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ELECTRONIC STRUCTURE WITH A DIPOLE MOMENT CALCULATION OF THE LOW-LYING ELECTRONIC STATES OF THE KHe MOLECULE

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The KHe molecular system is extensively studied by multi-reference configuration interaction calculations. Potential energy curves are constructed for 20 lowest electronic states, and molecular parameters are extracted. A comparison of our results with previous works shows remarkable agreement. A further calculation of the dipole moment functions through a wide range of the internuclear separation is performed and their corresponding curves are presented. Charge transfer is detected from the change in the sign of these functions particularly for $R < R_e$. Negative dipole moment values near R_e are predicted for 3 excited states, $(1)^2\Pi$, $(3)^2\Sigma^+$ and $(1)^4\Pi$, which are of a relatively short-range strong-binding nature. On the other hand, weakly binding long-range excited states predict positive values of the dipole moment near R_e reflecting the K^-He^+ polarity.

INTRODUCTION

Recently, there has been much theoretical and experimental interest in the study of van der Waals molecules involving helium. In the investigation of the unique properties of such molecules, alkali metals are among the best candidates due to their simple electronic configuration and the presence of optically accessible electron transitions. Moreover, alkali metals are particularly important in helium nanodroplet isolation spectroscopy [1, 2] because they reside on the surface of superfluid He droplets whereas most other atoms or molecules move to the center. The experimental emission spectra of alkali metal-helium exciplexes were reported [3, 4]. Also, the exploration of the photoabsorption spectra of alkali metal-rare gas systems and the location of possible satellite peaks constitute strong tools for understanding the atmospheres of brown dwarfs and other astrophysical objects, such as extrasolar giant planets dominated by alkali-metal atoms [5—8]. These compounds are also considered to play a major role in exciplex laser field due to their repulsive ground state and a comparatively more stable first excited state [9—12]. Their potential as exciplex lasers has theoretically been confirmed for both diatomic and triatomic systems [13—15].

The work presented here uses an *ab initio* configuration interaction approach to study the electronic structure of the potassium-helium KHe molecule. In the following section, we present the computational details of the method used. In the third section, the result of the calculations is presented. We calculated potential energy curves and dipole moments for 20 electronic states. We displayed their spectroscopic constants, including the equilibrium position R_e, the well depth D_e, the harmonic frequency ω_e, the transition energy T_e, the barrier position R_e, and the barrier height relative to the disso-

ciation asymptote E_{max}. The comparison of our results with the previously published experimental and theoretical data is also presented and discussed.

COMPUTATIONAL DETAILS

The group theory gives important instructions how the molecular symmetry is related to the molecular polarity. If a molecule belongs to the C_{nv} group, where $n > 1$, then it cannot have a component of the dipole moment perpendicular to the symmetry axis because a dipole moment existing in one direction perpendicular to the axis is cancelled by an opposing dipole. A dipole moment in these molecules can be only parallel to the molecular axis. Being a heteronuclear diatomic molecule, KHe is of $C_{\infty v}$ point group symmetry; however, the MOLPRO software can only make use of Abelian point groups, which means that $C_{\infty v}$ is to be treated using the C_{2v} point group. placing the molecule along the + z-axis and keeping K at the origin. Potential energy curves (PECs) for the 20 lowest-lying electronic states of the KHe molecule in the representation $^{2S+1}\Lambda^{(\pm)}$ were investigated by performing multi-reference CI calculations (single and double excitations) using reference functions resulting from the state-averaged complete active space SCF approach. Davidson correction is introduced to estimate the effect of higher-order excitations. Among the 21 electrons for the KHe molecule, 16 inner electrons from the K atom were frozen in subsequent calculations so that 5 free electrons were explicitly treated. The active space contains 11 active orbitals listed as follows: 5σ(K: $3p_o$, $3d_o$; He: $1s$, $2s$, $3s$), 4π(K: $3p_{\pm1}$, $3d_{\pm1}$) and 2δ(K: $3d_{\pm2}$) distributed among the irreducible representations a_1, b_1, b_2, and a_2 of the C_{2v} symmetry as [6, 2, 2, 1]. The helium species is represented by the 6-311G basis set whereas the D_ef2-SVPD basis set is used for potassium. These basis sets have been taken from the EMSL Basis Set Library (http://www.emsl.pnl.gov/forms/basisform.html). The MOLPRO program [16] was used in this work.

RESULTS AND DISCUSSION

In Table 1 we present the numerical data for the 20 electronic states of the KHe molecule with the corresponding MRCI potential energy curves displayed in Fig. 1, *a* and *b*. The ground state is $X^2\Sigma^+$ correlating to K($3p^64s^1$; ^2S) + He($1s^2$; ^1S). As for all alkali-helium diatomic compounds, this ground state is repulsive at a short range but also slightly attractive at a long range. Our calculated values of the equilibrium bond length and potential depth are found to be $R_e = 7.63$ Å and $D_e = 0.724$ cm^{-1}, which are in good agreement with the available data in the literature [17—21], while those in [13, 22] show a closer equilibrium geometry and a deeper potential well. In the literature, the calculated R_e values [4l, 13, 15] are in excellent agreement with our value for the electronic state $(1)^2\Pi$ correlating to K($3p^64p^1$; $^2P^0$) + He($1s^2$; ^1S). The comparison with the other published data [21—25] indicates a stretched bond length at the equilibrium position with the average relative difference of 7.9 %. The potential well of the $(1)^2\Pi$ state is an issue of great importance for all first excited states in alkali-helium compounds, which determines the stability of this state, and consequently, the possible wide range of applications in the laser field. Our calculations predict a well depth of $D_e = 80.19$ cm^{-1}, which is in perfect agreement with 77.06 cm^{-1} indicated in [13]. Higher stability for this electronic state is shown by comparing our value to those given in the literature [13, 15, 21—24]. An apparent increase in stability is reported in [25] with $D_e = 480$ cm^{-1}. Allard [26] studied theoretically the emission profiles for KHe with spin-orbit interactions and predicted well depths of 212 cm^{-1} and 193 cm^{-1} for $(1)^2\Pi_{3/2}$ and $(1)^2\Pi_{3/2}$, respectively. Among all published results, only those presented by Mullamphy *et al.* [20] show a shallower potential well of $D_e = 43$ cm^{-1}, which is about half of the present calculated value, at a greater bond length of 4.7 Å. At this point and with the lack of any experimental value for the potential well depth of this $(1)^2\Pi$ state, it is quite interesting to mention that for alkali-helium compounds the D_e value for $(1)^2\Pi$, and consequently, its stability decreases as we go from Li to K. In fact, an experiment made by Havey *et al.* [27] presented a well depth of 850±100 cm^{-1} for $(1)^2\Pi$ of LiHe and 480±50 cm^{-1} for NaHe. This leads us to the conclusion that the well depth of the $(1)^2\Pi$ state of KHe is definitely less than 480 cm^{-1}. Acceptable agreement is obtained

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Spectroscopic constants of the lowest-lying doublet and quartet electronic states of the KHe *molecule*

State	R_e, Å	D_e, cm^{-1}	T_e, cm^{-1}	ω_e, cm^{-1}	R_{max}, Å	E_{max}, cm^{-1}
X$^2\Sigma^+$	7.63	0.724	0.00			
	7.30[a]	0.8984[a]				
	7.35[b]*	1.27[b]*				
	6.98[b]**	4.38[b]**				
	7.133[c]	0.935[c]				
	7.18[d]	0.98[d]				
	7.22[e]	1.184[e]				
	7.33[f]	0.77[f]				
	6.08[g]	6.255[g]				
(1)$^2\Pi$	3.05	80.19	11081.53			
	3.12[b]*	77.06[b]*	11800[b]			
	3.01[h,b]**	114.56[h,b]**				
	4.07[e]	43.58[e]				
	2.80[f]	225[f]				
	2.85[g]	168.99[g]				
	2.80[i]	190.00[i]				
	2.80[j]	245.00[j]				
	2.80[k]	480.00[k]				
	—	—	11914[l]*			
	3.08[l]**	—	12076[l]**			
	2.80[m]	—	11884[m]			
(2)$^2\Sigma^+$	Repulsive					
	10.85[e]	0.339[e]				
	7.40[h]	25[h]				
(3)$^2\Sigma^+$	3.17	375.52	20515.91		5.00	286.57
	3.14[h]	280[h]			5.36[h]	113[h]
(4)$^2\Sigma^+$	3.74	900.81	29022.38		5.57	667.38
	2.88[h]	119[h]				
(1)$^2\Delta$	4.18	15.51	42123.02			
	3.08[h]	50[h]				
(5)$^2\Sigma^+$	4.94	22.34	42231.24			
(1)$^4\Sigma^+$	6.05	12.33	167928.33			
(1)$^4\Delta$	6.05	12.29	169842.48			
(1)$^4\Pi$	6.92	5.70	170910.03			
(2)$^2\Delta$	6.07	11.5	171703.00			
(1)$^4\Sigma^-$	6.05	12.56	171816.41			
(1)$^2\Sigma^-$	6.08	11.43	172923.68			
(3)$^2\Delta$	5.87	16.02	181252.83	545.76		
(2)$^2\Sigma^-$	5.84	16.30	181506.79	1110.71		
(2)$^4\Pi$	Repulsive					
(3)$^4\Pi$	4.01	61.21	188628.46		5.14	128.46
(1)$^4\Phi$	6.20	9.13	189542.66			
(4)$^4\Pi$	2.90	236.46	191638.49	318.86		

First entry: The present work. [a]Ref. [17], [b]Ref. [13] (b*: ALDET-CI, b**: GUGA-CI), [c]Ref. [18], [d]Ref. [19], [e]Ref. [20], [f]Ref. [21], [g]Ref. [22], [h]Ref. [15], [i]Ref. [23], [j]Ref. [24], [k]Ref. [25], [l]Ref. [4](*l**: exp., *l***: Theor.), [m]Ref. [26].
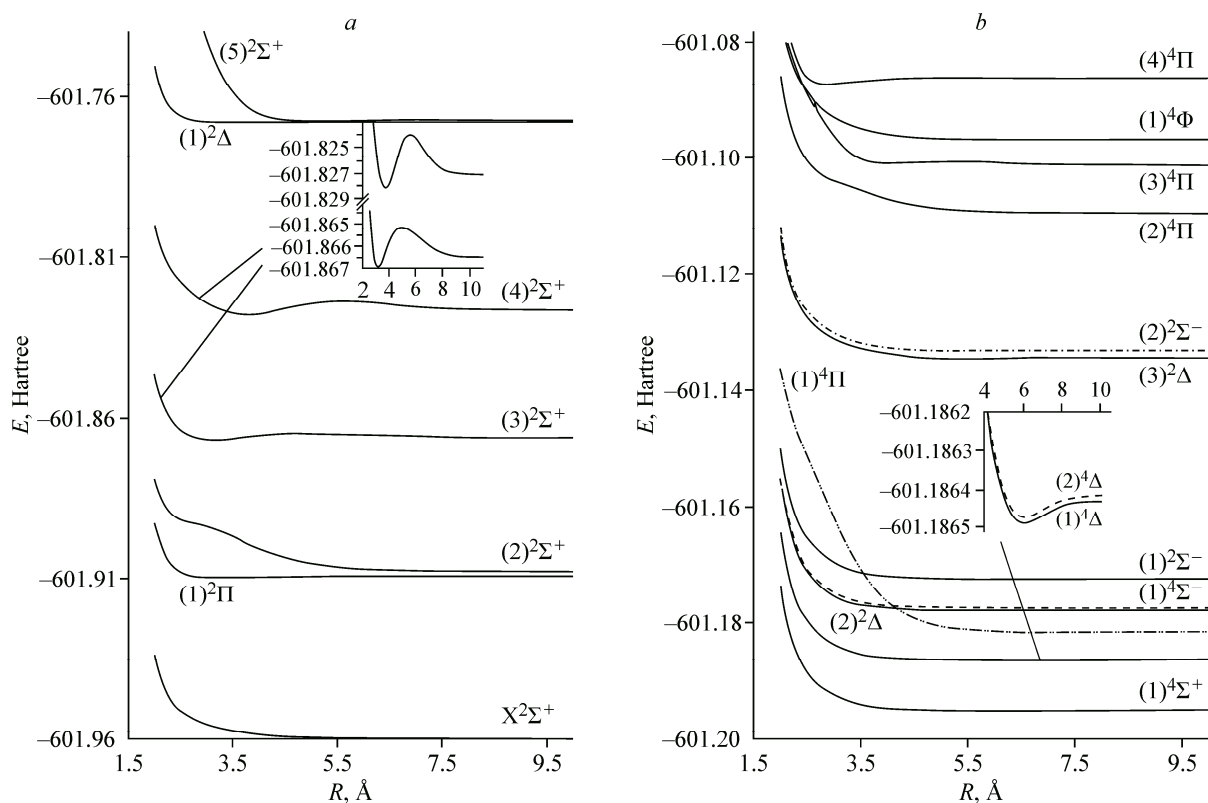
Fig. 1. Potential energy curves of the low-lying doublet electronic states of the KHe molecule between –601.96 and –601.71 Hartree (*a*); –601.2 and –601.08 Hartree (*b*)

when comparing the transition energy of $(1)^2\Pi$ of the value $T_e = 11081.53$ cm^{-1} with other theoretical works [4, 13, 26] with a relative difference of $6.7 \le \delta T_e/T_e \le 8.2$ %, noting that our calculations indicate a smaller transition energy than all other works. A relative difference of 7 % is recorded when compared to the experimental value of 11 914 cm^{-1} predicted by Enomoto *et al.* [4]. Another experimental study conducted by Reho *et al.* [3], on the emission spectrum of the KHe exciplex reported that excitation around $D_1(4^2P_{1/2} \leftarrow 4^2S_{1/2})$ of the K atoms with an energy of 12 985.17 cm^{-1} results in broad structure emission with an intensity maximum at ~12 000 cm^{-1}. The peak position near 12 750 cm^{-1} is obtained due to excitations around the $D_2(4^2P_{3/2} \leftarrow 4^2S_{1/2})$ fine structure level of the energy of 13 042.89 cm^{-1}.

In our calculation, the next excited state $(2)^2\Sigma^+$ is found to be purely repulsive, whereas Mullamphy *et al.* [20] predicted a slight dip of 0.339 cm^{-1} at 10.85 Å and Chattopadhyay [15] presented a slightly deeper well of 25 cm^{-1} at 7.40 Å. The available data in the literature for the $(3)^2\Sigma^+$, $(4)^2\Sigma^+$, $(1)^2\Delta$, and $(5)^2\Sigma^+$ electronic states is obtained theoretically [15]. Similarly to the data obtained by Chattopadhyay [15] for KHe, an avoided crossing is recorded between $(3)^2\Sigma^+$ and $(4)^2\Sigma^+$ near 4 Å (Fig. 1, *a*) in the present work. This result was found to be a common property for these two states of LiHe [28] and NaHe [29] molecules and which is responsible for the presence of potential barriers of these states. For the $(3)^2\Sigma^+$ state, our minimum position of 3.17 Å is in excellent agreement with the relative difference of 0.9 %, as compared with that of Chattopadhyay [15] while our potential well is deeper. Acceptable agreement is found for the present calculated position of the barrier $R_{max} = 5.00$ Å with a greater height of 286.57 cm^{-1} above the dissociation asymptote. However, for the $(4)^2\Sigma^+$ state we obtained a much deeper well of 900.81 cm^{-1} at a larger equilibrium position 3.74 Å. A barrier with a height of 667.38 cm^{-1} at 5.57 Å is detected for this state, which is not reported by Chattopadhyay [15]. By comparing with the same reference [15], poor agreement is found for $(1)^2\Delta$ where we predict a smaller minimum of 15.51 cm^{-1} with a larger bond length of 4.18 Å. The study of the states from
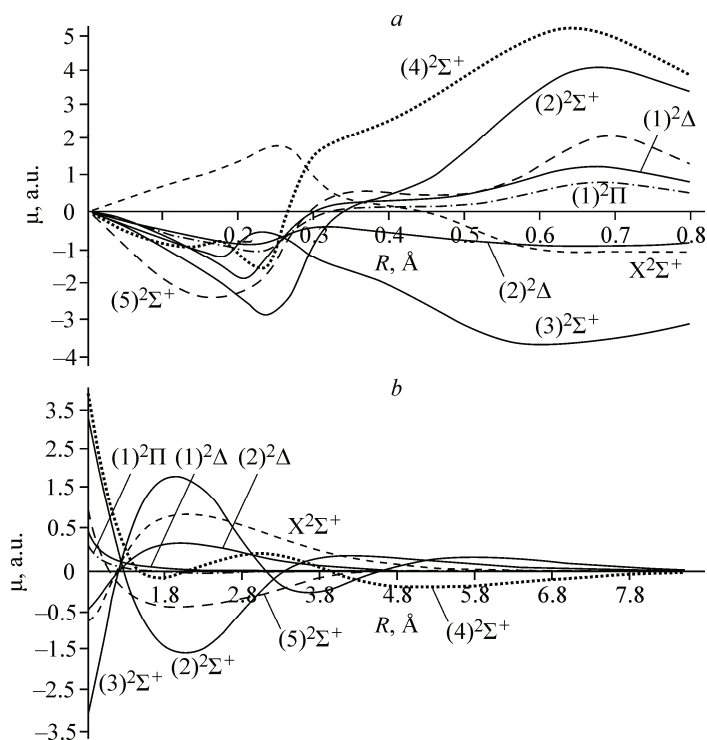
Fig. 2. Dipole moment curves of doublet states, $X^2\Sigma^+$, $(1)^2\Pi$, $(2)^2\Sigma^+$, $(3)^2\Sigma^+$, $(4)^2\Sigma^+$, $(5)^2\Sigma^+$, $(1)^2\Delta$, and $(2)^2\Delta$ for internuclear distances ranging between 0 and 0.8 Å (*a*); 0.8 and 8.8 Å (*b*)

$(5)^2\Sigma^+$ to $(2)^2\Sigma^-$ show that all these states exhibit a long-range weakly-binding nature. Another perturbation is noticed between the two high-lying $(2)^4\Pi$ and $(3)^4\Pi$ states, leading to an avoided crossing between their PECs near 3.4 Å. The $(1)^4\Phi$ state has a quite similar weakly-binding nature with slight dip of 9.13 cm^{-1} at 6.20 Å. For the highest lying calculated state $(4)^4\Pi$ we predict a relatively short-range bonding at 2.9 Å and larger stability with a 236.46 cm^{-1} potential well.

For a diatomic molecule, the knowledge of the dipole moment function over a wide range of the internuclear separation is of great theoretical and practical significance. In particular, it reflects the electron-density distribution in the molecule in different electronic states, and it is of maximum importance near the equilibrium geometry R_e. Figs. 2, 3, and 4 represent the dipole moment functions μ of the doublet and quartet electronic states of the KHe molecule. As can be seen, smooth and continuous dipole moment functions for all states have been obtained, which can be used to assess the quality of our investigation. The sign of the dipole moment depends on the orientation of the internuclear axis. Positive values correspond to the excess electron density near the K atom, which is fixed at the origin. Moreover, the change in the sign of the dipole moment function indicates the electronic charge migration inside the molecule. It is worth mentioning that, for the relatively short-range binding states

$(1)^2\Pi$, $(3)^2\Sigma^+$, and $(4)^4\Pi$, which are the most stable among the considered states, the dipole moment function is negative at R_e with the respective values of -0.0117 a.u., -0.1368 a.u., and -0.01727 a.u., suggesting the K^+He^- polarity. This is consistent with electronegativity arguments according to the Allred-Rochow scale
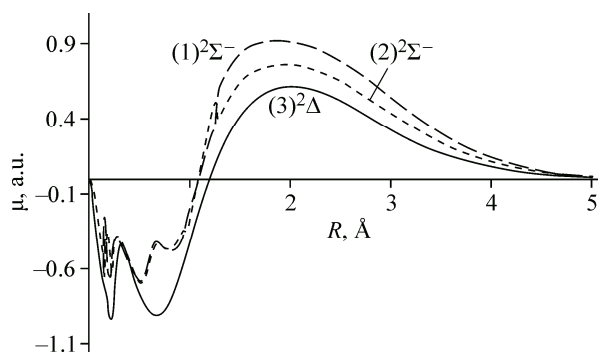

Fig. 3. Dipole moment curves of the doublet states $(3)^2\Delta$, $(1)^2\Sigma^-$, and $(2)^2\Sigma^-$
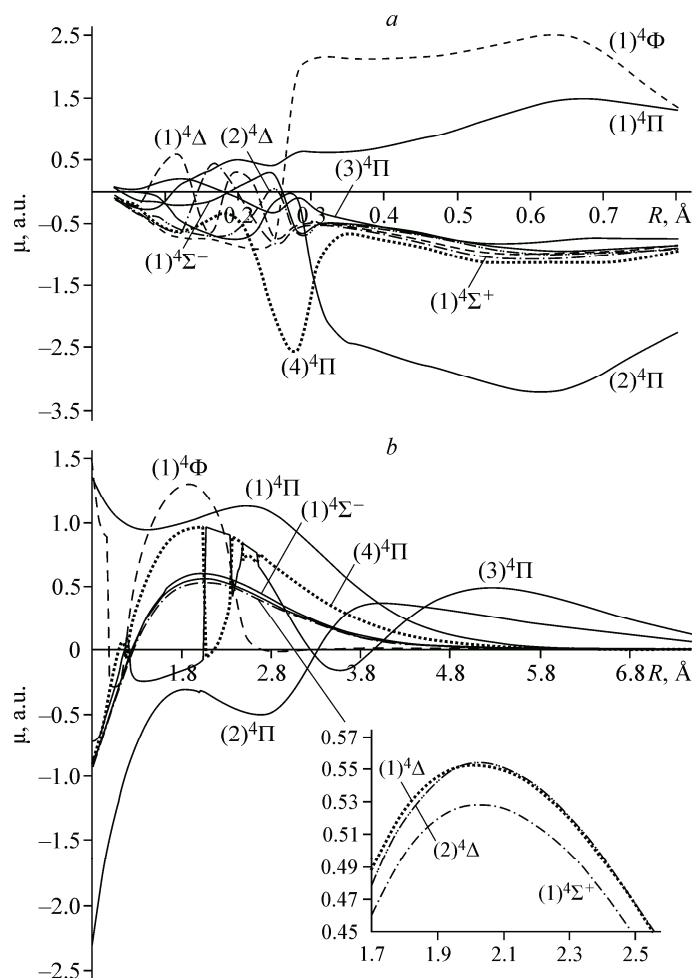
Fig. 4. Dipole moment curves of all quartet states for internuclear distances
ranging between 0 and 0.8 Å (*a*); 0.8 and 7.5 Å (*b*)

(E.N. of He = 5.50 while E.N. for K = 0.91). We may attribute this to the formation of a Rydberg state where an electron in the K atom is shifted to higher excited states, leaving a vacancy such that the He atom can approach and fill the low density space near K. On the contrary, the long-range weakly binding states exhibit positive dipole moment values reflecting the K^-He^+ polarity near R_e, ranging between 0.00057 a.u. for $(2)^2\Sigma^-$ < μ < 0.1060 a.u. for $(4)^2\Sigma^+$ with an average value of 0.01086 a.u. At large internuclear separations, all dipole moment curves asymptotically reach a zero value reflecting the proper dissociation of the molecule into neutral species K+He.

CONCLUSIONS

In this work we have performed an *ab initio* MRCI calculations related to the electronic structure of KHe molecule. The PECs and spectroscopic constants for 20 electronic states were reported along with their dipole moment curves. Most of these states reflect the weakly bound nature of such a van der Waals molecule. The comparison with the published results shows overall good agreement.

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