Infrared absorption spectra of vinyl radicals isolated in solid Ne

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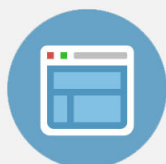Infrared depletion spectra of 2-aminopyridine2-pyridone, a Watson–Crick mimic of adenineuracil
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Infrared absorption spectra of vinyl radicals isolated in solid Ne

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Irradiation of samples of solid Ne near 3.0 K containing ethene (C_2H_4) with vacuum ultraviolet radiation at 120 nm from synchrotron yielded new spectral lines at 3141.0, 2953.6, 2911.5, 1357.4, 677.1, 895.3, and 857.0 cm^{-1}. These features are assigned to α-CH stretching (ν_1), CH_2 antisymmetric stretching (ν_2), CH_2 symmetric stretching (ν_3), CH_2-bending (ν_5), HCCH *cis* bending (ν_7), CH_2 out-of-plane bending (ν_8), and α-CH out-of-plane bending (ν_9) modes of C_2H_3, respectively, based on results of ^{13}C- and D-isotopic experiments and quantum-chemical calculations. These calculations using density-functional theory (B3LYP and PW91PW91/aug-cc-pVTZ) predict vibrational wavenumbers, IR intensities, and isotopic ratios of vinyl radical that agree satisfactorily with our experimental results. © *2008 American Institute of Physics.*
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I. INTRODUCTION

The vinyl radical (C_2H_3) plays an important role in the combustion of hydrocarbons.[1,2] It is a key intermediate in an addition reaction of an acetylenic bond and in the decomposition of ethenoid compounds; in these reactions, the vinyl radical plays an important role also in stereochemistry.[3] The vinyl radical was found also in extraterrestrial planetary atmospheres at low temperature.[4,5] Being the simplest open-shell olefinic radical, the vinyl radical serves as a crucial test molecule for quantum-chemical calculations.

Despite its significant role in free-radical chemistry, spectral observations of C_2H_3 have been limited. The $\widetilde{A} \leftarrow \widetilde{X}$ and the $\widetilde{B} \leftarrow \widetilde{X}$ electronic transitions were observed in regions of 400–530 (Refs. 6–8) and 225–238 nm,[9] respectively. In the infrared (IR) region, only a few lines were reported. Upon codeposition at 12 K of a stream of Ar subjected to microwave discharge with a gaseous mixture of C_2H_2/Ar, Jacox and Olson assigned an IR absorption line near 900 cm^{-1} to C_2H_3 isolated in solid Ar;[10] a line at 895.4 cm^{-1} was also reported for C_2H_3 isolated in solid Ne, produced upon codeposition of discharged Ne with acetylene.[11] Shepherd *et al.* produced C_2H_3 via vacuum ultraviolet (vuv) photolysis of ethene isolated in solid Ar and assigned this line at 900.8 cm^{-1} to an out-of-plane bending mode (ν_8) based on deuterium and ^{13}C-isotopic-substitution experiments.[12] Tanskanen *et al.*[13] generated vinyl radicals via an annealing-induced reaction of H atom with ethyne (C_2H_2) in various solid noble-gas matrices and assigned an additional line at 1356.7 cm^{-1} to the CH_2-bending (ν_5) mode of C_2H_3 isolated in solid Ar; they reported also electron para-

magnetic resonance spectra of C_2H_3 in solid Ar. Jacox observed lines at 1359.8 cm^{-1} (ν_5), 677.0 cm^{-1} (ν_7), and 897.4 cm^{-1} (ν_8) for C_2H_3 in solid Ne upon codeposition of ethene with discharged Ne.[14]

Kanamori *et al.* used an IR diode laser to measure rotationally resolved IR absorption spectra of gaseous vinyl generated on photolysis of vinyl halides at 193 nm; a *c*-type band with origin at 895.4 cm^{-1} was reported for ν_8.[15] Letendre *et al.*[16] photodissociated several precursors at selected wavelengths to produce vibrationally excited species and then monitored their IR emission with time-resolved Fourier-transform (FT) spectra. They assigned these emission bands to all nine vibrational modes of vinyl but observed that line positions and relative intensities of these IR bands differed much from theoretical predictions for the corresponding vibrational modes of vinyl. Subsequently, Sattelmeyer and Schaefer performed a high-level theoretical treatment of vinyl in the ground electronic state by means of coupled-cluster theory with equations of motion for ionized states with inclusion of single and double excitations (EOMIP-CCSD).[17] Vibrational wavenumbers of C_2H_3 predicted with this method are similar to those predicted earlier with CCSD(T)/TZ2P.[18] Sattelmeyer and Schaefer suggested that vibrational mode ν_5 of gaseous C_2H_3 might have been misassigned by Letendre *et al.*[16] because their experimental value of 1277 cm^{-1} differs greatly from the predicted value of 1419 cm^{-1}.[17] Pushkarsky *et al.* reported the transition $\widetilde{A} \leftarrow \widetilde{X}$ of jet-cooled C_2H_3 and CD_2CH via action spectra recorded on monitoring the H or D fragment using $1+1'$ resonance-enhanced multiphoton-ionization detection upon photolysis of C_2H_3.[8] In addition to several vibrational modes of the $\widetilde{A}$ state, they reported $\nu_7 = 674 \pm 2$ cm^{-1} for state $\widetilde{X}$ of C_2H_3; this value is much smaller than the value of 758 cm^{-1}

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reported previously by Letendre *et al.*[16] To observe further vibrational features of C_2H_3 and to clarify these assignments, further investigation is obviously worthy.

Here, we report the IR absorption spectra of vinyl radical and its D- and ^{13}C-isotopic variants upon irradiation of Ne matrix samples containing C_2H_4 and corresponding isotopic species with vuv light at 120 nm. Observed absorption lines are assigned to seven vibrational modes of vinyl in solid Ne; four of them are new.

II. EXPERIMENTS

We performed vuv photolysis experiments with a new matrix-isolation/FTIR system coupled to an undulator beamline of a synchrotron at National Synchrotron Radiation Research Center in Taiwan. The vuv radiation was dispersed from beamline 21U9A2, which is a side branch of the white-light beamline of undulator U9 (having permanent magnets at 9 cm periodic spacing) in the storage ring (1.5 GeV). The energy or wavelength of this white-light branch beamline becomes tunable on varying the gap of the U9 undulator, which generates photons with resolution of ~2% and flux of ~10^{16} photons s^{-1} in the vuv and extreme UV range. This U9 white-light side branch provides photons with energies in the span from 5 to ~80 eV. By means of a gas filter cell placed at the focus of the first mirror in the U9 undulator, higher harmonics generated by the U9 undulator were suppressed.[19,20] The gas filter cell was filled with noble gas, e.g., Ne, Ar, Xe, or Kr, depending on the desired photon energy. When the desired photon energy is less than 11.8 eV (wavelength greater than 105 nm), a LiF window plate is installed downstream from the beamline. The LiF plate serves additionally to suppress light from higher harmonics. In our unpublished work, the absorption of the pure solid C_2H_4 features two broad bands at about 120 and 170 nm and the shoulder at about 157 nm in the wavelength of 105–200 nm. In this work, we thus selected wavelengths of 170, 157, and 120 nm of vuv light for photolysis of matrix samples.

The vacuum of the cryochamber is provided by a turbo-molecular pump which is, in turn, backed by a scroll pump; the pressure of the chamber is typically less than 1 $\times 10^{-8}$ Torr. A CsI window cooled to ~3.0 K serves as a cold substrate for a matrix sample. A closed-cycle cryogenic system (Janis RDK-415) was employed to cool the target. This cryostat is situated on the plate of a differential rotary-seal stage of which the rotatable angle is 360°. Thus, the CsI window can be rotated freely to face deposition, photolysis, or detection port.

The gaseous mixtures were prepared according to standard manometric procedures in an ultrahigh vacuum system designed for that purpose. The rate of deposition was regulated in a range/μmol s^{-1} [2, 5] and monitored with a flow transducer. A gaseous mixture of C_2H_4 and Ne (1/1000, 0.03 mol Ne) was typically deposited over 2 h before vuv irradiation.

IR absorption spectra were recorded at various stages of experiments with a FTIR spectrometer (Bomem, DA8) equipped with a globar (SiC) source, a KBr beam splitter,

and a Hg/Cd/Te detector (Belov Technology Co., Inc., IPH4800L) to cover the spectral range of 500–4000 cm^{-1}. Typically 400 scans at resolution of 0.5 cm^{-1} were recorded at each stage of the measurement. C_2H_4 (99.99%, Matheson Gases), Ne (99.999%, Scott Specialty Gases), [13]C_2H_4 (isotopic purity of ~99%, Cambridge Isotope Laboratories), and C_2D_4 (isotopic purity of ~98%, Cambridge Isotope Laboratories) were used without further purification.

III. THEORETICAL CALCULATIONS

The energies, equilibrium structures, vibrational wave-numbers, and IR intensities were calculated with the GAUSSIAN 03 program.[21] We used density-functional theory for calculations of two types: the B3LYP method uses Becke's three-parameter hybrid exchange functionals[22] and a correlation functional of Lee *et al.* with both local and nonlocal terms;[23] the PW91PW91 method uses exchange and correlation functionals of Perdew and Wang.[24] Dunning's correlation-consistent polarized valence triplet-zeta basis set, augmented with s, p, d, and f functions[25] (aug-cc-pVTZ), was used in both cases. Analytic first derivatives were utilized in geometry optimization, and vibrational wavenumbers were calculated analytically at each stationary point.

IV. RESULTS AND DISCUSSION

A. Experimental observations

Although vinyl halides are excellent precursors of vinyl radicals in the gaseous phase, photodissociation of vinyl chloride isolated in an Ar matrix produced only HCl and C_2H_2 because of the matrix cage effect.[26] Previous investigators successfully produced vinyl isolated in a matrix by reaction of H atoms with C_2H_2,[13] or by photodissociation or photoionization of C_2H_4.[12,14] The undulator beam of radiation from a synchrotron is much more intense than conventional vuv light generated from a flow of H_2 or inert gases subjected to a microwave discharge; we, thus, expect to form more vinyl in these photolysis experiments on C_2H_4 so that weaker absorption lines of vinyl become observable. We tuned synchrotron radiation to wavelengths of 170, 157, and 120 nm for irradiation of matrix samples and monitored the intensity of the known vibrational mode (ν_8) of C_2H_3. Among all three wavelengths tested, photolysis of C_2H_4 at 120 nm yielded the largest proportion of vinyl radicals.

1. Irradiation experiments with C_2H_4 in natural abundance

A partial spectrum of the matrix sample of C_2H_4/Ne (1/1000) after deposition at 3.0 K is shown in Fig. 1(a) with regions of 600–1400 and 2800–3250 cm^{-1}. The IR spectrum exhibits lines due to C_2H_4 at 826.4 (ν_{10}), 950.3 (ν_7), 1442.9 (ν_{12}), 1890.3 ($2\nu_7$), 2989.5 (ν_{11}), 3079.6 ($\nu_2+\nu_{12}$), and 3106.5 (ν_9) cm^{-1}.[27] Trace (B) of Fig. 1 is a difference spectrum recorded after irradiation of the matrix sample at 120 nm for 1.5 h. The difference spectrum was obtained on subtracting the spectrum recorded before vuv irradiation from that recorded after irradiation; lines pointing upward indicate production, whereas those pointing downward indi-
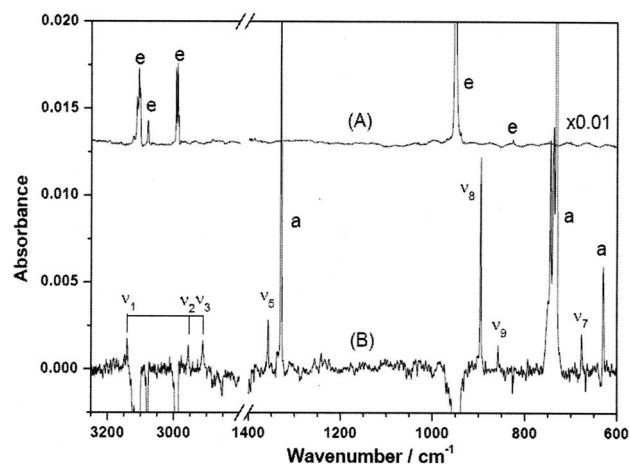
FIG. 1. (A) Partial IR absorption spectra of a C_2H_4/Ne (1/1000) matrix sample before irradiation: (B) Difference spectrum after irradiation at 120 nm for 1.5 h. Ethyne is marked as a, ethene is marked as e, and vinyl is marked according to the assigned vibrational modes.

cate destruction. To avoid interference due to destruction of C_2H_4 and to present better the newly produced lines, we also present a C_2H_4-stripped spectrum in Fig. 2(a). The stripped spectrum was derived on subtracting the spectrum of C_2H_4 [Fig. 1(a)], reduced by an appropriate factor, from that recorded after irradiation so that most lines due to C_2H_4 are
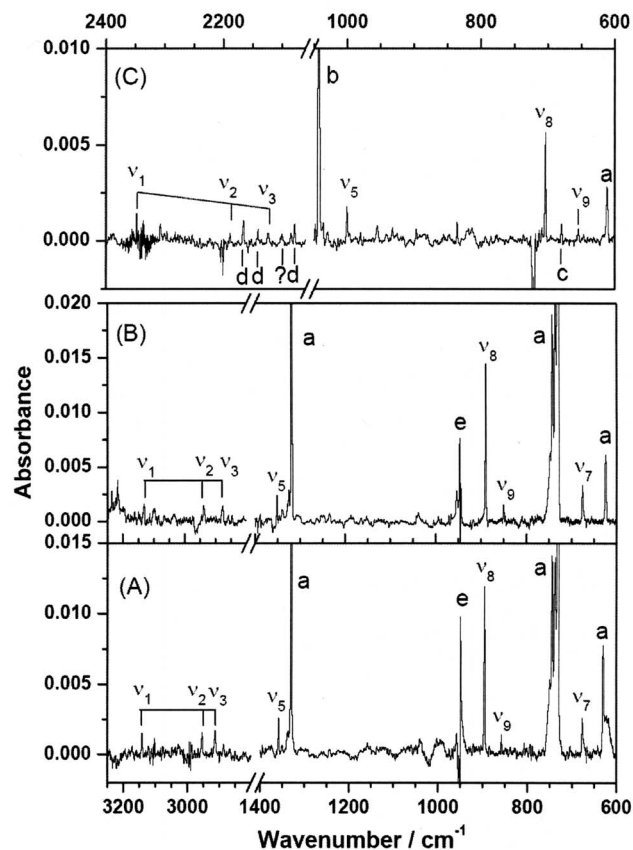

FIG. 2. Partial ethene-stripped IR absorption spectra of C_2H_4/Ne matrix samples with isotopic variants after irradiation at 120 nm for 1.5 h. (A) C_2H_4/Ne (1/1000), (B) $^{13}C_2H_4/Ne$ (1/1000), and (C) C_2D_4/Ne (1/1000). C_2H_2 and $^{13}C_2H_2$ are marked as a, C_2D_2 is marked as b, HCCD is marked as c, C_2H is marked as d, C_2H_4 and $^{13}C_2H_4$ are marked as e, and vinyl is marked according to the assigned vibrational modes.

attenuated. For regions of intense C_2H_2 absorption, the spectrally stripped spectra show slightly greater noise levels.

After irradiation, intensities of lines due to C_2H_4 decreased by $\sim 75\%$ and intense lines appeared at 630.1, 732.0, 1330.4, 1958.9, 3283.9, and 3332.1 cm^{-1}; these features are readily assigned to ν_4, ν_5, $\nu_4 + \nu_5$, ν_2, ν_3, and ν_1 of acetylene (C_2H_2), respectively.[27] Due to the breaking of symmetry in solid Ne, inactive modes of ν_1, ν_2, and ν_4 for acetylene are observed in the spectra. Some of these features are marked a in Figs. 1(b) and 2(a). A feature at 1835.6 cm^{-1} (not shown in the figure) corresponds to the C=C stretching mode of C_2H.[11] Some absorptions with weak intensities of vibronic structures of C_2H were also found at 2165.8, 2141.2, and 2078.9 cm^{-1} and are assigned to $\widetilde{X}(0,5^1,0)$, $\widetilde{X}(0,5^3,0)$, and $\widetilde{X}(0,1^1,1)$, respectively, based on previous reports.[28–30] Lines at 1357.4, 895.3 and 677.1 cm^{-1} correspond well with reported vibrational modes of vinyl: ν_5 [1356.7 cm^{-1} in Ar (Ref. 13) and 1359.8 cm^{-1} in Ne (Ref. 14)], ν_8 [895.16 cm^{-1} in gas[15] and 895.4 cm^{-1} in Ne (Ref. 11)], and ν_7 [674 $\pm$ 2 cm^{-1} in gas[8] and 677.0 cm^{-1} in Ne (Ref. 14)]; they are marked as ν_5, ν_8, and ν_7 in Figs. 1(b) and 2(a). Additional features are evident at 3141.0, 2953.6, 2911.5, and 857.0 cm^{-1}, marked as ν_1, ν_2, ν_3, and ν_9, respectively, in Figs. 1(b) and 2(a); their intensity variations are similar to those of ν_5, ν_7, and ν_8 bands of vinyl at various stages of photolysis but do not correlate with the known IR absorption lines of small hydrocarbons. We, thus, tentatively assign these features to other vibrational modes of vinyl, which were unreported in earlier experiments. Observed lines of vinyl are listed in Table I, with previous experimental results in solid Ar (Ref. 13) and Ne (Refs. 11 and 14) and in the gaseous phase[16] listed for comparison.

2. ^{13}C-isotopic experiments

A matrix sample of $^{13}C_2H_4/Ne=1/1000$ was used in this experiment. The $^{13}C_2H_4$-stripped spectrum of the matrix sample in regions of 600–1400 and 2800–3250 cm^{-1} recorded after irradiation at 120 nm for 1.5 h is shown in Fig. 2(b). Wavenumbers of new lines for all isotopic species are listed in Table II.

Results of the ^{13}C-isotopic experiment and the experiment performed with natural abundance showed almost identical spectra except that lines were slightly redshifted. The most intense vibrational mode ν_8 shifts slightly from 895.3 to 889.3 cm^{-1}. The ^{13}C-isotopic ratio of 889.3/895.3 =0.9933, defined as the ratio of the vibrational wavenumber of isotopic species to that of the natural species, is near the value of 0.9925 reported in solid Ar.[12] The ν_5 line at 1357.4 cm^{-1} shifts to 1351.3 cm^{-1} and the ^{13}C-isotopic ratio 0.9955 is similar to the value 0.9956 reported for C_2H_3 in solid Kr by Tanskanen et al.[13] The ^{13}C-isotopic ratios of lines of vinyl near 3000 cm^{-1} are 0.9970, 0.9949, and 0.9957, corresponding to lines at 3131.6, 2938.4, and 2899.1 cm^{-1}, respectively, for $^{13}C_2H_3$. The lines at 857.0 and 677.1 cm^{-1} for $^{12}C_2H_3$ shift to 849.8 and 676.0 cm^{-1}, respectively, and yield ^{13}C-isotopic ratios of 0.9916 and 0.9984.

TABLE I. Vibrational wavenumbers (cm^{-1}) and relative intensities (listed in parentheses) of C_2H_3 observed experimentally or calculated with various theoretical methods.

Mode	Approximate description	CCSD(T)/TZ2P[a]	EOMIP-CCSD[b]	PW91PW91[c]	B3LYP[c]	Gas[d]	Ar matrix[e]	Ne matrix[c]
$\nu_1(a')$	α-CH stretch	3215 (1.4)	3298 (1.4)[f]	3181 (0.5)[f]	3240 (0.5)[f]	3235 (7)[f]		3141.0 (2.0)[f]
$\nu_2(a')$	CH_2 antisym. stretch	3156 (1.4)	3222 (6.1)	3072 (2.7)	3137 (4.2)	3164 (11)		2953.6 (3.0)
$\nu_3(a')$	CH_2 sym. stretch	3049 (1.3)	3118 (6.0)	2976 (6.8)	3042 (7.1)	3103 (0.5)		2911.5 (2.6)
$\nu_4(a')$	C=C stretch	1609 (4.3)	1689 (1.4)	1616 (2.7)	1650 (2.9)	1700 (0.1)		
$\nu_5(a')$	CH_2 bend	1411 (8.5)	1419 (10.6)	1346 (12)	1395 (11)	1277 (100)	1356.7[g]	1357.4 (24)
$\nu_6(a')$	HCCH *trans* bend	1098 (8.9)	1077 (12.5)	1006 (11)	1048 (11)	1099 (43)		
$\nu_7(a')$	HCCH *cis* bend	764 (23.0)	730 (29.8)	678 (32)	708 (31)	758 (11)[h]	(677.0) [g]	677.1 (32)
$\nu_8(a'')$	CH_2 out-of-plane bend	944 (100)	965 (100)	886 (100)	929 (100)	955 (32)[i]	900.8[g]	895.3 (100)
$\nu_9(a'')$	α-CH out-of-plane bend	830 (12.9)	850 (13.7)	787 (18)	821 (28)	895 (93)		857.0 (9.6)

[a]Reference 18.
[b]Reference 17.
[c]This work.
[d]Reference 16.
[e]Reference 13.
[f]Intensities are normalized to the most intense feature; observed IR intensities are estimated by integrating the areas of the corresponding lines. IR intensities for ν_8 are calculated to be 72.9 and 69.6 km mol^{-1} for PW91PW91 and B3LYP respectively.
[g]In solid Ne (Ref. 14), 1359.8 (ν_5) and 897.4 cm^{-1} (ν_8) were reported for C_2H_3 in solid Ne. Reference 11 reported ν_8=895.4 cm^{-1} for C_2H_3 in solid Ne.
[h]Pushkarsky *et al.* reported 674±2 cm^{-1} for ν_7 of gaseous C_2H_3 (Ref. 8).
[i]Kanamori *et al.* reported 895.16 cm^{-1} for ν_8 of gaseous C_2H_3 (Ref. 15).

3. Deuterium-isotopic experiments

A matrix sample with C_2D_4/Ne=1/1000 was irradiated with vuv light at 120 nm for 1.5 h in this experiment. The C_2D_4-stripped spectrum of the irradiated matrix sample is shown in Fig. 2(c). Wavenumbers of observed lines of vinyl radicals are listed in Table II. Wavenumbers of the known ν_8 and ν_5 bands of vinyl shift from 895.3 and 1357.4 cm^{-1} of

C_2H_3 to 704.8 and 1000.4 cm^{-1} of C_2D_3, yielding isotopic ratios of 0.7872 and 0.7370, respectively, consistent with previous experiments in solid Kr.[13]

Abundant lines appear in the spectral region of 2000–2200 cm^{-1}. Small impurities from matrix samples might be a source providing H atoms on irradiation. The lines at 2165.8, 2141.2, 2078.9, and 2098.4 cm^{-1} were found

TABLE II. Comparison of IR wavenumbers (cm^{-1}) and ^{13}C- and D-isotopic ratios (defined as the ratio of wavenumber of the isotopic species to that of C_2H_3, listed in parentheses) of C_2H_3.

| Mode	C_2H_3 B3LYP	C_2H_3 Expt.	$^{13}C_2H_3$ B3LYP	$^{13}C_2H_3$ Expt.	C_2D_3 B3LYP	C_2D_3 Expt.
$\nu_1(a')$	3240.0	3141.0	3228.1 (0.9963)	3131.6 (0.9970)	2420.8 (0.7472)	2348.0 (0.7475)
$\nu_2(a')$	3137.1	2953.6	3126.0 (0.9965)	2938.4 (0.9949)	2326.7 (0.7414)	2192.5 (0.7423)
$\nu_3(a')$	3042.3	2911.5	3035.7 (0.9978)	2899.1 (0.9957)	2216.4 (0.7285)	2124.1 (0.7296)
$\nu_4(a')$	1650.0		1592.6 (0.9652)		1568.0 (0.9503)	
$\nu_5(a')$	1395.2	1357.4	1389.3 (0.9958)	1351.3 (0.9955)	1018.2 (0.7298)	1000.4 (0.7370)
$\nu_6(a')$	1047.6		1032.8 (0.9859)		856.3 (0.8174)	
$\nu_7(a')$	708.1	677.1	706.7 (0.9980)	676.0 (0.9984)	512.5 (0.7238)	
$\nu_8(a'')$	928.5	895.3	921.0 (0.9919)	889.3 (0.9933)	733.2 (0.7897)	704.8 (0.7872)
$\nu_9(a'')$	820.7	857.0	814.0 (0.9918)	849.8 (0.9916)	624.3 (0.7607)	654.5 (0.7637)
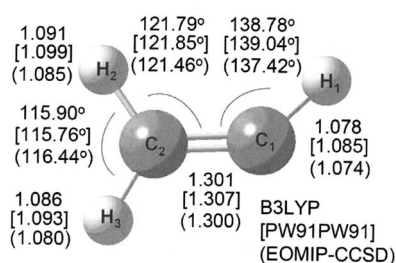
FIG. 3. Geometries of C_2H_3 calculated with the B3LYP/aug-cc-pVTZ and PW91PW91/aug-cc-pVTZ (in bracket) methods. Results of EOMIP-CCSD/cc-pVQZ from Ref. 17 are listed in parentheses for comparison. The unit of bond length is Å.

also in experiments with natural abundance. The former three lines are assigned to $\widetilde{X}(0,5^1,0)$, $\widetilde{X}(0,5^3,0)$, and $\widetilde{X}(0,1^1,1)$ of C_2H, respectively,[28–30] and the latter line is unknown. This line was observed also in an experiment performed on vuv photodissociation of a matrix sample of C_2H_2. In general, the isotopic ratios of deuterium substitution of C—H stretching modes have a range of 0.725–0.745. For instance, the value is 0.7362 for the CH_2 symmetric stretch (ν_{11}) of C_2H_4 and it is 0.7416 for the C—H stretching mode (ν_3) of C_2H_2. New lines at 2192.5 and 2124.1 cm^{-1} might, thus, correlate with lines at 2953.6 and 2911.5 cm^{-1}, respectively, yielding isotopic ratios of 0.7423 and 0.7296, respectively. The sharp line appearing at 2348.0 cm^{-1} suffered from interference from lines of parent molecule C_2D_4; it might correlate with the C—H stretching mode of vinyl at 3141.0 cm^{-1}, yielding an isotopic ratio of 0.7475. In the small wavenumber region, one weak line at 654.5 cm^{-1} is readily recognized as a new line. The deuterium-isotopic ratio might be either $654.5/677.1=0.9666$ for ν_7 or $654.5/857.0=0.7637$ for ν_9 of vinyl. According to an acceptable deuterium-isotopic ratio and the absorption intensity relative to ν_8, the line at 654.5 cm^{-1} for C_2D_3 is expected to correspond to the line at 857.0 cm^{-1} (ν_9) of C_2H_3. We found no possible new line in the spectral range of 500–700 cm^{-1}, perhaps because ν_7 of C_2D_3 is predicted to lie near 490 cm^{-1}, beyond our detection limit at 500 cm^{-1}.

The wavenumbers of new lines and derived isotopic ratios in various isotopic-substitution experiments are listed in Table II. To provide further information for the assignments we undertook calculations as follows.

B. Quantum-chemical calculations

We performed quantum-chemical calculations with the B3LYP and PW91PW91 methods by using the aug-cc-pVTZ basis set to locate a stable structure of C_2H_3. Geometries predicted with B3LYP and PW91PW91/aug-cc-pVTZ for vinyl are shown in Fig. 3, with those predicted previously by Sattelmeyer and Schaefer[17] by using EOMIP-CCSD/cc-pVQZ listed in parentheses for comparison. C_2H_3, predicted with B3LYP/aug-cc-pVTZ, has bonds C_1—H_1, C_2—H_2, C_2—H_3, and C_1=C_2 with lengths of 1.078, 1.091 1.086, and 1.301 Å, respectively, similar to corresponding values of 1.074, 1.085, 1.080, and 1.300 Å calculated previously with EOMIP-CCSD/cc-pVQZ.[17] Bond angles of vinyl, 138.78°

for $\angle H_1C_1C_2$, 121.79° for $\angle C_1C_2H_2$, and 115.90° for $\angle H_2C_2H_3$, are also similar to corresponding values of 137.42°, 121.46°, and 116.44° from EOMIP-CCSD/cc-pVQZ.

Table I compares vibrational wavenumbers and corresponding relative IR intensities of C_2H_3 predicted with the B3LYP and PW91PW91 methods in this work and with EOMIP-CCSD/cc-pVQZ and CCSD(T)/TZ2P reported previously;[17,18] previous experimental results are listed for comparison. The vibrational wavenumbers from these theoretical predictions are shown to agree within 10% of previous experimental values except ν_5 of gaseous C_2H_3 reported by Letendre et al.[16] In contrast, predicted relative IR intensities vary greatly from those reported by Letendre et al.,[16] as shown in Table I. The three known vibrational wavenumbers of matrix-isolated C_2H_3—ν_5, ν_7, and ν_8—agree satisfactorily with those predicted with PW91PW91 and B3LYP but deviate by 6%–12% from those reported by Letendre et al. Predicted displacement vectors for each vibrational mode of vinyl are available from the Electronic Physics Auxiliary Publication Service (EPAPS).[31] An approximate description of vibrational modes is also contained in Table I.

Table II lists vibrational wavenumbers of $^{13}C_2H_3$ and C_2D_3 and, parenthetically, ^{13}C- and D-isotopic ratios for vibrational wavenumbers of C_2H_3 predicted with B3LYP/aug-cc-pVTZ; as those predicted for C_2H_3 with PW91PW91 are similar, they are omitted.

C. Assignments of vibrational modes of C$_2$H$_3$

According to the absorption spectra of gaseous ethene in the vuv region, the selected photolysis wavelengths at 170, 157, and 120 nm can excite ethene to 3s, 3p, and 6s Rydberg states, respectively.[32] Earlier investigations showed that photolysis of gaseous partially deuterated ethene at 123.6 nm (from a Kr resonance lamp) yielded mainly hydrogen, ethyne, ethane, and butane.[33] Lin et al. who investigated the photodissociation dynamics of C_2H_4 at 157 nm reported that H-elimination and H_2-elimination channels are equally important; isotopic and site effects on the branching ratios of distinct H_2-elimination channels have also been observed.[34] It is, thus, expected that irradiation of a matrix sample of C_2H_4 isolated in solid Ne with vuv light produces initially mainly H, H_2, C_2H_2, and C_2H_3.

As indicated in Table I, observed lines at 1357.4, 677.1, and 895.3 cm^{-1} in this work agree with previous results of matrix-isolated C_2H_3. Four additional related lines that we observed at 3141.0, 2953.6, 2911.5, and 857.0 cm^{-1} are, thus, expected to be associated with other vibrational modes of C_2H_3. The line at 857.0 cm^{-1} fits satisfactorily with the value $\nu_9=850$ cm^{-1} predicted with the EOMIP/CCSD method[17] but is ~4.5% and 8.9% greater than those predicted with B3LYP and PW91PW91 methods. Observed wavenumbers of the three C—H stretching modes are 5.0%–9.1%, 1.3%–4.0%, and 3.1%–6.2% smaller than those predicted with EOMIP, PW91PW91, and B3LYP, respectively; these deviations are typical for C—H stretching modes.

Predicted ^{13}C- and D-isotopic ratios for C_2H_3 are com-

pared to experimental results in Table II; the satisfactory agreement further supports our assignments. For ^{13}C substitution, the largest deviation between experimental and predicted isotopic ratios for seven observed modes of $^{13}C_2H_3$ is 0.0021, within errors typically of $\sim$0.003. For D substitution, the largest deviation between observed and predicted isotopic ratios for six modes of C_2D_3 is 0.0072 (ν_5). A possibility exists that ν_5 (predicted at 1018.2 cm^{-1}) and $2\nu_7$ mode (with ν_7 predicted at 512.5 cm^{-1}) of C_2D_3 might be interacting with each other so that the levels are shifted slightly. As ν_7 of C_2D_3 is beyond our detection limit, no information is available.

Based on observed ^{13}C- and D-isotopic shifts and comparison of observed vibrational wavenumbers, relative intensities, and isotopic ratios with values predicted with quantum-chemical calculations, we conclude that observed new lines at 3141.0, 2953.6, 2911.5, and 857.0 cm^{-1} are due to vibrational modes of $\nu_1 - \nu_3$ and ν_9 of C_2H_3 radical.

Although we scrutinized our spectra carefully, the modes ν_4 (predicted at 1650 cm^{-1} by B3LYP) and ν_6 (predicted at 1048 cm^{-1}) of vinyl remained to be unobserved. A reason for the absence of ν_4 is likely its small intensity or possible interference from water lines. In contrast, the ν_6 mode is predicted to have an intensity similar to that of ν_5 (Table I). It is unclear why we are unable to observe the ν_6 line of C_2H_3 in solid Ne. Although a weak broad line near 1040 cm^{-1} might be ascribed to ν_6, we identified no corresponding line near 850 cm^{-1} as predicted for C_2D_3.

Vibrational wavenumbers reported by Letendre *et al.*[16] for gaseous C_2H_3 differ by -80, 81, and 60 cm^{-1} (-6.3%, 10.7%, and 6.3%), respectively, from those reported previously and in this work for the ν_5, ν_7, and ν_8 modes of C_2H_3 isolated in a Ne matrix. Those reported by Letendre *et al.* for gaseous C_2H_3 differ by 94, 210, 192, and 38 cm^{-1} (2.9%, 6.6%, 6.2%, and 4.2%), respectively, from the new features, $\nu_1 - \nu_3$ and ν_9, observed in this work. The deviations between vibrational wavenumbers of C_2H_3 in its gaseous state reported by Letendre *et al.*[16] and those in its matrix-isolated state are much greater than one expects ($<3\%$).[35] Further investigation of the IR spectrum of gaseous C_2H_3 is warranted.

V. CONCLUSION

We irradiated matrix samples of C_2H_4/Ne near 3.0 K with synchrotron radiation at 120 nm and observed IR absorption lines of vinyl radical. Features at 3141.0(ν_1), 2953.6(ν_2), 2911.5(ν_3), 1357.4(ν_5), 677.1(ν_7), 895.3(ν_8), and 857.0(ν_9) cm^{-1} are assigned based on observed ^{13}C- and D-isotopic shifts and theoretical predictions of line positions, infrared intensities, and isotopic ratios of C_2H_3. Considering the exceptionally large deviations of these vibrational wavenumbers from those reported for gaseous C_2H_3, further work on vibrational spectrum of gaseous C_2H_3 is desirable.

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