A Theoretical Study on the Excited States of the KCCH Radical

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Abstract. Based on the C_{2v} symmetry, the low-lying electronic states of the KCCH radical was studied in the complete active space self-consistent field (CASSCF) and multi-configurational second-order perturbation theory (CASPT2) methods. For the low-lying electronic states of KCCH, the calculated harmonic vibrational modes are in agreement with theoretical reports. Moreover, the electron transitions of KCCH, from $X^1\Sigma^+$ to $2^1\Sigma^+$, $1^1\Pi$, $2^1\Pi$, $1^1\Sigma^-$, $1^3\Sigma^+$, $1^3\Pi$, $2^3\Pi$ and $1^3\Sigma^-$, are predicted at 5.43, 5.59, 7.87, 5.50, 5.15, 5.73, 5.53 and 6.82 eV, respectively. The CASSCF/CASPT2 potential energy curves (PECs) were calculated for K^+ -loss dissociation from the $1^3\Sigma^+$, $2^3\Sigma^+$, $1^3\Pi$, $2^1\Sigma^-$, $1^1\Pi$ and $2^1\Pi$ states. Analyses of electron transition and dissociation curves show the ionic properties in the metal–ligand bond for KCCH. The dissociation energy of the KCCH ($X^1\Sigma^+$) $\rightarrow$ CCH($1^1\Sigma$) + $K^+(S^0)$ is 4.423 eV at the CASSCF/CASPT2 level.

1 Introduction

Over the past 30 years, the investigations for the metal monoacetylides have been progressed steadily, which include both theory and experiment, and have focused mainly on the alkali and alkaline-earth metals. To introduce organic groups into organic and organometallic compounds in substitution or addition reactions, organolithium species have been widely utilized to produce new and exotic compounds. The MCCH molecule used in nucleophilic substitution reactions to create large alkynes is the simplest alkynyl derivatives of organoalkali metal compounds in a monomeric state^[1].

Experimentally, the structure of alkali metal monomeric KCCH has been determined by means of millimeter/submillimeter rotational spectroscopy and Fourier transform microwave (FTMW) spectroscopy in the different frequency ranges^[2-3]. With these precise experimental results given, an opportunity is offered for an updated theoretical investigation by means of *ab initio* quantum chemical methods.

Theoretically, Veillard Alain used the Linear Molecule Program of Mclean and Yoshimine has calculated a self-consistent field wave function for the KCCH, which finds that a highly ionic compound and the long-range inductive effects play a major role in electronic transfers^[4]. Scalmani et al. had investigated the electronic properties of the molecule by means of a variety of theoretical models ranging from semiempirical techniques to Hartree–Fock (HF-SCF) and standard post-HF methods and a number of density functional theory (DFT) techniques^[5]. Gauss, J. et al. had calculated the equilibrium structure of KCCH using the coupled-cluster singles and doubles (CCSD) approach^[6].

However, they did not give an available information for the excited electronic states of these species.

To the best of our knowledge, there is a lack of the theoretical studies on excitation spectroscopy and dissociation of the KCCH radical, which makes us conduct a comprehensive investigation into providing accurate interpretation and prediction for the excited states. In numerous applications, the CASSCF and CASPT2 methods have been shown to be effective for theoretical studies of excited states of molecules^[7].

2 Computation methodology

In this work, the reference functions were performed to compute the first-order wave function and the second-order energy in the full configuration interaction space at the CASSCF/CASPT2 levels with an applied level shift of 0.3, which employs the large atomic natural orbital (ANO-RCC) basis sets^[8] in all the calculations. All calculations made use of the MOLCAS 7.8 programs.

The equilibrium geometries of the low-lying electronic states of the KCCH radical were calculated in C_{2v} symmetry by using the CASSCF optimization method which had the weight values of the CASSCF reference functions larger than 80% in the first-order wave functions. We chose the 10 valence electrons as the active electrons and presented the electron configuration of the ground state as (core)(8σ)²(9σ)²(10σ)²($3\pi_x$)²($3\pi_y$)².

The active space includes the 10 electrons and 13 orbitals (10, 18) for KCCH radical. The CASSCF calculations on all stationary points were performed using the above active space. On the basis of the corresponding optimized geometries, the effects of dynamic electron correlation were included by performing CASPT2 calculations at all CASSCF

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stationary points to compute the dynamic correlation energies, the adiabatic excitation energies, vertical excitation energies and dissociation energies. Using the CASPT2 energy differences, the oscillator strengths were computed with the CAS state interaction (CASSI) program^[9]. In addition, Multi-configurational linear response (MCLR) was used to calculate the harmonic vibrational frequencies^[10].

3 Results and discussion

3.1. Optimized geometries

Figure 1 shows the atom labels of the KCCH radical. Calculations were performed by means of the CASSCF and CASPT2 methods, using the VDZP and VTZP basis sets of ANO-RCC. The experimental and calculated bond lengths (in Å) and rotational constants (in GHz) for the $X^1\Sigma^+$ states of the KCCH are listed in Table 1. And the leading configurations and their CI coefficients for the low-lying electronic states of the KCCH radical are listed in Table 2. At the CASSCF and CASPT2 levels, the $X^1\Sigma^+$ states is predicted to be the ground state. From the Table 1, we can see that, for the obtained band

lengths $r(K-C)$ using the VDZP and VTZP basis sets of ANO-RCC, the calculated values of the CASPT2 method are closer to the experimental values than the ones of the CASSCF method and other theoretical calculation methods. While, for both levels, most of the obtained band lengths $r(C-C)$ and $r(C-H)$ are slightly longer than the ones in the experiment and some other theoretical calculation methods. At the CASPT2 level, the band lengths $r(C-C)$ and $r(C-H)$ of KCCH molecule in the VTZP basis set of ANO-RCC are in agreement with those in the experiment. So, in order to match the calculated values and experimental values better, and decrease the workload of calculation, we will use the VTZP basis set of ANO-RCC at the CASPT2 level in the following calculations. For KCCH radical, a dominant electronic configuration of $(core)(10\sigma)^2(3\pi_x)^2(3\pi_y)^2$ with the coefficient of -0.95 at the $X^1\Sigma^+$ state is shown in Table 2. The plots of the occupied orbitals for the $X^1\Sigma^+$ state and low-lying transition states of KCCH radical are shown in Figure 2 and Figure 3, respectively.

Fig.1. Atom labels for the KCCH radical in this work

Table 1. Experimental and calculated bond lengths (in Å) and rotational constants (in GHz) for the $X^1\Sigma^+$ of KCCH.

States	Method /Basis set	Optimized Structure			B
		$r(K-C)(\text{\AA})$	$r(C-C)(\text{\AA})$	$r(C-H)(\text{\AA})$	
$X^1\Sigma^+$	CASSCF/ANO-RCC-VDZP	2.629	1.243	1.077	2.509
	CASSCF/ ANO-RCC-VTZP	2.633	1.230	1.067	2.519
	CASPT2/ ANO-RCC-VDZP	2.591	1.249	1.076	2.565
	CASPT2/ ANO-RCC-VTZP	2.569	1.234	1.064	2.571
	^a exp.	2.540	1.233	1.06	2.598
$2^1\Sigma^+$	CASPT2/ ANO-RCC-VTZP	2.896	1.275	1.067	---
$1^1\Pi$	CASPT2/ ANO-RCC-VTZP	3.086	1.278	1.066	---
$2^1\Pi$	CASPT2/ ANO-RCC-VTZP	2.340	1.270	1.062	---
$2^1\Sigma^-$	CASPT2/ ANO-RCC-VTZP	2.416	1.277	1.066	---
$1^3\Sigma^+$	CASPT2/ ANO-RCC-VTZP	4.843	1.210	1.060	---
$1^3\Pi$	CASPT2/ ANO-RCC-VTZP	2.768	1.290	1.066	---
$2^3\Sigma^+$	CASPT2/ ANO-RCC-VTZP	3.073	1.279	1.066	---
$1^3\Sigma^-$	CASPT2/ ANO-RCC-VTZP	2.337	1.271	1.061	---

^aThe experimental values are taken from Ref. 3.

Table 2. Configurations (the weights exceed 5%), CI coefficients, adiabatic and vertical excitation energies, and oscillator strengths for the ground and low-lying excited states of KCCH.^a

State	Configuration		Ea(eV)		Ev(eV)	<i>f</i>
	Occupation	Coeff.	CASSCF	CASPT2		
$2^1\Sigma^+$	$(10\sigma)^2(3\pi_x)^2(3\pi_y)^2$	0.95	0	0	0	$<10^{-8}$
	$(3\pi_x)^\alpha(3\pi_y)^2(5\pi_y)^\beta$	0.95	5.60	5.40	5.43	
$1^1\Pi$	$(3\pi_x)^\alpha(3\pi_y)^2(10\sigma)^\beta$	-0.95	4.32	4.12	5.59	5.0×10^{-2}
$2^1\Pi$	$(3\pi_x)^\alpha(3\pi_y)^2(12\sigma)^\beta$	-0.71	5.99	5.79	7.87	6.8×10^{-2}
$2^1\Sigma$	$(3\pi_x)^2(3\pi_y)^\alpha(5\pi_y)^\beta$	-0.95	5.53	5.34	5.50	$<10^{-8}$
$1^3\Sigma^+$	$(10\sigma)^\alpha(3\pi_x)^2(3\pi_y)^2(11\sigma)^\alpha$	0.93	3.92	3.75	5.15	$<10^{-8}$
$1^3\Pi$	$(3\pi_x)^2(3\pi_y)^\alpha(5\pi_y)^\alpha$	0.95	5.51	5.29	5.73	$<10^{-8}$
$2^3\Sigma^+$	$(3\pi_x)^\alpha(3\pi_y)^2(11\sigma)^\alpha$	-0.95	4.30	4.11	5.53	$<10^{-8}$
$1^3\Sigma^-$	$(3\pi_x)^\alpha(3\pi_y)^2(12\sigma)^\alpha$	-0.73	5.92	5.72	6.82	$<10^{-8}$

^a“ α ” and “ β ” represent a singly occupied orbital with an up or down spin respectively.

Fig.2. Plots of the occupied orbitals for the $X^1\Sigma^+$ state in this work. **Fig.3.** Plots of some transition orbitals for the $X^1\Sigma^+$ state in this work

3.2. The calculations on the adiabatic and vertical Excitation Energies

As the Table 2 shows, we also explore the adiabatic excitation energies (E_a) of the low lying excited states of KCCH. The comparisons the E_a values at the CASSCF and CASPT2 levels indicate that, to calculate the excitation energies, the dynamical electron correlation effects should be considered. For the $1^3\Sigma^+$ state, the E_a value at the CASPT2 level is 3.75 eV, which is the corresponding energy gap between the highest occupied

molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

Using the Franck-Condon theory, we also calculated the vertical excitation energies (E_v) for the eight linear excited states at the CASPT2 level. The E_v value of the $1^1\Pi$ state is 5.59 eV, and the calculated oscillator strength of it is 5.0×10^{-2} . Expect for the $1^1\Pi$ and $2^1\Pi$ state, the calculated oscillator strengths of other states are less than 10^{-8} . Since the oscillator strengths of all the triplet excited states are less than 10^{-8} , the transitions from the $X^1\Sigma^+$ state to the triplet states are spin forbidden transitions, which reflects exactly selection rule.

Table 3. Harmonic vibrational frequencies for the low-lying electronic states of KCCH

State	CASPT2			CASSCF						
	$\nu_1(a1)$	$\nu_2(a1)$	$\nu_3(a1)$	$\nu_1(a1)$	$\nu_2(a1)$	$\nu_3(a1)$	$\nu_4(b1)$	$\nu_5(b1)$	$\nu_4(b2)$	$\nu_5(b2)$
$X^1\Sigma^+$	3387	1978	299	3358	1989	281	656	109	656	109
HF ^a	3427	2095	367	3487	2155	367	658	117	671	106
MP2 ^a	3439	1989	376	3430	1987	358	652	109	648	125
BLYP ^a	3247	1942	380	3347	1942	380	620	113	620	113
B1LYP ^a	3366	2009	379	3436	2018	389	670	117	670	117
mPW1PW91 ^a	3438	2014	383	3430	2013	377	636	115	695	115
$2^1\Sigma^+$	3371	1843	168	3268	1846	145	---	---	---	---
$1^1\Pi$	3358	1825	109	3284	1825	90	160i	366	669	99
$2^1\Pi$	3392	1852	200	3305	1832	165	---	---	---	---
$2^1\Sigma$	3363	1836	175	3287	1841	149	630	140	240i	273
$1^3\Sigma^+$	3440	2061	31	---	---	---	---	---	---	---
$1^3\Pi$	3357	1825	112	3283	1824	92	762i	131	670	96
$2^3\Sigma^+$	3397	1852	207	3311	1834	174	---	---	---	---
$1^3\Sigma^-$	3361	1805	178	3286	1831	152	603	143	221i	269

^aThe values are taken from Ref. 5.

3.3. The Harmonic Vibrational Frequencies

At the CASSCF and CASPT2 levels, we calculate the harmonic vibrational frequencies for the ground and excited states of KCCH in Table 3. It is clear that, for all of the low-lying electronic states, there are three harmonic vibrational frequencies at the CASPT2 level. For the $X^1\Sigma^+$ state, The calculated $\nu_1(a_1)$ C-H stretching mode is 3387 cm^{-1} , which is in agreement with that (3366 cm^{-1}) at the BLYP level.

According to the investigated literatures, the harmonic vibrational frequencies of the low-lying excited states are firstly calculated in this paper. As the Table 3 shows, the excited states are given three harmonic vibrational frequencies at the CASPT2 level, but there are seven calculated values for the $1^3\Pi$, $1^3\Sigma^-$, $1^1\Sigma^-$ and $2^1\Sigma^+$ states at the CASSCF level. Moreover, there is one imaginary frequency for the $1^3\Pi$, $1^3\Sigma^-$, $1^1\Sigma^-$ and $2^1\Sigma^+$ states, indicating that they are not energetic minimum points.

3.4. C-K bond dissociation

To further understand the ground and low-lying excited state properties, we have, in Figure 4, described the PECs (potential energy curves of six low-lying electronic states ($X^1\Sigma^+$, $2^1\Pi$, $1^1\Pi$, $2^1\Sigma^-$, $1^3\Pi$ and $2^3\Sigma^+$) for KCCH radical at the CASSCF/CASPT2 levels, which employed the ANO-RCC-VTZP basis set at the active space including the 10 electrons and 13 orbitals.

The KCCH systems in the four excited states at the $r(\text{C-K})$ value of $6.0\text{ \AA}$ will be called as K^+ -loss dissociation asymptote products of the respective states. As the Figure 4 shows, along the $X^1\Sigma^+$ state, the energy increases monotonically with the $r(\text{C-K})$ value, and there no barriers along the $X^1\Sigma^+$ state of PEC. The CASSCF/CASPT2 energy difference between the asymptote product and the reactant for $X^1\Sigma^+$ state is considered the predicate dissociation energy. The CASSCF/CASPT2 dissociation energy is evaluated to be 4.423 eV for the $\text{KCCH}(X^1\Sigma^+) \rightarrow \text{CCH}(1^1\Sigma) + \text{K}(S^0)$. At the same time, the curves of the $2^1\Pi$ and $2^3\Sigma^+$ states are separated at the beginning, then also tend to coincidence quickly. Otherwise, it is obvious that because the $1^3\Pi$ and $1^1\Pi$ states are the same state.

Fig.4. PEC curves for KCCH

4 Conclusion

In this paper, we reported a combined CASSCF and CASPT2 study of the low-lying electronic states of the KCCH radical in C_{2v} symmetry for the first time. For the $X^1\Sigma^+$ state of the KCCH radical, the calculated harmonic vibrational frequencies are in agreement with theoretical data.

The E_a value of the $1^3\Sigma^+$ state at the CASPT2 level is 3.75 eV , which is the corresponding energy gap between the HOMO and the LUMO.

In our work, we reported for the first time the eight linear excited states for KCCH at the CASPT2 level.

In addition, we indicated that the spin forbidden transitions from the $X^1\Sigma^+$ state to the triplet states. Finally, we have given the PECs of five low-lying electronic states for KCCH radical with the CASSCF/CASPT2(10,13)/ANO-RCC-VTZP level. And the dissociation energy of the $\text{KCCH}(X^1\Sigma^+) \rightarrow \text{CCH}(1^1\Sigma) + \text{K}(S^0)$ is 4.423 eV at the CASSCF/CASPT2 level.

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