

# Photoinduced Isomerization of *trans*-Acetylene Radical Anion to Vinylidene Radical Anion in 2-Methyltetrahydrofuran

Yoshiteru Itagaki and Masaru Shiotani\*

Faculty of Engineering of Hiroshima University, Higashi-Hiroshima 739-8527, Japan

Received: February 9, 1999; In Final Form: April 25, 1999

Photoinduced reactions of *trans*-HC≡CH<sup>−</sup> in a glassy 2-MTHF matrix were studied by ESR and electron absorption (EA) spectroscopy. ESR and EA spectra were interpreted with the aid of the results of molecular orbital (MO) calculations. The *trans*-HC≡CH<sup>−</sup> was generated and stabilized in the 2-MTHF matrix at 77 K by ionizing irradiation. The ESR parameters observed for the radical anion are  $A_1 = 5.3$ ,  $A_2 = 4.6$ ,  $A_3 = 4.5$  mT for two equivalent <sup>1</sup>H atoms,  $A_{\perp} = 1.5$ ,  $A_{\parallel} = 4.2$  mT for two equivalent <sup>13</sup>C atoms, and  $g_1 = 2.0009$ ,  $g_2 = 2.0024$ ,  $g_3 = 2.0029$  for the **g** tensor. By illuminating with light of  $\lambda \geq 430$  nm, the *trans*-HC≡CH<sup>−</sup> was found to be irreversibly isomerized into the vinylidene radical anion, H<sub>2</sub>C=C<sup>−</sup>, in the matrix. The experimental ESR parameters of H<sub>2</sub>C=C<sup>−</sup> [ $A_1 = 5.4$ ,  $A_2 = 6.0$ ,  $A_3 = 5.7$  mT for two equivalent protons,  $g_1 = 2.0026$ ,  $g_2 = 2.0008$ ,  $g_3 = 2.0026$ ] were fully consistent with the results obtained by semiempirical MO methods, (1) INDO and Analytical Dipolar Calculation method (ANADIP) for isotropic and anisotropic <sup>1</sup>H hyperfine (hf) couplings, respectively, and (2) AM1 for the **g** tensor, for a geometrical structure optimized by ab initio method (Gaussian90/uhf/6-31++G\*\*). The structure of the anions was in agreement with the results obtained from the EA spectroscopic study. The photoinduced isomerization was initiated by the light absorption at  $\lambda \geq 430$  nm of *trans*-HC≡CH<sup>−</sup>. The EA band at  $\lambda_{\max} = 374$  nm observed for H<sub>2</sub>C=C<sup>−</sup> was attributed to the electron transition from the <sup>2</sup>B<sub>2</sub> ground state and to the <sup>2</sup>A<sub>1</sub> excited state.

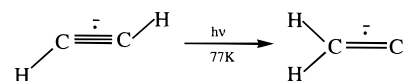
## 1. Introduction

Acetylene is one of the simplest hydrocarbons and a fundamentally important chemical in organic chemistry. The electronic structure of acetylene and its related compounds have been extensively studied both spectroscopically and theoretically, and a number of interesting observations have been reported. For example, a *trans*-bent structure has been reported for acetylene in an excited state<sup>1,2</sup> and also for a radical anion form.<sup>20,21</sup> The interaction between acetylene and some metal atoms has been studied by inert gas matrix isolation (MI) ESR and IR methods.<sup>3–15,18</sup> Kasai<sup>3,4</sup> has reported on ESR results of Al–acetylene and Li–acetylene complexes, and concluded that the former is a  $\sigma$ -complex (Al atom occupying the *trans* site to the unpaired electron orbital) but the latter a  $\pi$ -complex. Manceron et al.<sup>5</sup> have carried out an IR study on the Li–acetylene complex and reported that the acetylene moiety has a *cis*-bent structure.<sup>4</sup> Recently, Picos et al.<sup>6</sup> have reported a *cis*-bent acetylene radical anion stabilized in the ZSM-5 zeolite.

Photoinduced reactions of some alkali metal–acetylene complexes have also been studied.<sup>4,7,8</sup> For example, the Li–*cis*-acetylene complex was reported to be isomerized into Li–vinylidene by photoillumination.<sup>8</sup> A similar observation has been reported for the Na–*cis*-acetylene complex.<sup>7</sup> Nguyen<sup>9</sup> has theoretically predicted that the Li atom interaction with C<sub>2</sub>H<sub>2</sub> stabilizes the vinylidene form and increases the potential energy barrier from the vinylidene form to the acetylene form. However, the potential barrier is evaluated to be quite large in the case of metal-free anions as well ( $\sim 44$  kcal·mol<sup>−1</sup>).<sup>16</sup> Muto et al.<sup>20</sup> have reported an ESR study of the acetylene radical anion in a glassy

3-methylpentane (3-MP) matrix generated by  $\gamma$ -ray irradiation at 77 K. However, the transformation to the vinylidene radical anion was not observed, probably due to its nonpolar soft nature of the matrix.

In the present study the acetylene radical anion was generated in the frozen 2-MTHF glassy matrix at 77 K, and the isomerization was observed in such a polar and rigid matrix. Furthermore, the radical anion produced in 2-MTHF was confirmed to have a *trans*-bent structure based on the comparison of the ESR results with the theoretical calculations, especially on anisotropic <sup>1</sup>H hyperfine (hf) and **g** tensor components. Detailed ESR studies following the photoinduced reaction of the *trans*-acetylene radical anion were carried out using two isotope-labeled acetylenes, DC≡CD and H<sup>13</sup>C≡<sup>13</sup>CH. By photoillumination with the light of  $\lambda \geq 430$  nm it was observed that an intramolecular radical conversion takes place from the *trans*-acetylene radical anion to the vinylidene radical anion. This is the first experimental evidence showing the photoinduced isomerization of the *trans*-HC≡CH<sup>−</sup> in a metal-free system.



The ESR hf structures were much simpler than those previously reported for the metal-bonded systems because they consisted of only the nucleus belonging to acetylene (<sup>13</sup>C and H or D).

An electronic absorption (EA) spectroscopic study on the radical anions was also carried out. The assignment of absorption bands was discussed in terms of molecular orbitals calculated by employing the *semiempirical* method (roh/AM1). The theoretical results were fully consistent with the experimental data.

\* To whom correspondence should be addressed. E-mail: mshiota@ipc.hiroshima-u.ac.jp. Tel/Fax: +81-(824)-24-7736.

## 2. Experiment

The chemicals used in the present experiments were 2-methyltetrahydrofuran (2-MTHF), 3-methylpentane (3-MP), HC≡CH (Takachiho Kougyou, 99%), H<sup>13</sup>C≡<sup>13</sup>CH (CEA, 99 <sup>13</sup>C atom %) and DC≡CD (99 D atom %). 2-MTHF was dried using metallic Na. The HC≡CH, H<sup>13</sup>C≡<sup>13</sup>CH, and DC≡CD were used as received. Solutions containing 1 mol % HC≡CH, H<sup>13</sup>C≡<sup>13</sup>CH, or DC≡CD in 2-MTHF were prepared in a Spectrosil ESR sample tube or an optical quartz cell on a vacuum line after several freeze and thaw cycles. The radical anions of HC≡CH, H<sup>13</sup>C≡<sup>13</sup>CH, and DC≡CD were generated in the frozen 2-MTHF glassy matrix by ionizing radiation using  $\gamma$ -rays from <sup>60</sup>Co at 77 K. Photoillumination was performed using a tungsten lamp with Toshiba filters of R60, Y45, and UV35 whose cutoff efficiency was 50% at  $\lambda = 600, 450,$  and 350 nm, respectively. ESR and EA spectra were recorded with a Bruker ESP-300 spectrometer and a HITACHI U-3400, respectively, in the dark at 77 K.

## 3. Calculation Methods

The optimized structures of the radical anions were calculated by employing an ab initio method of the Gaussian 90 program (uhf/6-31++G\*\*) on a Convex system at the Information Processing Center, Hiroshima University. Both isotropic and anisotropic (dipole) <sup>1</sup>H hyperfine (hf) couplings were evaluated on the basis of the INDO spin densities for the optimized structure. The dipole terms were calculated using a program of "ANADIP (Analytical Dipole)".<sup>22,23</sup>

The principal values of **g** tensor were evaluated using the following equation.

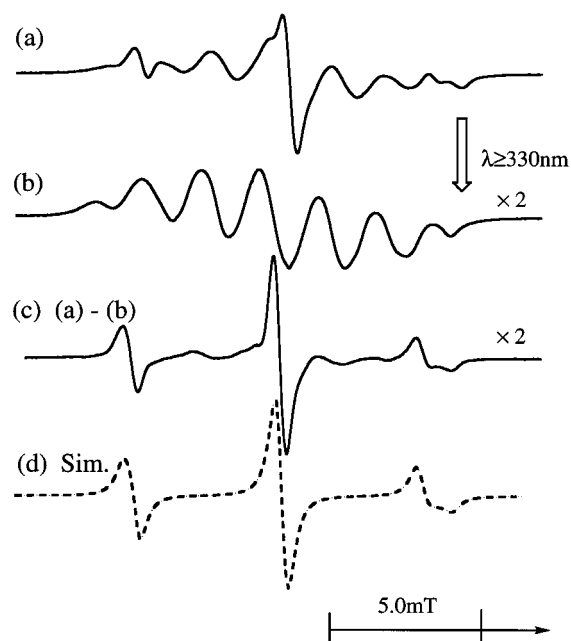
$$g_{ii} = 2.0023 - 2 \sum_n \sum_{kj} \frac{\langle \phi_o | \xi_k L_{ik} \delta_k | \phi_n \rangle \langle \phi_n | L_{ij} \delta_j | \phi_o \rangle}{E_n - E_o} \quad (i = x, y, z) \quad (1)$$

where  $\phi_o$  and  $\phi_n$  are the ground and excited-state molecular orbitals, and  $E_o$  and  $E_n$  the corresponding energies. Affixes  $k$  and  $j$  correspond to the  $k$ th and  $j$ th atom in the molecule.  $L_{ik}$  and  $L_{ij}$  are the  $i$ th component of orbital angular momentum operator, which is effective for the orbitals of the  $k$ th and  $j$ th atoms, and  $\xi_k$  is the spin-orbital coupling constant for the  $k$ th atom. The orbitals ( $\phi_o$  and  $\phi_n$ ) and energies ( $E_o$  and  $E_n$ ) were evaluated by a semiempirical rohf/AM1 method for the optimized structures.

The assignments of the electron absorption spectra were carried out using semiempirical rohf/AM1 method for the optimized structures.

## 4. Results and Discussions

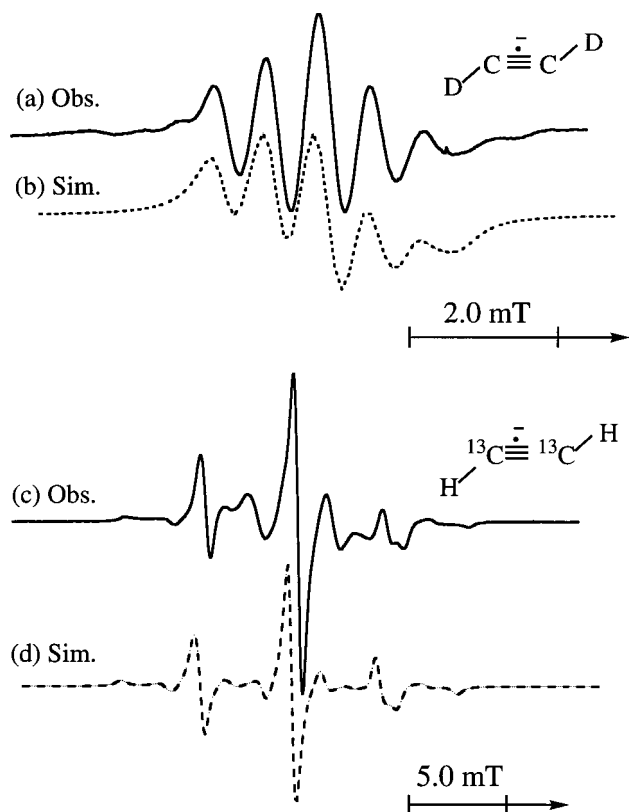
**a. Generation of *trans*-Acetylene Radical Anion.** The ESR spectrum of  $\gamma$ -irradiated 2-MTHF containing 1 mol % HC≡CH at 77 K consists of at least two components, i.e., a sharp central singlet at **g** = 2.0023 due to trapped electron ( $e_t^-$ ) and a broad septet hf line with ca. 1.9 mT hf coupling attributable to the 2-MTHF radical (2-methyl-2-tetrahydrofuryl radical). When the glassy sample was illuminated with the light of  $\lambda \geq 580$  nm, the singlet of  $e_t^-$  disappeared and concomitantly a triplet became visible, as shown in Figure 1a. The newly appeared triplet was observed for only the sample containing HC≡CH and was attributed to a solute radical. The results suggest that the triplet is attributable to the radical formed by an electron attachment to HC≡CH, i.e., acetylene radical anion or radical generated secondarily via the radical anion. Upon further



**Figure 1.** ESR spectra of a solid solution of 1 mol % of HC≡CH in 2-MTHF irradiated by  $\gamma$ -rays at 77 K: (a) observed after illumination with light of  $\lambda \geq 580$  nm; (b) after illumination with light of  $\lambda \geq 330$  nm; (c) spectrum obtained by subtracting spectrum (b) from spectrum (a); (d) spectrum simulated to (c) by using the <sup>1</sup>H hf couplings and **g** tensor listed in Table 1 and a Gaussian line width of  $\Delta H_{msl} = 0.45$  mT.

illumination of the sample with light of  $\lambda \geq 330$  nm, the spectrum due to the solute radical completely disappeared and only the spectrum due to the 2-MTHF radical was observed (Figure 1b). An ESR spectrum of the solute anion radical was obtained by subtracting the spectrum in Figure 1b from that in Figure 1a. The result is shown in Figure 1c; the triplet pattern affected by slight **g** and <sup>1</sup>H hf anisotropy is clearly revealed. The triplet was reproduced in spectral simulation by using the following ESR parameters. **A** and **g** tensors:  $A_1 = 5.3, A_2 = 4.6, A_3 = 4.5$  mT for two equivalent hydrogens,  $g_1 = 2.0009, g_2 = 2.0024, g_3 = 2.0029$  (Figure 1d). No appreciable change was observed in the simulated spectra when the orientation of  $\tilde{A}$  tensor relative to the  $\tilde{A}$  tensor within the  $x$ - $y$  molecular plane was changed from 0° to 30°. The spectral pattern should change significantly if the radical has a *cis*-structure, since the bending of the C-H bonds results in rotation of the  $\tilde{A}$  tensor in the opposite directions (we thank one of the reviewers for suggesting this comment).

When DC≡CD was used instead of HC≡CH, the triplet was changed into an anisotropic quintet due to two magnetically equivalent deuteriums, as shown in Figure 2a; the hf splitting decreased, as expected, by a factor of 6.5, the ratio of the nuclear magnetic moment of <sup>1</sup>H and <sup>2</sup>D. Thus, the triplet was attributable to the two magnetically equivalent protons belonging to the solute molecule. Three isomer radical ions of acetylene, *trans*-HC≡CH<sup>-</sup> isomers, *cis*-HC≡CH<sup>-</sup>, and H<sub>2</sub>C=C<sup>-</sup>, are candidate species responsible for the triplet because they have two magnetically equivalent protons. The <sup>1</sup>H hf coupling constants of the latter two radical anions have been reported to be considerably larger than the presented values: 6.3–7.3 mT for *cis*-HC≡CH<sup>-</sup><sup>13,14</sup> and 5.7–6.0 mT for H<sub>2</sub>C=C<sup>-</sup>.<sup>8,13,24</sup> The parameters we observed are very close to those reported for the *trans*-HC≡CH<sup>-</sup> in 3-MP by Muto et al.<sup>20</sup> Thus, the *trans*-HC≡CH<sup>-</sup> was concluded to be formed in 2-MTHF by ionizing radiation at 77 K.

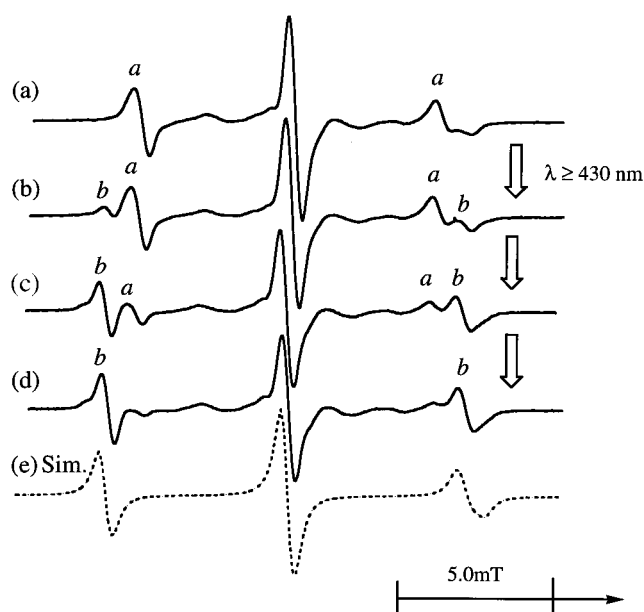


**Figure 2.** Experimental ESR spectra of (a) *trans*-DC≡CD<sup>-</sup> and (c) *trans*-H<sup>13</sup>C≡<sup>13</sup>CH<sup>-</sup> in the 2-MTHF matrix at 77 K together with the simulated spectra (dotted lines) calculated by using the EPR parameters given in the text.

The ESR spectrum of *trans*-H<sup>13</sup>C≡<sup>13</sup>CH<sup>-</sup> in 2-MTHF at 77 K is shown in Figure 2c. The spectrum consists of an anisotropic triple-triplet due to two sets of magnetically equivalent protons and carbons. The following axially symmetric hf couplings were obtained for the two equivalent <sup>13</sup>C atoms from computer simulations:  $A_{\perp}({}^{13}\text{C}) = 1.5$  mT and  $A_{\parallel}({}^{13}\text{C}) = 4.2$  mT (Figure 2d). The perpendicular value is slightly different from the reported one for the same radical anion in the 3-MP matrix:<sup>20</sup>  $A_{\perp}({}^{13}\text{C}) = \text{ca. } 0$  mT and  $A_{\parallel}({}^{13}\text{C}) = 4.2$  mT.

**b. Photoinduced Isomerization.** When the sample showing the spectrum of *trans*-HC≡CH<sup>-</sup> was illuminated with  $\lambda \geq 430$  nm, the outer components of the triplet (marked as "a" in Figure 3) decreased with a concomitant increase of peaks further out in the spectrum (marked as "b" in the figure). After 20 min of photoillumination, signals "a" were completely replaced by the spectrum of the new triplet signals, "b". The latter triplet has the following ESR parameters:  $A_1({}^1\text{H}) = 5.4$  mT,  $A_2({}^1\text{H}) = 6.0$  mT,  $A_3({}^1\text{H}) = 5.7$  mT,  $g_1 = 2.0026$ ,  $g_2 = 2.0008$ ,  $g_3 = 2.0026$ . Note that, in this case too, no appreciable change was observed in the theoretical spectra when the principal directions of <sup>1</sup>H hf values relative to the **g** tensor in the *x-y* molecular plane were changed from 0° to 30°. The total radical concentration was found to be constant in the course of the photoillumination. This result strongly suggests that the present photoinduced reaction can be due to an intramolecule radical conversion, not an intermolecular conversion.

The newly appeared triplet has a larger <sup>1</sup>H hf coupling than the *trans*-HC≡CH<sup>-</sup>. Either *cis*-HC≡CH<sup>-</sup> or H<sub>2</sub>C=C<sup>-</sup> can be a candidate radical for it because they have two magnetically equivalent protons and large <sup>1</sup>H hf splittings comparable to the present experimental ones. However, these two are indistinguishable based only on the value of the <sup>1</sup>H hf coupling.

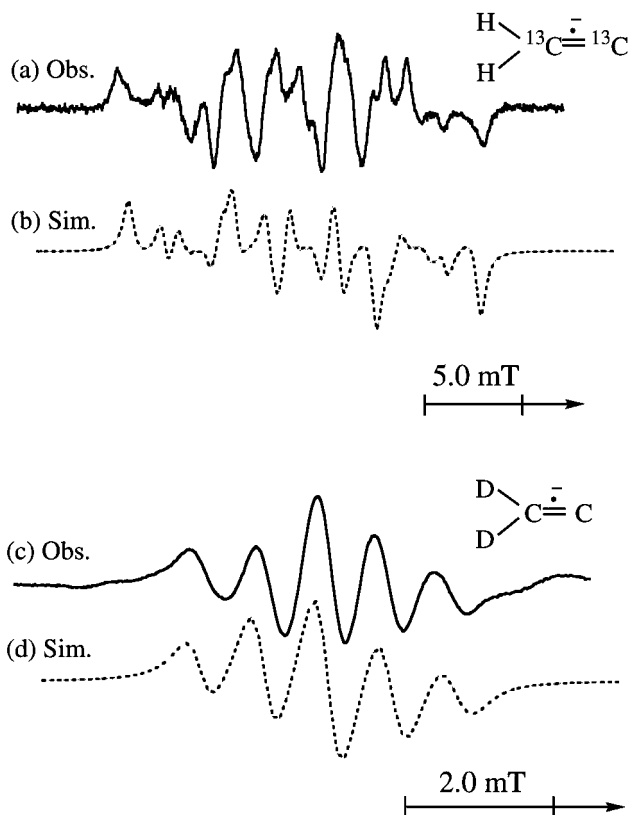


**Figure 3.** Successive change in the ESR spectrum of *trans*-HC≡CH<sup>-</sup> (a) to that of H<sub>2</sub>C=C<sup>-</sup> upon illumination with light of  $\lambda \geq 430$  nm. Spectrum (a) was observed immediately after  $\gamma$ -irradiation at 77 K in dark. Spectra (b), (c), and (d) were recorded after 5, 10, and 20 min illumination. (e) spectrum simulated to (d) by using the <sup>1</sup>H hf couplings and **g** tensor listed in Table 1 and a Gaussian line width of  $\Delta H_{\text{msl}} = 0.45$  mT.

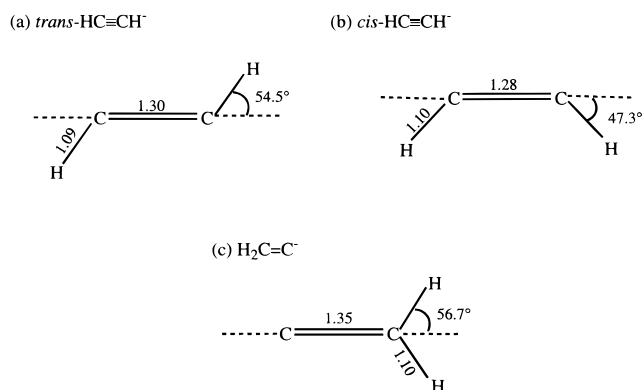
Observation of <sup>13</sup>C hf coupling is essential for the identification because *cis*-HC≡CH<sup>-</sup> has two equivalent carbons, whereas H<sub>2</sub>C=C<sup>-</sup> has two nonequivalent carbons. Thus, the same experiments were repeated using H<sup>13</sup>C≡<sup>13</sup>CH as the solute. In the ESR spectrum recorded before the photoillumination, the axial symmetric hf coupling were clearly observed for the two equivalent <sup>13</sup>C atoms of *trans*-H<sup>13</sup>C≡<sup>13</sup>CH<sup>-</sup> as mentioned in the foregoing section. The ESR spectrum observed after photoillumination turned out to be too complicated to determine accurate <sup>13</sup>C anisotropic splittings from a direct spectrum analysis (see Figure 4a). It is obvious, however, that the spectrum consists of two nonequivalent carbons because the triplet due to the two equivalent protons cannot be seen separately in the spectrum. Furthermore, this spectrum has almost the same line shape as that reported by Taarit et al.<sup>24</sup> Thus the radical formed after the photoillumination can be attributable to H<sub>2</sub>C=C<sup>-</sup> and the possible occurrence of *cis*-HC≡CH<sup>-</sup> was ruled out.

The best fit simulation spectrum of H<sub>2</sub>C=C<sup>-</sup> was obtained by using the following <sup>13</sup>C hf splittings:  $A_1 = 2.1$  mT,  $A_2 = 1.7$  mT,  $A_3 = 2.4$  mT for carbon of H<sub>2</sub>C= and  $A_1 = 5.8$  mT,  $A_2 = 0.5$  mT,  $A_3 = 1.0$  mT for that of =C<sup>-</sup> (Figure 4b). Note that the values noted in the beginning of this section were used for the <sup>1</sup>H hf couplings and **g** values in the simulation. The <sup>1</sup>H hf couplings were fairly well reproduced by the theoretical calculations for H<sub>2</sub>C=C<sup>-</sup>, as will be mentioned. Furthermore, they are in agreement with the values reported for Li<sup>+</sup>(H<sub>2</sub>C=C<sup>-</sup>) by Kasai.<sup>10</sup> Furthermore, we confirmed that the same reaction proceeded when DC≡CD was used instead of HC≡CH (Figure 4c). Thus, it was concluded that the photoisomerization from *trans*-HC≡CH<sup>-</sup> to H<sub>2</sub>C=C<sup>-</sup> occurred in a rigid glassy matrix of 2-MTHF at 77 K.

**c. Theoretical Calculations of  $\tilde{A}$  and  $\tilde{g}$  Tensor Components.** It was concluded in the previous sections that the *trans*-HC≡CH<sup>-</sup> was formed in the irradiated solid solution of acetylene in 2-MTHF at 77 K and was isomerized to H<sub>2</sub>C=C<sup>-</sup> by the photoillumination with  $\lambda \geq 430$  nm. In this section the



**Figure 4.** ESR spectra of (a)  $\text{H}_2^{13}\text{C}=\text{C}^{13}\text{C}^-$  and (c)  $\text{D}_2\text{C}=\text{C}^-$  in the 2-MTHF matrix at 77 K together with the simulated spectra (dotted lines) calculated by using EPR parameters given in the text.

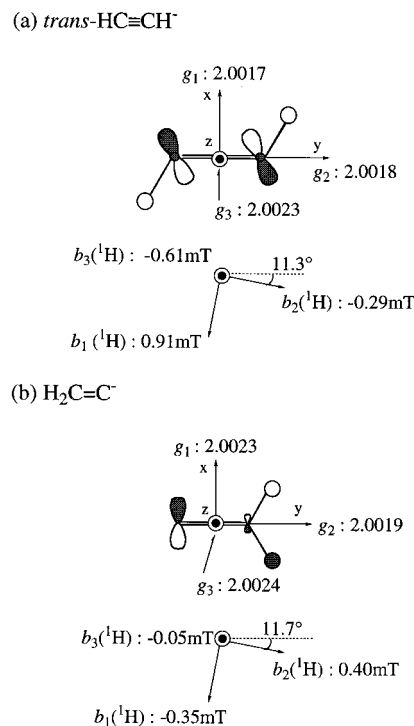


**Figure 5.** Optimized structures of (a)  $\text{trans-HC}\equiv\text{CH}^-$ , (b)  $\text{cis-HC}\equiv\text{CH}^-$ , and (c)  $\text{H}_2\text{C}=\text{C}^-$  by the ab initio method (Gaussian 90/uhf/6-31++G\*\*). The bond length is in Å.

ESR  $\tilde{A}$  and  $\tilde{g}$  tensor components of the radical anions were theoretically calculated and compared with the experimental ones.

The optimized structures of  $\text{trans-HC}\equiv\text{CH}^-$ ,  $\text{cis-HC}\equiv\text{CH}^-$ , and  $\text{H}_2\text{C}=\text{C}^-$  were calculated by the ab initio (uhf/6-31++G\*\*) method and resulted in all the planar ones. The geometrical parameters calculated are summarized in Figure 5. Total energies were  $-76.751$ ,  $-76.741$ , and  $-76.770$  hartree for  $\text{trans-HC}\equiv\text{CH}^-$ ,  $\text{cis-HC}\equiv\text{CH}^-$ , and  $\text{H}_2\text{C}=\text{C}^-$ , respectively;  $\text{H}_2\text{C}=\text{C}^-$  was calculated to be the most stable anion among these three anions. Consistent with the present results, ab initio MP2 level of calculations Eriksson et al. also resulted in the radical anion of  $\text{H}_2\text{C}=\text{C}^-$  being the most stable.<sup>19</sup>

The isotropic and anisotropic hf couplings were calculated by the INDO method and ANADIP,<sup>22,23</sup> respectively, for the optimized geometries of three radical anions (uhf/6-31++G\*\*).



**Figure 6.** Theoretical principal values and axes of  $^1\text{H}$  hf and  $\mathbf{g}$  tensors for (a)  $\text{trans-HC}\equiv\text{CH}^-$  and (b)  $\text{H}_2\text{C}=\text{C}^-$  obtained by INDO and ANADIP calculations for the optimized structures given in Figure 5.

The calculated  $^1\text{H}$  hf couplings and  $\mathbf{g}$  values are summarized in Table 1 and compared with experimental ones. The calculated isotropic  $^1\text{H}$  hf couplings to the equivalent protons are 4.12 ( $\text{trans-HC}\equiv\text{CH}^-$ ), 8.60 ( $\text{cis-HC}\equiv\text{CH}^-$ ), and 8.08 mT ( $\text{H}_2\text{C}=\text{C}^-$ ). The isotropic  $^1\text{H}$  hf coupling (4.9 mT) observed before the photoillumination is very close to the value calculated for  $\text{trans-HC}\equiv\text{CH}^-$ ; for the latter two radical anions the calculated hf values were about 2 times larger than the experimental one.

In addition to the isotropic  $^1\text{H}$  hf couplings, the anisotropic  $^1\text{H}$  hf couplings and their principal axes were evaluated by the ANADIP method based on the INDO spin density distribution for the three different  $\text{C}_2\text{H}_2$  radical anions. The calculated results for  $\text{trans-HC}\equiv\text{CH}^-$  and  $\text{H}_2\text{C}=\text{C}^-$  are summarized in Figure 6 together with the schematic representation of the associated singly occupied molecular orbitals (SOMOs). The anisotropic  $^1\text{H}$  hf couplings calculated for  $\text{trans-HC}\equiv\text{CH}^-$  are  $b_1(^1\text{H}) = 0.91$ ,  $b_2(^1\text{H}) = -0.29$ , and  $b_3(^1\text{H}) = -0.61$  mT. They are in rather good agreement with the experimental ones:  $b_1(^1\text{H}) = 0.5$ ,  $b_2(^1\text{H}) = -0.2$ , and  $b_3(^1\text{H}) = -0.3$  mT. Furthermore the anisotropic  $^1\text{H}$  hf couplings calculated for  $\text{H}_2\text{C}=\text{C}^-$  agreed fairly well with the experimental values derived from the spectrum obtained after the photoillumination:  $b_1(^1\text{H}) = -0.3$ ,  $b_2(^1\text{H}) = 0.3$ , and  $b_3(^1\text{H}) = 0.0$  mT (exp) vs  $b_1(^1\text{H}) = -0.35$ ,  $b_2(^1\text{H}) = 0.40$ , and  $b_3(^1\text{H}) = -0.05$  mT (cal). For both  $\text{trans-HC}\equiv\text{CH}^-$  and  $\text{H}_2\text{C}=\text{C}^-$  the principal axes of  $b_1$  and  $b_2$  were calculated to be in the molecular plane, but with about  $11^\circ$  deviation from the molecular  $x$ ,  $y$  axes (see Figure 6), whereas, the axis of  $b_3$  was calculated to be parallel to the molecular  $z$ -axis, as expected. We have confirmed that no appreciable spectral change was observed in the calculated spectra when the orientation of the  $\mathbf{A}$  tensor relative to the  $\mathbf{g}$  tensor was changed from  $0^\circ$  to  $30^\circ$ , as mentioned already. This suggests that the calculated anisotropic  $^1\text{H}$  hf couplings can be directly compared with the experimental values.

The theoretical  $\mathbf{g}$  tensor components were calculated for the three different radical anions of  $\text{C}_2\text{H}_2$ . The results are sum-



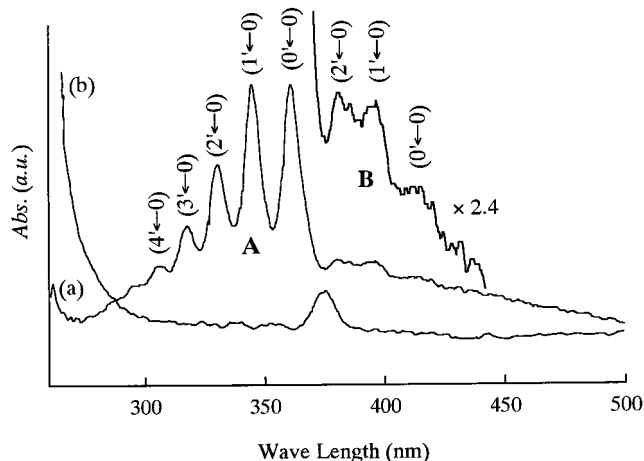
TABLE 1: Experimental  $^1\text{H}$  and  $^{13}\text{C}$  hf Couplings in mT and  $g$  Values of  $\text{C}_2\text{H}_2^-$  Radical Anions Together with Calculated Ones

$\text{C}_2\text{H}_2^-$ radical	matrix	$g_{\text{iso}}$	$a_{\text{iso}}$	principal values <sup>a</sup>			ref	
				$x$	$y$	$z$		
Experimental Values								
<i>trans</i> - $\text{HC}\equiv\text{CH}^-$	2-MTHF	$g$	2.0021	2.0024	2.0009	2.0029	this work	
		$^1\text{H}$	4.8	(-0.2)	0.5	(-0.3)		
	3-MP	$^{13}\text{C}$	2.4	1.8	(-0.9)	(-0.9)	20	
		$g$	2.0020	2.0023	2.0011	2.0027		
<i>cis</i> - $\text{HC}\equiv\text{CH}^-$	HZSM-5	$^1\text{H}$	4.8	(-0.1)	0.5	(-0.5)	6	
		$^{13}\text{C}$	1.4-1.5	2.8	(-1.4)	(-1.4)		
	Ar	$g$	2.0021	2.0032	2.0008	2.0023	8	
		$^1\text{H}$	6.5	(-0.4)	0.3	0.1		
$\text{Li}^+(\text{cis}\text{-}\text{HC}\equiv\text{CH}^-)$	Ar	$^{13}\text{C}$	13.0	(-0.8)	2.0	(-1.1)	17	
		$g$	2.0023	2.0008	2.0032	2.0029		
	Ar	$^1\text{H}$	6.65	(-0.45)	0.45	0	8	
		$^{13}\text{C}$	7.4 ± 1					
$\text{H}_2\text{C}=\text{C}^-$	2-MTHF	$g$	2.0020	2.0008	2.0026	2.0026	this work	
		$^1\text{H}$	5.7	0.3	(-0.3)	0		
	MgO	$^{13}\text{C}_1$	(-2.1)	0.4	0	(-0.3)	24	
		$^{13}\text{C}_2$	1.4	(-2.4)	4.4	(-1.9)		
$\text{Li}^+(\text{H}_2\text{C}=\text{C}^-)$	Ar	$^1\text{H}$	5.8	4.1	(-2.1)	(-2.1)	8	
		$^{13}\text{C}_1$	3.6	2.0008	2.0031	2.0023		
	Ar	$g$	2.0021	2.0008	2.0031	2.0023	8	
		$^1\text{H}$	5.7	0.2	(-0.2)	0		
Theoretical Values								
<i>trans</i> - $\text{HC}\equiv\text{CH}^-$ uhf/INDO + ANADIP		$g$	2.0019	2.0018	2.0017	2.0023	this work	
		$^1\text{H}$	4.12	-0.29	0.91	-0.61		
		$^{13}\text{C}$	8.61	1.97	-0.99	-0.98		
PWP/IGLO-III		$^1\text{H}$	4.885	-0.305	0.610	-0.305	6	
		$^{13}\text{C}$	2.993	2.420	-1.210	-1.210		
		$g$	2.0022	2.0017	2.0024	2.0024		this work
<i>cis</i> - $\text{HC}\equiv\text{CH}^-$ uhf/INDO + ANADIP		$^1\text{H}$	8.60	-0.36	0.70	-0.34	6	
		$^{13}\text{C}$	13.8	-0.53	1.12	-0.59		
		$^1\text{H}$	6.500	-0.252	0.504	-0.252		
PWP/IGLO-III		$^{13}\text{C}$	13.215	-0.839	1.678	-0.839	19	
		$^1\text{H}$	6.12	-0.41	0.51	-0.10		
		$^{13}\text{C}$	7.44	-0.89	1.79	-0.90		
$\text{H}_2\text{C}=\text{C}^-$ uhf/INDO + ANADIP		$g$	2.0019	2.0019	2.0023	2.0024	this work	
		$^1\text{H}$	8.08	0.40	-0.35	-0.05		
		$^{13}\text{C}_1$	-2.09	0.42	-0.11	-0.32		
		$^{13}\text{C}_2$	1.66	-2.49	4.39	-1.90		
PWP/IGLO-III		$^1\text{H}$	5.382	0.296	-0.148	-0.148	6	
		$^{13}\text{C}_1$	-1.603	0.382	-0.191	-0.191		
		$^{13}\text{C}_2$	1.86	-2.415	4.830	-2.415		

<sup>a</sup> Principal values of hf are shown as a dipole term,  $b_{ii}$  ( $i = x, y, z$ ). <sup>b</sup> The  $^{13}\text{C}_1$  and  $^{13}\text{C}_2$  corresponds to protonated and unprotonated carbons, respectively;  $\text{H}_2\text{C}_1=\text{C}_2$ .

marized in Table 1 and Figure 6. The experimental and theoretical  $g$  values can be seen for the *trans* anion:  $g_1 = 2.0009$ ,  $g_2 = 2.0024$ ,  $g_3 = 2.0029$  (exp) vs  $g_1 (=g_x) = 2.0017$ ,  $g_2 (=g_y) = 2.0018$ ,  $g_3 (=g_z) = 2.0023$  (cal). Note that the axes of  $x$ ,  $y$ ,  $z$  refer to the molecular system. A rather large difference can be seen for the  $g_1$  value. This may come from the AM1 calculations, which overestimate the energy differences between the SOMO and other orbitals,  $\Delta E = E_n - E_o$ . However, consistent with our attribution of the experimental spectrum, the negative shift of  $g_1$  from the free electron value ( $g = 2.0023$ ) is reproduced from the *trans* anion, but not for the *cis* anion. Furthermore, the calculated  $g$  values for  $\text{H}_2\text{C}=\text{C}^-$  were found in a range comparable with the experimental ones, although the agreement is not perfect.

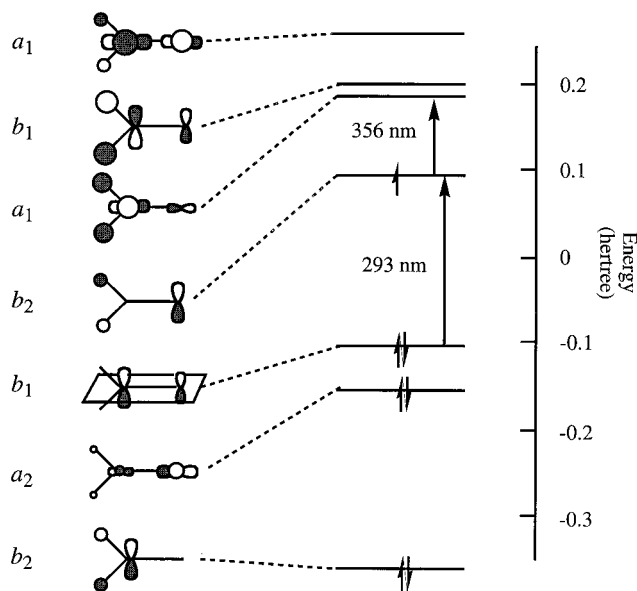
**d. Electronic Absorption Spectra.** Figure 7 shows the electronic absorption (EA) spectra of (a) *trans*- $\text{HC}\equiv\text{CH}^-$  and (b)  $\text{H}_2\text{C}=\text{C}^-$  in 2-MTHF at 77 K. The former shows a strong absorption band at a region from 300 to 362 nm with the vibrational structures of  $1120\text{--}1390\text{ cm}^{-1}$  (A) and a weak band at  $\lambda \geq 420\text{ nm}$  with that of ca.  $1060\text{ cm}^{-1}$  (B). These parameters are summarized in Table 2. The EA spectrum of *trans*- $\text{HC}\equiv\text{CH}^-$



**Figure 7.** Electronic absorption spectra of (a) *trans*- $\text{HC}\equiv\text{CH}^-$  and (b)  $\text{H}_2\text{C}=\text{C}^-$  in 2-MTHF at 77 K. (a) and (b) were observed immediately after the  $\gamma$ -ray irradiation and after 20 min light illumination with  $\lambda \geq 430\text{ nm}$ .

**TABLE 2: Vibronic and Vibrational Transition Parameters of *trans*-CH≡CH<sup>-</sup> in 2-MTHF**

	vibronic transitions (nm)					vibrational structure (cm <sup>-1</sup> )			
	(0' ← 0)	(1' ← 0)	(2' ← 0)	(3' ← 0)	(4' ← 0)	(1' ← 0')	(2' ← 1')	(3' ← 2')	(4' ← 3')
band A (strong)	360.9	343.7	329.7	317.2	306.3	1390	1230	1200	1120
band B (weak)	412.5	395.3		381.3		1060	930		



**Figure 8.** Energy level diagram of H<sub>2</sub>C=C<sup>-</sup> together with schematics of the associated molecular orbitals calculated by the semiempirical method using the rohf/AM1 level of theory for the optimized structure with 6-31++G\*\* basis sets (see Figure 5c). The arrows (†) marked in the figure show possible electron transitions in the radical anion.

CH<sup>-</sup> in the 3-MP matrix has been recently reported on by Muto et al.<sup>25</sup> The two absorption bands have been attributed to the electronic transitions from the ground state <sup>2</sup>A<sub>g</sub> to the excited states to <sup>2</sup>B<sub>u</sub> (strong band) with the vibrational structures to C≡C stretching for the former and to <sup>2</sup>A<sub>u</sub> (weak band) with those to H–C bending for the latter. In the present study we could fully confirm their EA spectral attribution to *trans*-HC≡CH<sup>-</sup>.

The photoinduced isomerization from *trans*-HC≡CH<sup>-</sup> to H<sub>2</sub>C=C<sup>-</sup> was observed to take place by light illumination with the light of λ ≥ 430 nm in 2-MTHF. This observation suggests that the photoreaction is initiated by the light absorption at the band B of *trans*-HC≡CH<sup>-</sup>, i.e., the electronic transition from ground state <sup>2</sup>A<sub>g</sub> to an excited <sup>2</sup>A<sub>u</sub> state.

The EA spectrum of H<sub>2</sub>C=C<sup>-</sup> shows a single sharp absorption at λ = 374 nm, which is not accompanied by vibrational structure. To assign the observed band, electronic energy levels were calculated for the radical anion by the semiempirical method employing the rohf/AM1 level. The resulting energy diagram is shown in Figure 8. The SOMO of H<sub>2</sub>C=C<sup>-</sup> resulted in a b<sub>2</sub> orbital. For the H<sub>2</sub>C=C<sup>-</sup> with C<sub>2v</sub> symmetry, the x, y, z components of the dipole moment operator, **r**, belong to the representations of B<sub>1</sub>, B<sub>2</sub>, and A<sub>1</sub>, respectively. Thus, the following five electron transitions are allowed; ⟨a<sub>1</sub>|z(a<sub>1</sub>)|a<sub>1</sub>⟩, ⟨b<sub>1</sub>|z(a<sub>1</sub>)|b<sub>1</sub>⟩, ⟨b<sub>2</sub>|z(a<sub>1</sub>)|b<sub>2</sub>⟩, ⟨b<sub>1</sub>|x(b<sub>1</sub>)|a<sub>1</sub>⟩, and ⟨b<sub>2</sub>|y(b<sub>2</sub>)|a<sub>1</sub>⟩. Referring the calculated electronic energy levels shown in Figure 8, the most probable electronic transition responsible for the observed band (λ = 374 nm) is that from the <sup>2</sup>B<sub>2</sub> state (or SOMO) to the lowest excited state <sup>2</sup>A<sub>1</sub> state (or LUMO), i.e., λ = 356 nm.

## 5. Concluding Remarks

The acetylene radical anion was successfully generated in a glassy 2-MTHF matrix by ionizing irradiation at 77 K. The ESR

spectra of normal as well as <sup>13</sup>C and <sup>2</sup>D isotopically labeled acetylene radical anions were observed in the matrix at the same temperature. The acetylene radical anions were attributed to a *trans*-bent geometrical structure based on the observed <sup>1</sup>H, <sup>2</sup>D, and <sup>13</sup>C hf couplings and **g** tensor. The *trans*-HC≡CH<sup>-</sup> was found to be photoisomerized to H<sub>2</sub>C=C<sup>-</sup> in the 2-MTHF matrix by illumination with the light of λ ≥ 430 nm. When 3-MP was used as a matrix molecule instead of 2-MTHF, however, no such isomerization reaction was observed: the *trans*-HC≡CH<sup>-</sup> decayed monotonically in the course of light illumination. The reason can be due to the nature of 3-MP, which gives a nonpolar and soft matrix at 77 K. 2-MTHF is a polar molecule that gives a rigid glassy matrix at 77 K. In fact, the electrons generated by ionizing irradiation are stabilized in 2-MTHF at 77 K, as observed in the present experiments. Such a polar and rigid nature of the 2-MTHF matrix can be responsible for the reason both *trans*-HC≡CH<sup>-</sup> and H<sub>2</sub>C=C<sup>-</sup> are thermally stable so that the photoisomerization reaction from the former to the latter was observed by the present ESR and EA spectroscopic study. Comparing the present case with that of Li<sup>+</sup>(HC≡CH)<sup>-</sup>, which was reported to be photoisomerized into Li<sup>+</sup>(H<sub>2</sub>C=C)<sup>-</sup>,<sup>8</sup> one expects 2-MTHF to behave like a countercationic species to stabilize the C<sub>2</sub>H<sub>2</sub> radical anions as Li<sup>+</sup> for the Li–acetylene complex.

The theoretical isotropic and anisotropic <sup>1</sup>H hf coupling were calculated for the optimized geometries of *trans*-HC≡CH<sup>-</sup> and H<sub>2</sub>C=C as well as the **g** tensors. By referring the theoretical ESR parameters with the experimental ones, we could reconfirm that our ESR spectral assignment was valid. Furthermore, the present theoretical calculations provided us important information about the orientation of <sup>1</sup>H hf principal values with respect to the **g** tensor components, the latter being generally coincident with molecular coordinate system.

By observing the electronic absorption spectrum of *trans*-HC≡CH<sup>-</sup> in the 2-MTHF matrix, the isomerization reaction was suggested to take place via the electron transition from <sup>2</sup>A<sub>g</sub> to <sup>2</sup>A<sub>u</sub>, which was observed as a weak absorption band at λ<sub>max</sub> ≤ 420 nm. Furthermore, the electronic absorption spectrum of H<sub>2</sub>C=C<sup>-</sup> with a maximum at λ<sub>max</sub> = 374 nm was suggested to be attributable to the electron transition from the ground state <sup>2</sup>B<sub>2</sub> to the excited state <sup>2</sup>A<sub>1</sub>.

**Acknowledgment.** The present study was partially supported by a subsidy for Science Research of the Japanese Ministry of Education (Grant No. 08240105). We thank Dr. Mikael Lindgren and Dr. Paul. H. Kasai for valuable comments.

## References and Notes

- (1) (a) Ingold, C. K.; King, G. W. *J. Chem. Soc.* **1953**, 2702. (b) Ingold, C. K.; King, G. W. *ibid.*, **1953**, 2704.
- (2) Innes, K. K. *J. Chem. Phys.* **1954**, *22*, 863.
- (3) Kasai, P. H.; McLeod, Jr, D.; Watanabe, T. *J. Am. Chem. Soc.* **1980**, *102*, 179.
- (4) Kasai, P. H. *J. Phys. Chem.* **1982**, *86*, 4092.
- (5) Manceron, L.; Andrews, L. *J. Am. Chem. Soc.* **1985**, *107*, 563.
- (6) Picos, E. A.; Werst, D. W.; Trifunac, A. D.; Eriksson, L. A. *J. Phys. Chem.* **1996**, *100*, 8408.
- (7) Kasai, P. H. *J. Am. Chem. Soc.* **1982**, *104*, 1165.
- (8) Kasai, P. H. *J. Am. Chem. Soc.* **1992**, *114*, 3299.

- (9) Nguyen, M. T. *J. Phys. Chem.* **1988**, 92, 1426.  
(10) Kasai, P. H.; McLeod, Jr. D. *J. Am. Chem. Soc.* **1975**, 97, 6602.  
(11) Ozin, G. A.; Power, W. J. *Inorg. Chem.* **1977**, 16, 212.  
(12) Ozin, G. A.; Power, W. J. *J. Am. Chem. Soc.* **1976**, 98, 6508.  
(13) Kasai, P. H. *J. Am. Chem. Soc.* **1983**, 105, 6704.  
(14) Cohen, D.; Basch, H. *J. Am. Chem. Soc.* **1983**, 105, 6980.  
(15) Manceron, L.; Andrews, L. *J. Phys. Chem.* **1985**, 89, 4094.  
(16) Sakai, S.; Morokuma, K. *J. Phys. Chem.* **1987**, 91, 3661.  
(17) Manceron, L.; Schrimpf, A.; Bornemann, T.; Rosendahl, R.; Faller, F.; Stockmann, H.-J. *Chem. Phys.* **1993**, 169, 219.  
(18) Chenier, J. H. B.; Howard, J. A.; Mile, B.; Sutcliffe, R. *J. Am. Chem. Soc.* **1983**, 105, 788.  
(19) Eriksson, L. A.; Wang, J.; Boyd, R. J. *Chem. Phys. Lett.* **1995**, 235, 422.  
(20) Matsuura, K.; Muto, H. *J. Phys. Chem.* **1993**, 97, 8842.  
(21) Matsuura, K.; Muto, H. *J. Chem. Phys.* **1991**, 94, 4078.  
(22) Edlund, O.; Lund, A.; Shiotani, M.; Sohma, J.; Thuomas, K.-Å. *Mol. Phys.* **1976**, 32, 49.  
(23) Edlund, O.; Sohma, J. *Mol. Phys.* **1975**, 29, 1229.  
(24) Taarit, Y. B.; Symons, M. C. R.; Tench, A. J. *J. Chem. Soc., Faraday Trans. 1* **1977**, 1149.  
(25) Kusumori, T.; Matsuura, K.; Muto, H. *J. Chem. Phys.* **1996**, 104, 8879.