{1/2}$ transition) excitation spectrum of Cs in bulk liquid helium cannot be reproduced if a simple spherical cavity is assumed, and has been attributed to a quadrupolar deformation of the bubble. 11 In this refinement of the bubble model, the spherical symmetry of the helium cavity (and hence the degeneracy of the excited atomic $n^2P$ states) is removed by a dynamic Jahn–Teller effect. 19 Analogously, Kanorsky et al. postulate a deformation of the bubble after electronic excitation of atomic Na in bulk liquid helium. 20 Describing the Na atom in terms of one-electron orbitals, they suggest that a few (from four to six) helium atoms can “flow” into the “waist” of the Na $p_z$ nodal plane into a potential energy well nearly 500 cm$^{-1}$ deep. 21 When the number of helium atoms on the $p_z$ nodal plane of Na reaches five, the lowering of the potential energy of the excited state combined with the increase in the repulsive energy of the Na($3s$)He interaction, results in a curve crossing that leads to radiationless transitions from both $D$ lines. 22 This model has been proposed as an explanation of the absence of fluorescence from optically excited Na and Li atoms in bulk liquid helium.

Analogous mechanisms also exist which account for the reduced $n^2P_{3/2} \rightarrow n^2S_{1/2}$ (as compared to $n^2P_{1/2} \rightarrow n^2S_{1/2}$) Cs and Rb fluorescence 11 in bulk helium. One such mechanism involves the rapid population transfer from the $n^2P_{3/2}$ state down to the $n^2P_{1/2}$ level, which becomes possible as the helium bath allows for partial L–S uncoupling. Under the perturbation of the surrounding liquid, L–S coupling is largely preserved in the case of Cs (large fine structure), while for Rb it is thought to be partially broken. Experimental evidence also points to an additional nonradiative decay channel from the $n^2P_{3/2}$ state that at present remains uncharacterized. 22

The case of K solvated in liquid helium stands as an intermediate between the total quenching observed for Li and Na and the spin–orbit-selective quenching in the case of the larger alkalis (Rb, Cs). In the case of K, quenching of both spin–orbit emission channels is observed, but while this quenching is substantial, it is not total. 23

Alkali atoms are predicted to reside on the surface of helium droplets due to the predominantly repulsive nature of the interaction of the alkali atom with helium. 24 Indeed, because of the large size of the Na atom, the well depth of the Na–He pair potential is calculated to be almost one-tenth of that between two helium atoms. 21 The atom is predicted to sit above a “dimple” formed on the helium surface at a distance from the surface larger than in the case of the bulk. 24 Experimental work has confirmed the surface site location by probing both bound–bound and bound–free transitions of the atom–droplet complex. 10 Emission from the $D_1$ and $D_2$ lines of K and Na excited on the helium droplet are of roughly equal intensity, 10 which stands in contrast to the findings in the bulk noted above. Furthermore, in the case...
of Li- and Na-doped He droplets, fluorescence can be easily observed,\textsuperscript{10} while it appears that in the bulk (see above) this process is fully quenched.

In this and the companion article, we focus on the interaction between excited alkali atoms and the helium surface. Using visible dispersed fluorescence measurements, we study the process in which He atoms are attracted to the node of the ne\textsuperscript{th} alkali atom, and characterize the photoinduced formation of K\textsuperscript{+}He and Na\textsuperscript{+}He (and possibly of K\textsuperscript{+}He\textsubscript{2} and Na\textsuperscript{+}He\textsubscript{2} exciplexes), complementing preliminary results for Na\textsuperscript{+}He which have been reported by us previously.\textsuperscript{25} Time-resolved studies of the dynamics of this process will be presented in the companion article. The comparison of K\textsuperscript{+}He exciplex formation with an extended analysis of what is known of Na\textsuperscript{+}He exciplex processes\textsuperscript{25} can further our ability to discern the extent to which behavior as a solute in bulk liquid helium can be used to predict surface behavior on a helium droplet and to improve our understanding of the interaction between liquid helium and the dopant atoms.

II. EXPERIMENT

A description of the methodology used for the production and study of alkali-doped He droplets in our laboratory will be presented here only in brief, as a more detailed exposition has already been given elsewhere.\textsuperscript{10} A beam of large He nanodroplets ((N)~10\textsuperscript{7}–10\textsuperscript{8}) is produced in a free jet expansion of He gas using a nozzle diameter of 20 \textmu m, stagnation pressure of 2.5 MPa, and nozzle temperatures of 16–20 K. After collimation by a 400 \textmu m skimmer, the droplets are doped with sodium or potassium atoms using the pickup technique which consists of passing the He droplet beam through a cell containing a pressure of ~10\textsuperscript{−2} Pa of the alkali atom of interest. The doped droplets are probed spectroscopically by collection of laser-induced fluorescence (LIF) by means of a standard spherical/elliptical mirror combination.\textsuperscript{26}

Emission spectra are measured by dispersing the collected photoinduced fluorescence through a 0.35 m spectrograph (MacPherson EU-700) with a dispersive power of 20 A/mm. A liquid-nitrogen-cooled charge-coupled device (CCD) (Princeton Instruments 1152UV, operated in a one-dimensional mode) is used to detect the photons exiting the monochromator. The entrance slit of the monochromator was set to 250 \textmu m, giving an instrumental resolution of approximately 54 cm\textsuperscript{−1}. Each emission spectrum consists of two five-minute frames, with maximum counts ranging from 3000 to 4000 counts per CCD strip.

III. RESULTS

A. Excitation spectra of Na and K atoms on He droplets

The excitation spectra of alkali atoms (Na, K) attached to large helium droplets, which have been discussed at length previously,\textsuperscript{10} will be briefly recounted here in the framework of the alkali atom–He exciplex formation. It has been previously observed that the spectrum begins slightly to the red of the free Na D\textsubscript{1} (3P\textsubscript{1/2}→3S\textsubscript{1/2}) and D\textsubscript{2} (3P\textsubscript{3/2}→3S\textsubscript{1/2}) lines (16 956.18 cm\textsuperscript{−1} and 16 973.38 cm\textsuperscript{−1}, respectively, and exhibits a long blue tail.\textsuperscript{10} This spectrum has previously been explained and successfully modeled as a composite of bound–bound and bound–free transitions occurring between the ground and first excited state of the Na atom–helium droplet pseudodiatom potential energy surface.\textsuperscript{10} Empirically, this conclusion has been supported through the measurement of excitation spectra employing wavelength-selective collection, separating the bound–bound from the bound–free contributions to the total LIF signal. The bound–free contribution was collected by scanning over the entire transition while collecting exclusively Na D-line fluorescence. Such fluorescence arises from excited Na atoms that have desorbed from the droplet surface within the natural lifetime of the P\textsubscript{3/2,1/2} excited states.

The existence of both bound–bound and bound–free components in the excitation spectra of alkali atoms on helium droplets can be explained through a simple consideration of the geometry of the alkali atom on the droplet surface. Upon n\textsuperscript{2}P→n\textsuperscript{2}S excitation, two symmetries (Σ and Π) become accessible to the alkali atom–helium droplet pseudodiatom. If the z-axis is assumed to be perpendicular to the surface, in the Σ configuration the lobe of the excited p\textsubscript{z} orbital intrudes into the droplet surface, causing a strong alkali atom–He droplet repulsion and desorption of the atom, accounting for the bound–free transitions described above. In the excitation of the p\textsubscript{x} or p\textsubscript{y} orbitals, on the other hand, an increase in both attraction and repulsion is expected and the balance between the two leads to the possibility of bound-to-bound transitions in which the droplet–atom complex is initially preserved\textsuperscript{10} (see below) in spite of the electronic excitation.

Unlike the lighter alkalis, potassium does emit some fluorescence in bulk liquid helium which increases when the atom is attached to helium droplets.\textsuperscript{23} It has been found that the general spectral characteristics of the excitation spectrum of Na attached to helium nanodroplets reappear in the case of potassium,\textsuperscript{10} i.e., the long blue tail and the presence of intensity at the gas phase D-line positions. It is interesting to note that in the case of potassium, there is no intensity to the red of the lower fine structure line, unlike in the case of Na. On the helium droplets, the fine structure splitting in potassium (57.72 cm\textsuperscript{−1}) is almost fully resolved, in contrast to Na for which the smaller splitting (17.20 cm\textsuperscript{−1}) is only partially resolved in the excitation spectrum.\textsuperscript{10} As in the case of Na, the excitation spectrum of potassium on helium droplets can be broken down into bound–free and bound–bound components through wavelength-selective emission studies.

B. Dispersed emission of Na\textsuperscript{+}He and K\textsuperscript{+}He

As mentioned above, the dispersed emission spectra obtained from K\textsuperscript{+} and Na\textsuperscript{+} atoms on helium droplets consist of two main features, the relative intensities of which change as a function of the excitation frequency. The high-energy feature, having an instrument-limited linewidth, is due to the emission of gas-phase atoms and corresponds to the bound–free component of the excitation spectra. The second emission feature is broad and structured and exhibits intensity spanning the range from 10 000 to 13 000 cm\textsuperscript{−1} (for K\textsuperscript{+} and...
12 000 to 16 800 cm\(^{-1}\) (for Na\(^+\)). This emission, substantially red-shifted from the atomic D line positions, corresponds to the bound–bound component of the excitation spectrum.

Figures 1 and 2 show, respectively, the emission spectra upon excitations of the \(D_1(4^2P_{3/2} \rightarrow 4^2S_{1/2})\) and \(D_2(4^2P_{3/2} \rightarrow 4^2S_{1/2})\) transitions of potassium on helium nanodroplets. It is found that excitation around the \(D_1\) energy (12 985.17 cm\(^{-1}\)) results in broad structured emission with a maximum of intensity at \(\sim 12 000\) cm\(^{-1}\), while excitations corresponding to the \(D_2\) fine structure level of K atoms (13 042.89 cm\(^{-1}\)) give rise to an equally broad, structured emission, exhibiting a maximum signal near 12 750 cm\(^{-1}\), at the red foot of the \(D_1\) atomic line. These differences will be discussed below.

### IV. DISCUSSION

#### A. Modeling the K\(^+\)-He and Na\(^+\)-He(A)\(1^2\Pi \rightarrow (X)1^2\Sigma^+\) emission neglecting spin–orbit interactions

Potential energy curves of the alkali/helium interactions are available in the literature.\(^{21,27,28}\) Experimental information on these curves is also available from studies of the red tail of the emission of alkali atoms in high-pressure helium gas.\(^{28,29}\) Figure 3 shows the potential curves of the \((A)\,1^2\Pi\) and \((B)\,2^2\Sigma^+\) state of K–He as calculated by Pascale neglecting spin–orbit effects.\(^{21}\) It can be seen from the figure that both the predominantly repulsive \(2^2\Sigma^+\) state and the attractive \(2^2\Pi\) state correlate to the atomic K(4\(P\)) asymptote. The ground state is of course repulsive at short range but also very weakly attractive at long range with a well depth of 1.6 cm\(^{-1}\) located at 7.2 Å. The dispersed emission spectra from K atoms on helium droplets (cf. Figs. 1 and 2) was modeled by use of these spin–orbit averaged potential curves.\(^{21}\) The bound vibrational levels of the \((A)\,1^2\Pi\) state were calculated using the LEVEL 6.0 program of LeRoy,\(^{30}\) which numerically solves the radial Schrödinger equation by use of the Numerov–Cooley algorithm. The vertical emission from the bound states of the well of the \((A)\,1^2\Pi\) potential to the repulsive wall of the \((X)\,1^2\Sigma^+\) state is calculated employing the BCONT program suite of LeRoy\(^{31}\) and fitting the level populations. The only adjustable parameters in this simulation were the populations of the upper levels. The vertical emission connecting the bound vibrational levels of the \((A)\,1^2\Pi\) state with the repulsive wall of the \((X)\,1^2\Sigma^+\) state gives only fair agreement with the experimental spectrum, and the discrepancy in the red tail is more pronounced than in the modeling of the Na\(^+\)-He emission discussed below.
TABLE I. Vibrational populations of the K–He (A) 1 \(^2\)I state upon optical excitation at energies corresponding to each of the two fine structure components (J = 3/2,1/2) of K(4P) atoms. The emission spectra were calculated by use of the BCONT program\(^a\) and the vibrational populations were the only free parameters in the fit. The spin–orbit averaged 1 \(^2\)I and 1 \(^2\)Σ potential energy surfaces of Pascale\(^b\) were used in predicting the emission.

<table>
<thead>
<tr>
<th>Vibrational level</th>
<th>Excitation energy (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v' = 0)</td>
<td>12 985.2 (J = 1/2)</td>
</tr>
<tr>
<td>(v' = 1)</td>
<td>13 042.9 (J = 3/2)</td>
</tr>
<tr>
<td>(v' = 2)</td>
<td></td>
</tr>
<tr>
<td>(v' = 3)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Reference 31.
\(^b\)Reference 21.

Table I gives the populations of the (A) 1 \(^2\)I state from the best fit to the data for each (J = 1/2 and J = 3/2) K excitation. It is seen from the table that there is no evidence of population in \(v' = 3\) from the best fit to the emission spectrum (shown in Fig. 1) obtained by excitation at the \(D_1\) K line (12 985.2 cm\(^{-1}\)). The fit to this data is given in the J = 1/2 column of the table and is shown as a dashed line in Fig. 1.

Emission due to excitation of the K-doped droplet at 13 042.89 cm\(^{-1}\) (which corresponds to the \(D_2\) excitation of the gas-phase K atom and is shown in Fig. 2) requires population in the \(v' = 3\) level to obtain the best fit between calculated and experimental spectra (see Table I, column J = 3/2) and is shown by the dashed line in Fig. 2.

Figure 4 shows a comparison of the Na\(^a\)He dispersed emission spectrum observed at 16 975.2 cm\(^{-1}\) with the simulated emission spectrum of the exciplex calculated from the potential energy surfaces of Pascale,\(^21\) shown in Fig. 5. The bound vibrational levels of the (A) 1 \(^2\)I state were again calculated using the LEVEL 6.0 program of LeRoy.\(^30\) On the basis of this excellent agreement, we have previously assigned the emission as arising from the bound–free transitions of an isolated Na\(^a\)He exciplex.\(^25\) It can be seen from Fig. 4 that while the calculation fails to reproduce the intensity in the red tail of the experimental emission, it does a better job reproducing this region than was found for the case of potassium. This failure will be revisited below. Table II summarizes the relative (A) 1 \(^2\)I vibrational populations that result for several excitation wavelengths. Excitations with higher excess energy result, as expected, in increased population in the higher vibrational levels of the Na\(^a\)–He exciplex.

B. Modeling the K\(^*\)–He(A) 1 \(^2\)I \(\rightarrow\) (X) 1 \(^2\)Σ emission including spin–orbit interactions

Successful modeling of the Na\(^a\)He emission spectra does not necessitate going beyond the "spin-free" approximation, and so the spin–orbit averaged potential energy surfaces of Pascale were found to be sufficient. In the case of K\(^a\)He, however, because of the much larger spin–orbit splitting of the K atom in comparison with Na (57.7 vs 17.2 cm\(^{-1}\)), it becomes necessary to include spin–orbit coupling in the potential energy surfaces. In so doing, it is possible to produce a more realistic model of the emission spectra.

FIG. 4. Emission spectrum collected upon excitation of Na atoms on helium nanodroplets. The thin line represents the calculated emission from the (A) 1 \(^2\)I state of NaHe based upon the NaHe potential curves of Pascale (Ref. 21).

FIG. 5. Cubic spline fit to the potential energy curves of Na(3P)–He as calculated by Pascale (Ref. 21). The well depth of the A \(^2\)I state is 499 cm\(^{-1}\). The original Pascale points are represented as hollow circles. The inset shows an expanded view of the X \(^2\)Σ state. The arrow represents the exciplex emission.

TABLE II. Vibrational populations of the Na–He (A) 1 \(^2\)I state obtained by fitting the emission spectra produced by optical excitation at several different energies of Na atoms attached to large helium droplets. The calculated emission spectra were produced using the BCONT program\(^a\) and the potential surfaces of Pascale,\(^b\) which neglect spin–orbit coupling.

<table>
<thead>
<tr>
<th>Vib. level</th>
<th>Excitation energy (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v' = 0)</td>
<td>16 955 16 961 16 975 17 047 17 151</td>
</tr>
<tr>
<td>(v' = 1)</td>
<td>0.35 0.33 0.30 0.24 0.10</td>
</tr>
<tr>
<td>(v' = 2)</td>
<td>0.34 0.34 0.32 0.25 0.22</td>
</tr>
<tr>
<td>(v' = 3)</td>
<td>0.24 0.25 0.26 0.26 0.27</td>
</tr>
</tbody>
</table>

\(^a\)Reference 31.
\(^b\)Reference 21.
spin–orbit coupling procedure has been explained fully in an earlier publication\textsuperscript{21} and is also discussed in depth in the companion article. In short, spin–orbit effects are accounted for through the introduction of a constant spin–orbit operator that leads to the atomic K 4 2P fine structure splitting (57.7 cm\textsuperscript{-1}). This approximation is expected to be very good at long range where we expect negligible perturbation of the K* electronic structure in the diatomic system. The resultant spin–orbit coupled K–He potential energy surfaces, separated asymmetrically by the 57.7 cm\textsuperscript{-1} spin–orbit splitting of the K 4 2P atom, can be used to recalculate the K*He exciplex emission spectra. In this model, at short range the 2 1/2 and 3 1/2 states have a splitting equal to 2/3 of the atomic value of 57.7 cm\textsuperscript{-1}. The vibrational level positions for the K–He diatomic potential energy surfaces as predicted by the LEVEL 6.0 program of LeRoy\textsuperscript{30} are reported in Table III.

The comparison of the experiment with the predicted exciplex emission for the case of D\textsubscript{1,2} excitation of K on helium droplets is shown in Figs. 1 and 2. In these figures the predicted emission from the spin–orbit averaged potential energy surfaces of Pascale are shown by the dashed lines, while the predicted emission using the potential energy surfaces formed by spin–orbit coupling the Pascale surface (thus forming K–He 1 2 3/2 and 1 2 1/2 surfaces) are shown as solid lines. These solid lines thus represent predictions in which contributions from both potential energy surfaces are allowed for, with the relative populations of each vibrational level as the only free parameters. Such fits represent an improvement over fits in which only one spin–orbit component is considered.

The populations resulting from our fits are shown in Table IV. It can be seen from the table that, for the spectrum produced by excitation at the K D\textsubscript{1} line, 72% of the emission intensity is attributable to emission from the 2 1/2 vibrational levels (predominantly \( v = 0 \)) and only 28% of the total emission intensity is modeled as arising from the 2 3/2 vibrational levels (predominantly \( v = 1 \)). In the case of excitation corresponding to the D\textsubscript{3} line, it is found from the fit that 62% of the emission intensity is from 1 2 3/2 vibrational levels while the balance of the emission comes from the 1 2 1/2 levels. While most of the emission intensity of a given fine structure atomic excitation comes from vibrational bands corresponding to the same spin, a certain percentage (28% in the case of \( J = 1/2 \) excitation and 38% in the case of \( J = 3/2 \) excitation) can be attributed to vibrational bands corresponding to the other spin–orbit coupled potential energy surface. It can also be seen from Table IV that the contribution of the 2 1/2 \( v' = 3 \) vibrational level is negligible, mirroring the \( v' = 3 \) absence in the spin–orbit averaged case.

It can be seen from both figures that the fit to the K*He emission, even using the spin–orbit coupled potential energy surfaces, is not as good as in the case of the Na*He emission, particularly toward the red. While for both K*He emission spectra the two features toward the blue end are well fit by the Pascale surfaces, the feature most to the red and the red tail are not fit well in either case. This point will be taken up again in the next section.

C. The triatomic Na*He\textsubscript{2} and K*He\textsubscript{2} exciplexes

Figures 1 and 2 attest to the reasonable agreement between the predicted and experimental K*He emission, except for the fact that the simulations fail to reproduce the lowest energy intensity as well as the small red tail of the observed emission spectrum. Inclusion of spin–orbit coupling did not significantly add intensity to this region. As noted above, this failure at the red end is more pronounced in the case of K*He but is also present in the Na*He case (cf. Fig. 4). This discrepancy may in fact point to the possible presence of Na*He\textsubscript{2} and K*He\textsubscript{2} exciplexes. A case can be made that such higher-order exciplex formation is in fact probable based upon the considerations reported below.

The spectrum obtained by K D\textsubscript{1} excitation at 12985 cm\textsuperscript{-1} [circles in Fig. 6(a)] was first fit empirically by three Gaussian lineshapes (shown as dashed curves in the figure), excluding the area between 10 000 and 11 500 cm\textsuperscript{-1}, i.e., the area of the tail discussed above. Holding these three Gaussian constant, another Gaussian line shape was added, and the fit range was expanded to include the entire spectrum. The parameters of this additional Gaussian, given as the dash-dotted line shape in Fig. 6(a), show that this missing intensity (now corrected for the original failure at the red-

### Table III. Vibrational level positions found by adding spin–orbit coupling to the K–He potential energy surfaces of Pascale. The calculated vibrational positions were found through use of the LEVEL program. The spin-averaged asymptote is normalized to the K(4S)+He(1S) asymptote.

<table>
<thead>
<tr>
<th>Vibrational level</th>
<th>( 1\Pi_{1/2} ) surface</th>
<th>( 1\Pi_{3/2} ) surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v' = 0 )</td>
<td>12 810.2 cm\textsuperscript{-1}</td>
<td>12 849.3 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>( v' = 1 )</td>
<td>12 885.6 cm\textsuperscript{-1}</td>
<td>12 925.1 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>( v' = 2 )</td>
<td>12 939.0 cm\textsuperscript{-1}</td>
<td>12 978.6 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>( v' = 3 )</td>
<td>12 973.8 cm\textsuperscript{-1}</td>
<td>13 013.7 cm\textsuperscript{-1}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reference 25.  
\textsuperscript{b}Reference 21.

### Table IV. Vibrational populations of the K–He \((A)1\,1\Pi_{3/2}\) states as fit to the emission obtained from excitation at energies corresponding to the K D\textsubscript{1} line (second column) and D\textsubscript{2} line (third column) on He\textsubscript{+}. The calculated emission spectra were calculated using the BCINT program with the spin–orbit averaged potential energy surfaces of Pascale\textsuperscript{b} and the populations were the only free parameters in the fit.

<table>
<thead>
<tr>
<th>Vibrational level</th>
<th>Excitation energy (cm\textsuperscript{-1})</th>
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</thead>
<tbody>
<tr>
<td>( v' = 0(\Pi_{1/2}) )</td>
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<tr>
<td>( v' = 1(\Pi_{1/2}) )</td>
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<tr>
<td>( v' = 3(\Pi_{3/2}) )</td>
<td>0.014</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reference 31.  
\textsuperscript{b}Reference 21.
most maximum of the emission spectrum) is centered at 10 950 cm$^{-1}$. The final fit is shown as the solid curve in the figure, with the experimental data given as hollow circles. The parameters of the fit are reported in Table V.

The center of the additional Gaussian represents a shift of $\sim 2000$ cm$^{-1}$ from the excitation frequency. This shift is about twice the shift of the center of the K*He exciplex emission as discussed in the text. The solid arrow corresponds to the center of the Na*He 2 Gaussian. The dash-dot curve is added in a final fit to the experimental spectrum. The parameters of the fit are given in Table V.

The center of the additional Gaussian represents a shift of $\sim 2000$ cm$^{-1}$ from the excitation frequency. This shift is about twice the shift of the center of the K*He exciplex emission as discussed in the text. The solid arrow corresponds to the center of the Na*He 2 Gaussian. The dash-dot curve is added in a final fit to the experimental spectrum. The parameters of the fit are given in Table V.

### TABLE V. Parameters (P) of the Gaussian lineshapes fit to the $D_1$ and $D_2$ K*He emission spectra and to the Na*He ($3p^+; 3p^+$) emission; center ($v_c$) in cm$^{-1}$, full width at half maximum ($\Delta v_c$) in cm$^{-1}$, and normalized area ($A_c$).

<table>
<thead>
<tr>
<th></th>
<th>Na*He 16 975.2 cm$^{-1}$</th>
<th>Excitation$^a$</th>
<th>K*He 13 042.9 cm$^{-1}$</th>
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<td>$v_1$</td>
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<td>10 950</td>
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<td>$v_3$</td>
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FIG. 6. Experimental spectrum (hollow circles) obtained exciting the K $J=1/2(A)$ and $J=3/2(B)$ fine structure lines. The fits (solid lines) represent the addition of a redmost Gaussian (dash-dot curve) to the original fit composed of the dashed Gaussians. The dash-dot Gaussian may be representative of K*He$_2$ emission as discussed in the text. The solid arrow corresponds to the center of this Gaussian, and the dashed arrow to the center of the emission as a whole (excluding the "tail"). The parameters of the fit are given in Table V.

FIG. 7. Experimental spectrum (hollow circles) obtained exciting Na on He at 16 975 cm$^{-1}$. The fits (solid lines) represent the addition of a redmost Gaussian (dash-dot curve) to the original fit composed of the dashed Gaussians. The dash-dot Gaussian may be representative of Na*He$_2$ emission as discussed in the text. The solid arrow corresponds to the center of this Gaussian, and the dashed arrow to the center of the emission as a whole (excluding the "tail"). The parameters of the fit are given in Table V.

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**V. CONCLUSIONS**

We have found that K*He and Na*He exciplexes are formed upon $n^2P_{3/2,1/2}$ optical excitation of K and...
Na atoms doped onto the surface of large helium droplets. This conclusion has been reached by modeling the redshifted dispersed emission spectra collected following the above electronic excitations.

Alkali atoms are known to reside as a surface species on helium droplets. Thus this exciplex formation process is a surface phenomenon, and is not observed for alkali atoms in bulk liquid helium. The nodal plane of $P$-state alkali atoms located in bulk liquid helium is thought to attract a ring of helium atoms, causing the quenching of alkali fluorescence in the bulk liquid. The dissipation of energy following exciplex formation on the droplet surface can open a desorption channel for the exciplex which is not present in bulk liquid helium.

In both the $K^\oplus$–He and Na$^\ominus$–He case, we attribute exciplex formation exclusively to the case wherein $\Pi$ symmetry is assumed by the alkali atom–helium droplet pseudopotential. In cases in which $\Sigma$ symmetry is assumed by the system, desorption of the alkali atom is predicted to occur and exciplex formation is not possible as the He atoms of the droplet are repelled by the Na$^\ominus$ electron cloud as opposed to being attracted into the nodal plane as occurs in the $\Pi$ symmetry case.

In comparison with the predictive accuracy of the NaHe (A)$^1\Pi$ surface of Pascale for the vibrational structure of the NaHe (A)$^1\Pi\rightarrow(X)$1$^2\Sigma$ experimental emission, we find that our KHe results necessitate the inclusion of spin–orbit coupling of the original A$^1\Pi$ surface in order to achieve reasonable agreement with experiment. While the KHe agreement is sufficient for assignment of the emission to the (A)$^1\Pi\rightarrow(X)$1$^2\Sigma$ transition of KHe, there are deviations that are not accounted for by spin–orbit coupling of the 1$^2\Pi$ surfaces. This may be explained by slight deviations of the Pascale (A)$^1\Pi$ surface from the "true" surface in the region of its well. It is also possible that deviations in the lower (X)1$^2\Sigma$ state may be the cause this disagreement as such emission is highly sensitive to the positioning of the repulsive wall of the lower state. Although the calculation of the repulsive wall (in which correlation effects are small) is typically carried out with high precision, even small deviations can have large effects on the calculated emission. Therefore, it seems reasonable to attribute the disagreement between the experimental and predicted K$^\oplus$He emission spectra to the potential surfaces used in the calculation.

There is similar experimental–theoretical disagreement in the case of KHe and NaHe regarding the red tail of the emission spectra. As the disagreement in the red tail for KHe (where the intensity maxima are not well-modeled by the Pascale surfaces) and in the case of NaHe (in which all intensity maxima are well-accounted for by the emission calculated from the Pascale surfaces) is similar, it is reasonable to conclude that the potential energy surfaces are not the cause of disagreement in this case. Thus consideration of the failure of the predicted spectra to model the red tail of the experimental emission for both Na$^\oplus$He and K$^\oplus$He, coupled with the relative positioning of the difference spectra, has led to our tentatively assigning this minor portion of the red emission to fluorescence generated from Na$^\oplus$He$^2$ and K$^\oplus$He$^2$ exciplexes.

Recent photoionization measurements by F. Stienkemeier and co-workers, report the formation of K$^+He_n$ ($n\geq2$) complexes. The formation of those complexes is not addressed in our experiment, since the CCD detector is not sensitive in the region of their expected spectral emission.

ACKNOWLEDGMENTS

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This represents a reasonable first order approximation based on the successful AgHe$_2$ potential energy surfaces generated by the group of Takami, in which the well depth of the $1\ ^3\Sigma$ state of AgHe$_2$ was found to be almost exactly double that of AgHe with minimal change in $R_e$ at the MP4 level of theory [J. L. Persson, Q. Hui, Z. J. Jakubek, M. Nakamura, and M. Takami, Phys. Rev. Lett. 76, 1501 (1996)].