

Accurate vibrational spectra and reaction mechanism of the reaction of atomic hydrogen with acetonitrile

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Abstract

The reaction of atomic hydrogen with acetonitrile has been studied extensively at the B3LYP/6-311++G** level. The potential energy surface with zero-point energy correction is drawn. All reaction channels are fully investigated with the vibrational mode analysis to reveal the reaction mechanism. From the calculations, we conclude that the C-addition path is the most favorable and the major products are HCN, CH₄ and C₂H₆.

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1. Introduction

Acetonitrile (CH₃CN) is a colorless liquid with an aromatic odor, used in organic synthesis as a starting material for acetophenone, alpha-naphthaleneacetic acid, thiamine, acetamidine. It is used in the manufacturing of acrylic fibers, pharmaceuticals, perfumes, nitrile rubber, and pesticides. It can be released to the environment during its manufacture and use, from shale oil retorting and combustion of coal [1], incineration of polyacrylonitrile, from automobile exhaust and cigarette smoke. Acetonitrile burns with a luminous flame. When heated to decomposition, it emits highly toxic fumes of cyanides [2]. Moreover, acetonitrile is an important intermediate in a number of combustion processes [3]. The unimolecular reaction of CH₃CN is of minor importance [4], however, the bimolecular reactions of CH₃CN with the highly reactive radical species will be significant in flames. Meanwhile, the reactions of CH₃CN are regarded to be important in the atmospheric chemistry [5]. In this study, the atomic H is considered.

Begue et al. have calculated extensive the vibrational levels of CH₃CN by using a hybrid ab initio and DFT quartic force field [6]. Moreover, reactions of CH₃CN with F, Cl, O (³P), OH

and H have been extensively investigated [7–9], and methods of solving vibrational problems for CH₃CN has been discussed [10], but studies on the reaction mechanism of H+CH₃CN reaction system using vibrational analysis have not been reported. Recently, the analysis of the vibrational modes for the transition state and the intermediates has attracted great attentions. For example, the Mann was interested in the S_N2 reaction of Cl⁻+CH₃Cl [11] and McGrivern interested in the calculations of the dissociation energy of C–H and C–X [12], respectively. And the elucidation of reaction mechanisms via vibrational modes analysis gets more and more attentions [13–16]. In this work, we will use this method to set forth the reaction mechanism of H atom with acetonitrile. The vibrational modes and the force constants of the reactants, the transition states and products are analyzed. The relationships and the changes among them can confirm the rupture of the old bonds and the formation of the new bonds. All multi-atom molecules can produce infrared spectrum because of the rotation and vibration of atom groups. The characteristics of the normal mode vibrations are that all atoms reach their equilibrium points at the same time and come to the maximum simultaneously when vibrating, but the center of mass remains unchanged and the molecule as a whole does not rotate. If *n* is the atom number, for nonlinear molecules there are (3*n*–6) normal vibration modes and for linear molecules there are (3*n*–5) normal vibration modes. In a sense, the numerical values of the frequencies of a molecule can reflect the reaction potential barrier, namely the actual activation energy. If a bond is prolonged and weakened, the frequencies are red-shifted; on

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the contrary, if the bond is shortened and strengthened, the frequencies are blue-shifted. So the changes of vibrational modes must be relative to the transformations of the structures.

2. Computation method

The optimizations of the reactants, intermediates (IM) transition states (TS) and products are performed with the GAUSSIAN 98 programs [17] at the B3LYP/6-311++G** level. The computation procedures have been published previously and proved to be reliable to investigate the molecular structures [18,19]. The popular hybrid density functional B3LYP method, namely Becke's three-parameter nonlocal exchange functional [20] with the nonlocal correlation functional of Lee et al. [21], is used throughout the study. Subsequently, connections of the transition states and products are confirmed by intrinsic

reaction coordinate (IRC) calculations [22]. Structures of all species were fully optimized prior to analytical second derivative calculations and vibrational analysis, and the number of imaginary frequency (0 or 1) confirms whether a local minimum or a transition state. The zero-point vibration energy (ZPE, $1/2 \sum h\omega_1$) scaling and the thermal correction (TC) at 298.15 K calculated were performed.

3. Results and discussions

The optimized structures of various species involved in the reaction of H with CH₃CN are shown in Fig. 1. The total energies and the relative energies with zero-point energy correction are calculated and listed in Table 1. To elucidate the reaction mechanism, the profile of the potential energy surface is drawn (Fig. 2).

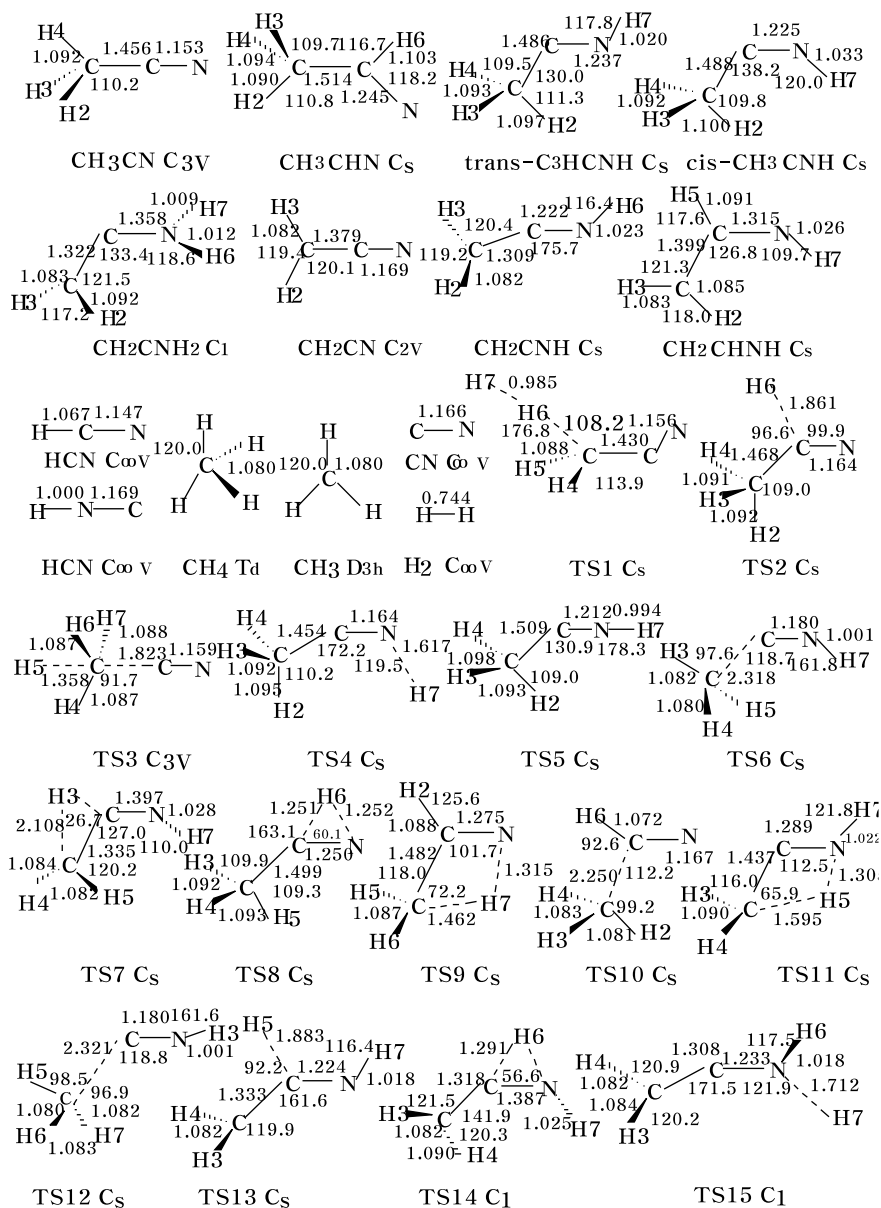


Fig. 1. The optimized geometrical parameters of various species involved in the H+CH₃CN reaction at B3LYP/6-311++G** level. Bond lengths are in Å and bond angles are in degree. Numbers beside the H atoms are sequence numbers to distinguish them.

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