A Theoretical Study on the Excited States of the KCCH Radical

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Abstract. Based on the C₃ᵥ 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 X1Σ⁻ to 21Σ⁺, 1Π₁, 2Π, 1Σ⁻, 1Π₀, 2Π and 1Σ⁺, 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 1Π₁, 2Π, 1Π₀, 2Π and 1Σ⁺ 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 (X1Σ⁻→CCH(1Σ⁺)+K⁺(S⁰)) is 4.423 eV at the CASSCF/CASPT2 level.

1 Introduction

Over the past 30 years, the investigations for the metal monocynetylides 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.

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 C₃ᵥ 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)(8σ²(9σ²)²(10σ²)(3π²)(3π²)(3π²). 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
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-configuration 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 XΣ+ 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 shown in Figure 2 and Figure 3, respectively.

Table 1. Experimental and calculated bond lengths (in Å) and rotational constants (in GHz) for the XΣ+ of KCCH.

| States   | Method /Basis set          | r(K-C)(Å) | r(C-C)(Å) | r(C-H)(Å) | B     |
|----------|----------------------------|-----------|-----------|-----------|-------|
| X1Σ+     | 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 |
|          | Exp.                       | 2.540     | 1.233     | 1.06      | 2.598 |
| 2Σ+      | CASPT2/ANO-RCC-VTZP        | 2.896     | 1.275     | 1.067     | ---   |
| 1Π       | CASPT2/ANO-RCC-VTZP        | 3.086     | 1.278     | 1.066     | ---   |
| 2Π       | CASPT2/ANO-RCC-VTZP        | 2.340     | 1.270     | 1.062     | ---   |
| 2Σ+      | CASPT2/ANO-RCC-VTZP        | 2.416     | 1.277     | 1.066     | ---   |
| 1Σ+      | CASPT2/ANO-RCC-VTZP        | 4.843     | 1.210     | 1.060     | ---   |
| 1Π       | CASPT2/ANO-RCC-VTZP        | 2.768     | 1.290     | 1.066     | ---   |
| 2Σ+      | CASPT2/ANO-RCC-VTZP        | 3.073     | 1.279     | 1.066     | ---   |
| 1Σ+      | CASPT2/ANO-RCC-VTZP        | 2.337     | 1.271     | 1.061     | ---   |

*The 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.  

| State   | Occupation | Coeff. | CASSCF | CASPT2 | Ev(eV) | f  |
|---------|------------|--------|--------|--------|--------|----|
| 2Σ+     | (10σ)2(3π)2(3π)2 | 0.95   | 0.95   | 0.95   | -0.71  | 7.87| 6.8×10^2 |
| 1Π      | (3σ)2(3π)2(10σ)2 | -0.95  | 4.32   | 4.12   | 5.59   | 5.0×10^2 |
| 2Π      | (3σ)2(3π)2(12σ)2 | -0.71  | 5.99   | 5.79   | 7.87   | 6.8×10^2 |
| 2Σ+     | (3σ)2(3π)2(5π)2 | -0.95  | 5.53   | 5.34   | 5.50   | <10^4 |
| 1Σ+     | (10σ)2(3π)2(3π)2(11σ)2 | 0.93   | 3.92   | 3.75   | 5.15   | <10^4 |
| 1Π      | (3σ)2(3π)2(5π)2 | 0.95   | 5.51   | 5.29   | 5.73   | <10^4 |
| 2Σ+     | (3σ)2(3π)2(11σ)2 | -0.95  | 4.30   | 4.11   | 5.53   | <10^4 |
| 1Σ+     | (3σ)2(3π)2(12σ)2 | -0.73  | 5.92   | 5.72   | 6.82   | <10^4 |

*a”α” and “β” represent a singly occupied orbital with an up or down spin respectively.
3.2. The calculations on the adiabatic and vertical Excitation Energies

As the Table 2 shows, we also explore the adiabatic excitation energies (Ea) of the low lying excited states of KCCH. The comparisons the Ea 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\(^1\)\(\Sigma^+\) state, the Ea 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 (Ev) for the eight linear excited states at the CASPT2 level. The Ev value of the 11\(^1\)\(\Pi\) state is 5.59 eV, and the calculated oscillator strengths of it is 5.0 \(\times\) 10\(^{-2}\). Expect for the 11\(^1\)\(\Pi\) and 21\(^1\)\(\Pi\) 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 X1\(^1\)\(\Sigma^+\) 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  |
|----------|---------|---------|
|          | \(v_1(a_1)\) | \(v_2(a_1)\) | \(v_3(a_1)\) | \(v_4(a_1)\) | \(v_5(a_1)\) | \(v_6(b_1)\) | \(v_7(b_1)\) | \(v_8(b_2)\) | \(v_9(b_2)\) |
| 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\(^2\)\(\Sigma^+\) | 3371   | 1843   | 168   | 3268   | 1846   | 145   | ---   | ---   | ---   | ---   |
| 1\(^1\)\(\Pi\) | 3358   | 1825   | 109   | 3284   | 1825   | 90    | 160i  | 366   | 669   | 99    |
| 2\(^2\)\(\Sigma\) | 3392   | 1852   | 200   | 3305   | 1832   | 165   | ---   | ---   | ---   | ---   |
| 1\(^1\)\(\Sigma^+\) | 3363   | 1836   | 175   | 3287   | 1841   | 149   | 630   | 140   | 240i  | 273   |
| 1\(^3\)\(\Pi\) | 3440   | 2061   | 31    | ---    | ---    | ---   | ---   | ---   | ---   | ---   |
| 2\(^2\)\(\Sigma^+\) | 3357   | 1825   | 112   | 3283   | 1824   | 92    | 762i  | 131   | 670   | 96    |
| 1\(^3\)\(\Sigma^1\) | 3397   | 1852   | 207   | 3311   | 1834   | 174   | ---   | ---   | ---   | ---   |
| 2\(^3\)\(\Sigma^+\) | 3361   | 1805   | 178   | 3286   | 1831   | 152   | 603   | 143   | 221i  | 269   |

\(^a\)The 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 \( \nu(a_1) \) 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 \( 1^3\Pi, 1^1\Sigma^- \) 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 (\( X^1\Sigma^+ \), \( 2^1\Pi \), \( 1^1\Pi \), \( 2^2\Sigma^- \), \( 1^1\Sigma^- \) and \( 2^1\Sigma^- \)) 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 \( r(C-K) \) value of 6.0 Å 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 \( r(C-K) \) 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 KCCH (\( X^1\Sigma^+ \)→CCH\(^-\)\( (1^1\Sigma^-) \)+K\(^+\)) state. At the same time, the curves of the \( 2^1\Pi \) and \( 2^2\Sigma^- \) states are separated at the beginning, then also tend to coincidence quickly. Otherwise, it is obvious that because the \( 1^1\Pi \) and \( 1^1\Pi \) states are the same state.

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 KCCH (\( X^1\Sigma^+ \)→CCH\(^-\)\( (1^1\Sigma^-) \)+K\(^+\)) is 4.423 eV at the CASSCF/CASPT2 level.

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