

Ab initio molecular orbital study of excited electronic states of the vinyl radical

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Abstract

Eight excited doublet electronic states of C_2H_3 have been studied using multireference configuration interaction calculations. Close agreement of the excitation energies with experiment is found for the \tilde{A}^2A' , $5^2A'$ ($\sigma-n$), and $3^2A'$ ($\pi-R$) states where the experimental data are available. The undiscovered \tilde{B}^2A' ($n-\pi^*$) state is predicted to have the adiabatic and vertical excitation energies of 33530 and 38546 cm^{-1} , respectively. The $\pi-\pi^*$ \tilde{C}^2A' state with the vertical energy of 45001 cm^{-1} is predicted to be difficult to observe because of the small oscillator strength. © 1997 Elsevier Science B.V.

1. Introduction

The vinyl radical, C_2H_3 , plays an important role in hydrocarbon fuel combustion chemistry [1–3]. Thermal decomposition of C_2H_3 and its reactions with hydrogen [4] and oxygen [5] are of fundamental importance in combustion processes. C_2H_3 is also a significant intermediate in such chemical reactions as the addition to and the polymerization of an acetylenic bond, and the decomposition of ethenoid compounds. Identification of electronic spectra of vinyl is relevant to the measurements of its gas phase reactivity.

Geometry and energetics of the ground (\tilde{X}^2A') and the first excited (\tilde{A}^2A') states of C_2H_3 are well established. A visible absorption spectrum of the vinyl radical due to the $\tilde{A} \leftarrow \tilde{X}$ electronic transition has been observed by Hunziker et al. [6], using modulation spectroscopy. They detected a band origin at 20020 cm^{-1} with a vibrational progression

toward the blue with an observed maximum extinction coefficient of 30 $l\ mol^{-1}\ cm^{-1}$ at 23629 cm^{-1} and an estimated Franck–Condon maximum at 24815 cm^{-1} . Hunziker et al. [6] optimized the geometry of \tilde{A}^2A' C_2H_3 at the HF level, and calculated the vertical and adiabatic excitation energy to be 26100 and 18100 cm^{-1} , respectively, using the multireference configuration interaction (MRCI) approach. Paddon-Row and Pople [7,8] reported the adiabatic energy to be 18607 cm^{-1} at the UMP4//UHF/6-31G** level. A recent MRCI study by Wang et al. [9] with a better basis set gives the $\tilde{A} \leftarrow \tilde{X}$ vertical excitation energy of 25529 cm^{-1} .

Little is known about the electronic excited states of C_2H_3 higher than \tilde{A}^2A' . Fahr and Laufer [10] detected two absorption features at 59407 and 60713 cm^{-1} from the vacuum ultraviolet flash photolysis of $Sn(C_2H_3)_2$ and $Hg(C_2H_3)_2$ and assigned them as due to the transitions to the Rydberg states of vinyl radical. Fahr and Laufer used these bands to measure

the rate constant of the $C_2H_3 + O_2$ reaction [10]. Of theoretical calculations, Paddon-Row and Pople [7,8] considered a $n-\pi^*$ state within C_{2v} symmetry and found that adiabatically it lies 31512 cm^{-1} above the ground state. Wang et al. [9] obtained the vertical excitation energy for a $\pi-\pi^*$ ($2^2A'$) transition of 43910 cm^{-1} at the MRCI level.

We present here an ab initio MRCI study of the electronic spectra for C_2H_3 corresponding to the lowest lying eight excited doublet electronic states. For the first three excited states, we also discuss the equilibrium geometries and the adiabatic excitation energies. Using a recently developed method to theoretically investigate the vibronic spectra of polyatomic molecules and radicals [11], we calculated the vibronic spectrum of the $C_2H_3 \tilde{A}^2A' \leftarrow \tilde{X}^2A'$ transition and compared it to experiment. In the computations of vibrational overlap integrals and Franck–Condon factors, we took into account the distortions, displacements and normal mode mixings in the excited state.

2. Theoretical methods

Geometries of the ground and excited states of C_2H_3 have been optimized using the CASSCF method [12]. A small active space, including 3 electrons (C–C π bond and an unpaired electron) distributed at 11 orbitals ($7a' + 4a''$), was used for the calculations of the \tilde{X}^2A' and \tilde{A}^2A' states. For these states, we additionally carried out optimization employing the hybrid density functional B3LYP approach [13]. Vibrational frequencies for \tilde{X} and \tilde{A} have been calculated at the CASSCF(3,11) and B3LYP levels with the 6-311G(2+)G* basis set which is the standard 6-311G* basis set [14] with two additional sp diffuse functions on carbon with the exponents of 0.0438 and 0.013928 [15]. Geometries of \tilde{A}^2A' and other excited states have also been optimized at the CASSCF level with a larger (11,11) active space and ANO(2+) basis set. The (11,11) active space includes all valence electrons distributed at 11 orbitals, $9a' + 2a''$. ANO(2+) is the ANO basis set (4s3p2d for C, 3s2p for H) [16] augmented with several diffuse functions for the carbon atom (s exponents: 0.012138 and 0.00422482; p exponents: 0.0080150 and 0.0028052; d exponent: 0.028512)

[17]. Vertical and adiabatic excitation energies have been computed using internally contracted multireference configuration interaction (MRCI) method [18] with (5,6) and (7,7) active spaces. The CASSCF(11,11) wavefunction was used as a reference for the MRCI(5,6) and MRCI(7,7) calculations. Besides ANO(2+), the MRCI calculations have been carried out with the ANO(2+)** basis set which additionally includes polarization [3f]/(1f) functions on C and [3d]/(1d) functions on H [16]. For the $\tilde{A} \leftarrow \tilde{X}$ transition, adiabatic excitation energy has also been calculated by the restricted open shell coupled cluster (RCCSD(T)) method [19] with the ANO(2+)** and Dunning's correlation consistent pVTZ and aug-pVTZ basis sets [20]. Oscillator strength for each excited state has been calculated using MRCI(7,7)/ANO(2+)** transition moments and energies. For the calculations, we used GAUSSIAN 94 [21], MOLCAS-3 [22], and MOLPRO-96 [23] programs.

3. Results and discussion

3.1. Vertical excitation energies

Vertical excitation energies for the lowest lying eight doublet excited states of C_2H_3 are collected in Table 1. The \tilde{A}^2A' state corresponds to a $\pi-n$ transition. The $\tilde{A} \leftarrow \tilde{X}$ vertical energy is found to be in the $26000\text{--}27000\text{ cm}^{-1}$ range from various MRCI calculations. The most reliable value is 26102 cm^{-1} obtained at the MRCI(7,7)/ANO(2+)** level with Davidson correction for quadruple excitations, designated as MRCI + D(7,7). This value agrees well with previous theoretical results, 26100 cm^{-1} by Hunziker et al. [6] and 25529 cm^{-1} by Wang et al. [9] at the MRCI(5,6)/ANO level. The calculated vertical excitation energy is higher than the estimated Franck–Condon maximum at 24815 cm^{-1} in the experiment [6]. The calculated oscillator strength for $\tilde{A} \leftarrow \tilde{X}$ is 1.22×10^{-3} .

The second excited state, \tilde{B}^2A' , corresponds to a transition of the unpaired electron to a π^* antibonding orbital. At our best level, MRCI + D(7,7)/ANO(2+)**, the vertical excitation energy is 38546 cm^{-1} , and the oscillator strength for the $\tilde{B} \leftarrow \tilde{X}$ transition, 1.36×10^{-3} , is similar to that of

Table 1
Vertical and adiabatic excitation energies (cm^{-1}) for various excited states of C_2H_3

	$1^2A'$ π -n	$2^2A'$ n- π^*	$2^2A'$ π - π^*	$3^2A'$ n-R	$4^2A'$ n-R	$5^2A'$ σ -n	$3^2A'$ π -R	$4^2A'$ π -R
vertical energies ^a								
CASSCF(11,11)/ANO(2+)	28302	44889	48536					
MRCI(5,6)/ANO(2+)	26645	40374	45941					
MRCI + D(5,6)/ANO(2+)	26393	38281	45412					
MRCI(7,7)/ANO(2+)	26936	40434	45768	49771	54161	65691	59303	64247
MRCI + D(7,7)/ANO(2+)	26416	38784	45290	49901	54460	58093	59949	64881
MRCI(7,7)/ANO(2+) ^{**}	26851	40446	45787	50257	54540	66654	59878	64755
MRCI + D(7,7)/ANO(2+) ^{**}	26102	38546	45001	50422	54862	58991	60327	65202
experiment	24815 ^b				59407 ^c	60713 ^c		
oscillator strength ^d	1.22×10^{-3}	1.36×10^{-3}	3.05×10^{-4}	7.04×10^{-3}	0.0172	0.0190	0.0199	3.37×10^{-3}
adiabatic energies ^e								
	$1^2A'$ -pl. π -n	$1^2A'$ -tw. π -n	$2^2A'$ -pl. n- π^*	$2^2A'$ -tw. n- π^*	$2^2A'$ -pl. π - π^*	$2^2A'$ -tw. π - π^*		
CASSCF(11,11)/ANO(2+)	20003		39221	39043	40527	37543		
MRCI(5,6)/ANO(2+)	19536		35412	35769	39164	36582		
MRCI + D(5,6)/ANO(2+)	19252		33609	34007	38353	35736		
MRCI(7,7)/ANO(2+) ^{**}	18426	20894	33697	34542	37063	35078		
MRCI + D(7,7)/ANO(2+) ^{**}	19122	20866	33530	34068	37700	35212		
RCCSD(T)/ANO(2+) ^{**}	(19175) ^f							
RCCSD(T)/pVTZ	(19404) ^f							
RCCSD(T)/aug-pVTZ	(19812) ^f							
RCCSD(T)/aug-pVTZ	(19652) ^f							
experiment	20020 ^b							

^a The total energies of the ground state C_2H_3 (in hartree) at various levels are the following: CASSCF(11,11)/ANO(2+): -77.54024; MRCI(5,6)/ANO(2+): -77.70528; MRCI + D(5,6)/ANO(2+): -77.72957; MRCI(7,7)/ANO(2+): -77.71139; MRCI + D(7,7)/ANO(2+): -77.73968; MRCI(7,7)/ANO(2+)^{**}: -77.72335; MRCI + D(7,7)/ANO(2+)^{**}: -77.75250.

^b From ref [6].

^c From ref [9].

^d At the MRCI + D(7,7)/ANO(2+)^{**} level.

^e Without zero-point energy correction.

^f With zero-point energy correction.

$\tilde{A} \leftarrow \tilde{X}$. The energy is not very sensitive to the basis set and active space used in the MRCI calculations. On the other hand, the Davidson correction is essential. The vertical energy decreases by about 2000 cm^{-1} with the correction. The third doublet excited state has $2^2A'$ symmetry and a π - π^* character, and can be denoted as $\tilde{C} 2^2A'$. Previous calculations at the MRCI(5,6)/ANO level gave this state (represented by $\tilde{B} 2^2A'$ in that paper) a vertical energy of 43910 cm^{-1} [9]. The present calculations with the larger active space and basis set give 45001 cm^{-1} at the MRCI + D(7,7)/ANO(2+)^{**} level. The transition of $\tilde{C} \leftarrow \tilde{X}$ is weak and the oscillator strength is only 3.05×10^{-4} .

Of the higher states shown in Table 1, $5^2A'$ and $3^2A'$ are worth mentioning. The $5^2A'$ state is due to the σ -n transition of an electron moving from the C-C σ bond to the lone pair of the carbon atom. Our best vertical excitation energy is 58991 cm^{-1} which agrees fairly well with the experimental band observed by Fahr and Laufer at 59407 cm^{-1} [10]. The second band, at 60713 cm^{-1} , reported by these authors is apparently due to the π -R transition to the $3^2A'$ electronic state, although one cannot exclude the possibility of vibrational spacing mentioned in [10]. The best calculated vertical energy of $3^2A'$ is 60327 cm^{-1} . $5^2A'$ (σ -n) and $3^2A'$ (π -R) have large oscillator strength of 0.019 and 0.020, respectively.

The MRCI + D(7,7)/ANO(2+) ** calculations underestimate the energies of these two states by $\approx 400 \text{ cm}^{-1}$, but the energy difference between the two is reproduced within the accuracy of 30 cm^{-1} .

3.2. Geometries and adiabatic excitation energies

Optimized geometries of the \tilde{A} , \tilde{B} , and \tilde{C} excited states are shown in Fig. 1. For \tilde{A}^2A' , the bond

lengths and angles, calculated at three different levels of theory agree well with each other and with the earlier results of UHF calculations [7,8]. The major geometric changes in \tilde{A}^2A' as compared to the ground state are the elongation of the CC bond by 0.11–0.13 Å and the decrease of the C^2C^1H angle by $\approx 30^\circ$. The elongation of the CC bond is because the C–C π -bonding population is halved in the \tilde{A}^2A' state.

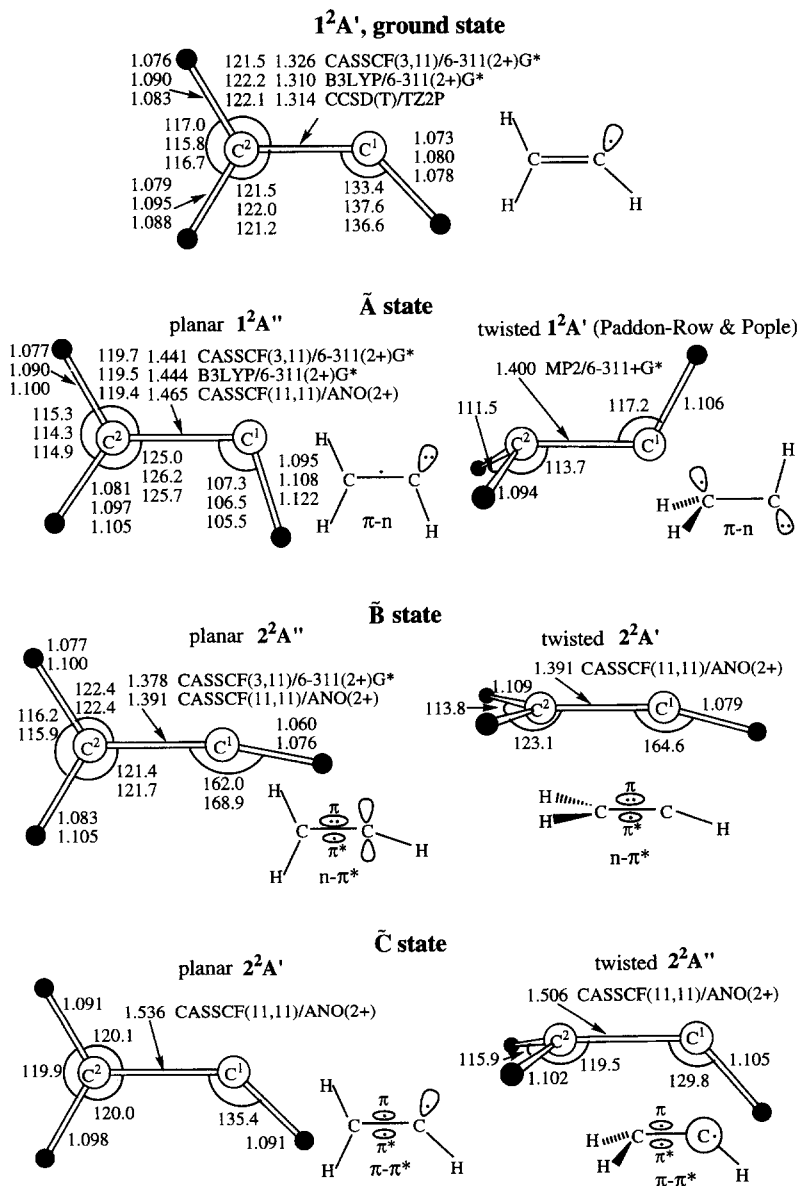


Fig. 1. Optimized geometries (bond lengths in Å, bond angles in degrees) and schematic presentation of the electronic structure for the ground and excited states of the vinyl radical. The MP2/6-311 + G* optimized geometry of the twisted $1^2A'$ structure is taken from [8].

The drastically bent C^2C^1H is caused by the large repulsion from the two σ -type lone-pair electrons of the C^1 atom. The adiabatic excitation energy at the MRCI + D(7,7)/ANO(2+)* level is 19175 cm^{-1} if the zero-point energy correction (ZPE), calculated at the B3LYP level, is taken into account. The ZPE is small, about 50 cm^{-1} . Our value for the adiabatic $\tilde{A}^2A'' \leftarrow \tilde{X}^2A'$ excitation energy is $500\text{--}1000\text{ cm}^{-1}$ higher than the earlier results of Hunziker et al. [6] and of Paddon-Row and Pople [7,8]. According to Paddon-Row and Pople [7,8], another minimum exists on the first excited doublet state PES. As shown in Fig. 1, it has non-planar C_s geometry with a twisted CH_2 group and the electronic term is $1^2A'$ (π -n). The electronic structure has been described [7,8] in terms of three nonbonding electrons, one of them occupying the tricoordinate carbon nonbonding AO and the remaining two occupying the bicoordinate carbon nonbonding AO. Both nonbonding AOs lie in the same plane. As a consequence, both carbon atoms are highly bent, i.e., C^2 is considerably pyramidalized and the C^2C^1H angle is 117.2° . At this geometry, $^2A''$ is the ground state. The adiabatic excitation energy for non-planar $1^2A'$ is calculated to be 20866 cm^{-1} at the MRCI + D(7,7)/ANO(2+)* level. Thus, this structure lies $\approx 1700\text{ cm}^{-1}$ higher in energy than planar $1^2A'$. At MP2/6-31G*, Paddon-Row's $1^2A'$ structure has no imaginary frequencies [8].

Two geometries have been optimized for the \tilde{B} (n - π^*) state. The planar structure has the $2^2A''$ electronic term. The non-planar C_s symmetric structure with a twisted CH_2 group is optimized for the $2^2A'$ state. Both planar $2^2A''$ and twisted $2^2A'$ have similar electronic structures and, consequently, similar bond lengths and bond angles. The unpaired electron is moved from the nonbonding AO of C^1 to the π^* antibonding orbital. This results in the elongation of the CC bonds to 1.39 \AA , and the C^2C^1H angles increase to $165\text{--}169^\circ$. In the twisted $2^2A'$ structure, the tricoordinated C^2 atom is not pyramidalized. The geometry of $2^2A'$ is quite different from that suggested by Paddon-Row and Pople for twisted $1^2A'$. This is due to the fact that the two geometries correspond to the stationary points on PES's of two different electronic states, the first and the second $^2A'$, and their electronic structures are different, π -n versus n - π^* . The MRCI + D(7,7)/ANO(2+)*

energy of the $2^2A'$ state calculated at Paddon-Row's geometry is by 1.8 eV higher than the energy at the twisted geometry optimized for $2^2A'$.

The adiabatic excitation energies for planar $2^2A''$ and twisted $2^2A'$ are close, 33530 and 34068 cm^{-1} , respectively. Paddon-Row and Pople [7,8] calculated the n - π^* state within C_{2v} symmetry with a linear C^2C^1H fragment and obtained the adiabatic energy of 31512 cm^{-1} at the UHF/6-31G* level. At this level, the C_{2v} structure has two imaginary frequencies and collapses to the twisted $1^2A'$ structure upon optimization allowing an out-of-plane distortion.

Two stationary points have been found on the PES for the π - π^* \tilde{C} excited state. For both planar $2^2A'$ and twisted $2^2A''$ states, the optimized geometry is characterized by the long CC distance ($1.51\text{--}1.54\text{ \AA}$), while the C^2C^1H angle ($130\text{--}135^\circ$) does not change much as compared to that in the ground state. The adiabatic excitation energies are calculated to be 37700 cm^{-1} for the planar $2^2A'$ structure and 35212 cm^{-1} for the twisted $2^2A''$.

For the four optimized geometries of \tilde{B} and \tilde{C} states we carried out the Hessian matrix calculations at the CIS/6-311(2+)G* level [24]. The results show that all of them, planar $2^2A''$ and $2^2A'$ as well as twisted $2^2A'$ and $2^2A''$, have no imaginary frequencies and correspond to minima on the PES's. Higher level calculations may change this conclusion. However, one can at least expect that the structures with lower energy, planar $2^2A''$ for the \tilde{B} state and twisted $2^2A''$ for \tilde{C} , are real minima.

3.3. Vibronic spectra

Vibrational frequencies of the ground and excited \tilde{A} state, calculated at various levels of theory are presented in Table 2. For the \tilde{X} state, Wang et al. [9] reported the CCSD(T)/TZ2P frequencies. The frequencies, calculated at the B3LYP/6-311(2+)G* level, agree well with the CCSD(T) ones. Therefore, we used the B3LYP frequencies of the ground and excited states for the calculations of the vibronic spectrum. In the \tilde{A} state, vibrational frequencies change substantially. For instance, frequency ν_2 (a') corresponding to a HCCH torsion increases from 820 to 1142 cm^{-1} . Two a' normal modes, Q_1 and Q_4 , responsible for the coupling between the C^2C^1H bending the C^2H rocking, increase their frequencies

Table 2

Vibrational frequencies (cm^{-1}) of the \tilde{X}^2A' and \tilde{A}^2A'' electronic states of C_2H_3 , calculated at various levels of theory

	\tilde{X}^2A'				\tilde{A}^2A''			
	UHF/ 6-31G* ^a	CASSCF/ 6-311(2+)G*	B3LYP/ 6-311(2+)G*	CCSD(T)/ TZ2P ^b	UHF/ 6-31G*	CASSCF/ 6-311(2+)G* ^a	B3LYP/ 6-311(2+)G*	
ν_1 (a')	827	762	713	764	ν'_1 (a')	1017	998	949
ν_2 (a'')	884	559	820	830	ν'_2 (a'')	1002	1513	1142
ν_3 (a'')	959	979	920	944	ν'_3 (a'')	779	904	850
ν_4 (a')	1194	1092	1046	1098	ν'_4 (a')	1386	1363	1290
ν_5 (a')	1407	1451	1391	1411	ν'_5 (a')	1257	1216	1191
ν_6 (a')	1635	1640	1651	1609	ν'_6 (a')	1656	1632	1531
ν_7 (a')	3279	3256	3038	3049	ν'_7 (a')	3268	3243	3020
ν_8 (a')	3372	3332	3136	3156	ν'_8 (a')	3369	3349	3141
ν_9 (a')	3431	3359	3236	3215	ν'_9 (a')	3157	3129	2942

^a From Ref. [7,8].^b From Ref. [9].

from 713 and 1046 cm^{-1} in \tilde{X}^2A' to 949 and 1290 cm^{-1} in \tilde{A}^2A'' . The frequency change in ν_1 and ν_4 is caused by the decrease of the $\text{C}^2\text{C}^1\text{H}$ bond angle in the excited state. The Q_5 and Q_6 normal modes, corresponding to the CC stretching coupled with the C^2H bending, exhibit a decrease of their frequencies from 1391 and 1651 cm^{-1} to 1191 and 1531 cm^{-1} , respectively. This is due to the elongation of the CC bond in the excited state. The ν_9 frequency of the C^1H stretch vibration also decreases from 3236 to 2943 cm^{-1} .

The greatest displacement was calculated due to the Q_1 and Q_4 normal coordinates; as seen in Table 3, ΔQ_1 and ΔQ_4 are 0.3327 and 0.3587 $\text{\AA amu}^{1/2}$, respectively. Q_5 , Q_6 , and Q_9 are also substantially displaced in the \tilde{A}^2A'' state, with ΔQ 's of 0.09–0.14 $\text{\AA amu}^{1/2}$. Besides the distortion and displacement described above, normal coordinates are rotated, i.e., mixed in the excited state. The corresponding Duschinsky matrices are shown in Table 3. The mixing between the a' modes, Q_2 and Q_3 , is relatively small. Q_1 , Q_4 , Q_8 , and Q_9 are rotated to a larger extent where the mixing is especially significant between Q_1 , Q_4 , and Q_9 . The third group of the rotated normal modes consists of Q_5 , Q_6 , and Q_7 . The largest mixing among the three is found between Q_5 and Q_6 .

The Duschinsky matrices, ΔQ 's, and B3LYP vibrational frequencies for the \tilde{X} and \tilde{A} states were used to calculate the vibronic overlap integrals and Franck–Condon factors, employing the algorithm

described earlier [11]. The calculated vibronic spectrum for the $\tilde{A}^2A'' \leftarrow \tilde{X}^2A'$ transition is shown in Fig. 2, and positions of the most intense peaks are compared to the experimental bands [6] in Table 4. In the experiment, the first band was observed at 20020 cm^{-1} . However, Hunziker et al. [6] did not rule out a possibility that the origin of the spectrum lies at a lower energy. MRCI/ANO(2+)* * calculations

Table 3

Duschinsky matrices and displacement of the normal modes ΔQ ($\text{\AA amu}^{1/2}$) in the excited \tilde{A}^2A'' state of C_2H_3

(a)				
	Q_1	Q_4	Q_8	Q_9
Q'_1	0.8928	0.3178	0.0943	0.3068
Q'_4	-0.2332	0.8499	0.1539	-0.5088
Q'_8	0.0160	-0.1342	-0.9923	-0.0600
Q'_9	0.4139	-0.1959	0.0642	-0.8098
ΔQ	0.3327	0.3587	0.0326	0.1023
(b)				
	Q_2	Q_3		
Q'_2	0.9061	-0.2965		
Q'_3	0.4999	0.9224		
ΔQ	0.0	0.0		
(c)				
	Q_5	Q_6	Q_7	
Q'_5	0.7325	0.1292	-0.2212	
Q'_6	-0.9805	0.5823	-0.0916	
Q'_7	-0.0414	-0.3670	0.9651	
ΔQ	0.0925	0.1445	0.0381	

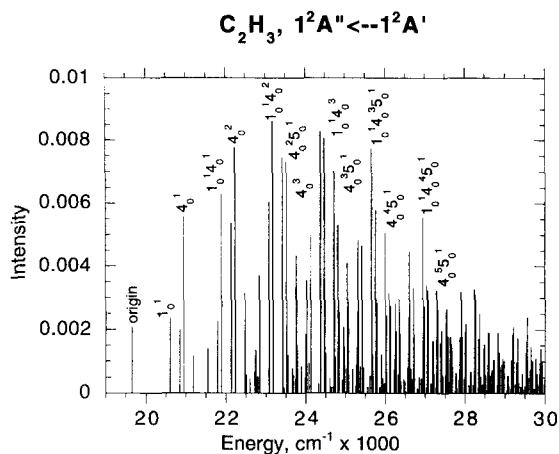


Fig. 2. Calculated vibronic spectrum for the $\tilde{A}^2A'' \leftarrow \tilde{X}^2A'$ transition in C_2H_3 .

give the spectral origin at 19175 cm^{-1} . In order to confirm this result, we additionally carried out RCCSD(T) calculations with the ANO(2+)**_{pVTZ} and aug-pVTZ basis sets. The adiabatic excitation energy calculated by RCCSD(T) with ZPE is in the $19404\text{--}19812\text{ cm}^{-1}$ range. The highest level result, RCCSD(T)/aug-pVTZ, where the basis set (5s3p3d2f for C and 4s3p2d for H) contains 161 contracted basis functions, is 19652 cm^{-1} . Since the calculated Franck–Condon factor for the origin is not much lower than those for the other intense peaks, we believe that the feature observed at 20020 cm^{-1} is truly the band origin. The best theoretical value underestimates the experimental result by 368 cm^{-1} . The accuracy may be increased using the RCCSD(T) method with pVQZ and pV5Z basis sets, which is beyond our computational facilities.

The calculated spectrum reproduces the main features of the observed one, as can be seen in Table 4. The spectrum contains two vibrational progressions with the spacings of 1290 and 949 cm^{-1} , compared to 1200 and 920 cm^{-1} in the observation, owing to the Q_1 and Q_4 normal modes. Additionally, Q_5 is active in the spectrum, with the frequency of 1191 cm^{-1} in the excited state. The ν_4' and ν_5' frequencies in $C_2H_3 \tilde{A}^2A''$ differ by about 100 cm^{-1} in our calculations, therefore, the peaks due to excitation of Q_4 and Q_5 , such as $4_0^1 5_0^1$ and 4_2^0 , 4_0^2 , $4_0^2 5_0^1$ and 4_0^3 etc., are quite close to each other and might merge if the resolution is not high enough. The calculated

maximum Franck–Condon factor occurs 3529 cm^{-1} above the origin ($1_0^1 4_0^2$), while the observed absorption maximum appears 4795 cm^{-1} above the origin and was assigned to 4_0^4 [6]. Franck–Condon factors nearly as large as those for the former are found for the transitions predicted to lie in the energy range between $\nu_{00} + 4000$ and $\nu_{00} + 5000\text{ cm}^{-1}$; it is likely that the observed maximum corresponds to one of these, particularly to $1_0^1 4_0^3$, which is predicted to lie at $\nu_{00} + 4819\text{ cm}^{-1}$. It is worth mentioning that the largest Franck–Condon factors are predicted for the transitions between 22232 and 25662 cm^{-1} , while the calculated vertical excitation energy is 26102 cm^{-1} . Thus, the simple assumption that “vertical excitation energy” = “absorption maximum”, often used in the theoretical analysis of electronic spectra, is violated here.

3.4. Correlation diagram between C_2H_3 and $C_2H_2 + H$

A diagram describing the correlation between the ground and valence excited states of C_2H_3 and its

Table 4
Experimental and calculated positions of the peaks (cm^{-1}), Franck–Condon factors, and assignment of the vibronic spectrum for the $\tilde{A}^2A'' \leftarrow \tilde{X}^2A'$ transition in the vinyl radical

Experimental band ^a	Theoretical peak	Franck–Condon factor	Assignment
20020	19652	0.0021	origin
21222	20942	0.0056	4_0^1
22148	21891	0.0063	$1_0^1 4_0^1$
22427	22133	0.0054	$4_0^1 5_0^1$
	22232	0.0077	4_0^2
23348	23082	0.0060	$1_0^1 4_0^1 5_0^1$
23629	23181	0.0086	$1_0^1 4_0^2$
	23423	0.0074	$4_0^2 5_0^1$
	23522	0.0073	4_0^3
24522	24372	0.0083	$1_0^1 4_0^2 5_0^1$
24815	24471	0.0081	$1_0^1 4_0^3$
	24713	0.0070	$4_0^3 5_0^1$
	24812	0.0053	4_0^4
25727	25662	0.0077	$1_0^1 4_0^3 5_0^1$
25981	25761	0.0058	$1_0^1 4_0^4$
	26003	0.0051	$4_0^4 5_0^1$
26918	26952	0.0056	$1_0^1 4_0^4 5_0^1$
27137	27293	0.0030	$4_0^5 5_0^1$

^a From ref. [6].

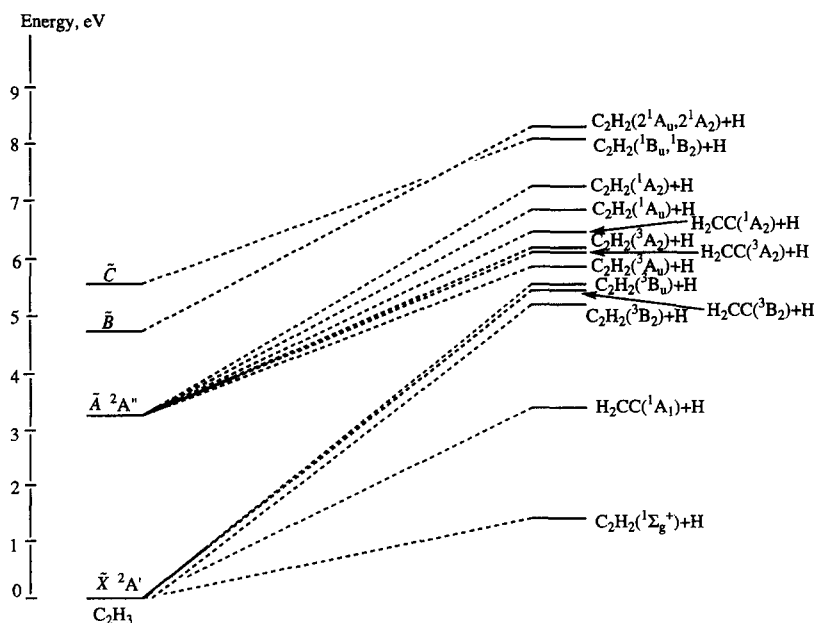


Fig. 3. Correlation diagram between the ground and valence excited states of C_2H_3 and its dissociation products $C_2H_2 + H$ and $H_2CC + H$.

dissociation products $C_2H_2 + H$ and $H_2CC + H$ is shown in Fig. 3. The correlation diagram is based on a simple symmetry consideration and the adiabatic excitation energies for acetylene and vinylidene were taken from the most accurate theoretical calculations¹, while the bond energies of C_2H_3 are taken as 3.47 eV ($H_2CC + H$) and 1.45 eV ($HCCH + H$) [30]. Both singlet and triplet states of C_2H_2 and H_2CC together with a hydrogen atom in the doublet state can be formed from the doublet states of C_2H_3 . Thus, adiabatically, the ground \tilde{X}^2A' state of the vinyl radical can dissociate to $C_2H_2(1^1\Sigma_g^+) + H$, $H_2CC(1^1A_1) + H$, $C_2H_2(\text{cis-}^3B_2 \text{ or trans-}^3B_u) + H$, and $H_2CC(3^1B_2) + H$. Dissociation of the first excited state, \tilde{A}^2A'' , can give six different products:

$\text{trans-}C_2H_2(1^1A_u \text{ and } ^3A_u)$, $\text{cis-}C_2H_2(1^1A_2 \text{ and } ^3A_2)$ as well as $H_2CC(3^1A_2 \text{ and } ^1A_2)$. $C_2H_3(\tilde{B}^2A'')$ is correlated to the 2^1A_u and 2^1A_2 singlet states and a triplet state of C_2H_2 originated from $^3\Sigma_u^-$. The \tilde{C}^2A' state of the vinyl radical is connected to $C_2H_2(1^1B_u \text{ and } ^1B_2)$ and a triplet state correlated to 3A_u .

The difference in the strengths of the C^1H and C^2H bonds is large for the ground state but becomes small for the \tilde{A} state of C_2H_3 . According to the recent results of Stanton and coworkers [27,29], vinylidene lies lower in energy than acetylene on the S_1 surface. Therefore, the C^1H bond in $C_2H_3 \tilde{A}^2A''$ is weaker than the C^2H bonds. Dissociation mechanism of the \tilde{B} and \tilde{C} states of the vinyl radical would apparently involve internal conversion to the \tilde{A} or \tilde{X} state. However, one cannot exclude that the dissociation takes place via intersystem crossing into the quartet manifold which we do not consider here. Experimental measurements of Lee and coworkers [31] have shown that upon the absorption of a 193 nm (51813 cm^{-1}) photon C_2H_3 fragments to $H + H_2CC(1^1A_1 \text{ or } ^3B_2)$, which are adiabatically correlated to the \tilde{X} state.

¹ The adiabatic excitation energies relative to the ground state acetylene are the following: 3.82 eV for 3B_2 , 4.16 eV for 3B_u , 4.44 eV for 3A_u , and 4.76 eV for 3A_2 states of C_2H_2 [25,26]; 5.43 and 5.78 eV for the 1A_u and 1A_2 states of C_2H_2 , respectively, [27]; 6.70 eV for the 1B_u and 1B_2 states and 6.94 eV for the 2^1A_u and 2^1A_2 states of C_2H_2 [28]; 4.07 eV for 3B_2 , 4.75 eV for 3A_2 , and 5.12 eV for 1A_2 states of H_2CC [29].

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References

- [1] H. Okabe, *Photochemistry of Small Molecules*, Wiley, New York, 1978.
- [2] W.C. Gardiner Jr. (Ed.), *Combustion Chemistry*, Springer, New York, 1984.
- [3] I.K. Puri (Ed.), *Environmental Implications of Combustion Processes*, CRC Press, Boca Raton, FL, 1993.
- [4] A. Fahr, A. Laufer, R. Klein, W. Braun, *J. Phys. Chem.* 95 (1991) 3218.
- [5] D.J. Donaldson, I.V. Okuda, J. Sloan, *J. Chem. Phys.* 193 (1995) 37.
- [6] H.E. Hunziker, H. Kneppel, A.D. McLean, P. Siegbahn, H.R. Wendt, *Can. J. Chem.* 61 (1983) 993.
- [7] M.N. Paddon-Row and J.A. Pople, *J. Phys. Chem.* 89 (1985) 2768.
- [8] M.N. Paddon-Row, reviewer's comments for this Letter.
- [9] J.-H. Wang, H.-C. Chang, Y.-T. Chen, *Chem. Phys.* 206 (1996) 43.
- [10] A. Fahr, A.H. Laufer, *J. Phys. Chem.* 92 (1988) 7229.
- [11] (a) A.M. Mebel, Y.-T. Chen, S.H. Lin, *Chem. Phys. Lett.* 258 (1996) 53; (b) A.M. Mebel, Y.-T. Chen, S.H. Lin, *J. Chem. Phys.* 105 (1996) 9007.
- [12] (a) H.B. Schlegel, M.A. Robb, *Chem. Phys. Lett.* 93 (1982) 43; (b) F. Bernardi, A. Bottoni, J.J.W. McDougall, M.A. Robb, H.B. Schlegel, *Faraday Symp. Chem. Soc.* 19 (1984) 137.
- [13] (a) A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648; (b) C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [14] R. Krishnan, M. Frisch, J.A. Pople, *J. Chem. Phys.* 72 (1988) 4244.
- [15] K.B. Wiberg, C.M. Hadad, J.B. Foresman, W.A. Chupka, *J. Phys. Chem.* 96 (1992) 10756.
- [16] P.-O. Widmark, P.-Å. Malmqvist, B.O. Roos, *Theor. Chim. Acta.* 77 (1990) 291.
- [17] L. Serrano-Andres, M. Merchan, I. Nebot-Gil, R. Lindh, B.O. Roos, *J. Chem. Phys.* 98 (1993) 3151.
- [18] (a) H.-J. Werner, P.J. Knowles, *J. Chem. Phys.* 89 (1988) 5803; (b) P.J. Knowles, H.-J. Werner, *Chem. Phys. Lett.* 145 (1988) 514.
- [19] P.J. Knowles, C. Hampel, H.-J. Werner, *J. Chem. Phys.* 99 (1994) 5219.
- [20] T.H. Dunning, *J. Chem. Phys.* 90 (1989) 1007.
- [21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. DeFrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, *Gaussian 94, Revision B.2*, Gaussian, Pittsburgh, PA, 1995.
- [22] MOLCAS-3, K. Andersson, M.R.A. Blomberg, M.P. Fulscher, G. Karlstrom, V. Kello, R. Lindh, P.-Å. Malmqvist, J. Noga, J. Olsen, B.O. Roos, A.J. Sadlej, P.E.M. Siegbahn, M. Urban, P.-O. Widmark, University of Lund, Sweden.
- [23] MOLPRO is a package of ab initio programs written by H.-J. Werner and P.J. Knowles, with contributions from J. Almlöf, R.D. Amos, M.J.O. Deegan, S.T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. Pitzer, A.J. Stone, P.R. Taylor, R. Lindh.
- [24] J.B. Foresman, M. Head-Gordon, J.A. Pople, M.J. Frisch, *J. Phys. Chem.* 96 (1992) 135.
- [25] J.K. Lundberg, R.W. Field, C.D. Sherrill, E.T. Seidl, Y. Xie, H.F. Schaefer III, *J. Chem. Phys.* 98 (1993) 8384.
- [26] Y. Yamaguchi, G. Vacek, H.F. Schaefer III, *Theor. Chim. Acta* 86 (1993) 97.
- [27] J.F. Stanton, C.-M. Huang, P.G. Szalay, *J. Chem. Phys.* 101 (1994) 356.
- [28] M. Peric, S.D. Peyerimhoff, R.J. Buenker, *Mol. Phys.* 62 (1987) 1339.
- [29] J.F. Stanton, J. Gauss, *J. Chem. Phys.* 101 (1994) 3001.
- [30] K.M. Ervin, J. Ho, W.C. Lineberger, *J. Chem. Phys.* 91 (1989) 5974.
- [31] B.A. Balko, J. Zhang, Y.T. Lee, *J. Chem. Phys.* 97 (1992) 935.