Infrared Absorption Spectra of Vinyl Radical Isolated in Solid Ne

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The vinyl radical (C_2H_3) plays an important role in hydrocarbon combustion and possibly also in astrochemistry. Vinyl is the simplest open-shell olefinic molecule and is an important reactive intermediate in high temperature reactions with hydrogen and oxygen. It is also found in low temperature extraterrestrial planetary atmospheres and paid attention to its implication in stereochemistry. It can serve as a crucial test to aid an understanding of the chemistry of unsaturated hydrocarbons in the atmosphere and in combustion.

Despite its significant role in free-radical chemistry, spectral observations of C_2H_3 have been limited; only the most intense line near 900 cm^{-1} was extensively investigated. Letendre *et al*., photodissociated several precursors at selected wavelengths to produce highly vibrationally excited species and then monitored its IR emission with time-resolved Fourier-transform spectroscopy. They reported all nine vibrational modes of vinyl, but the observed line positions and relative intensities of these IR lines differed much from theoretical predictions on corresponding vibrational modes of vinyl.

Here we report the IR absorption spectrum of vinyl radical upon irradiation of Ne matrix samples containing C_2H_4 with vacuum ultraviolet light at 120 nm generated from a synchrotron. The spectral assignments of vinyl are based on quantum-chemical calculations and isotopic-substituted experiments. Observed absorption lines are assigned to seven of nine vibrational modes of vinyl; four of them are new.

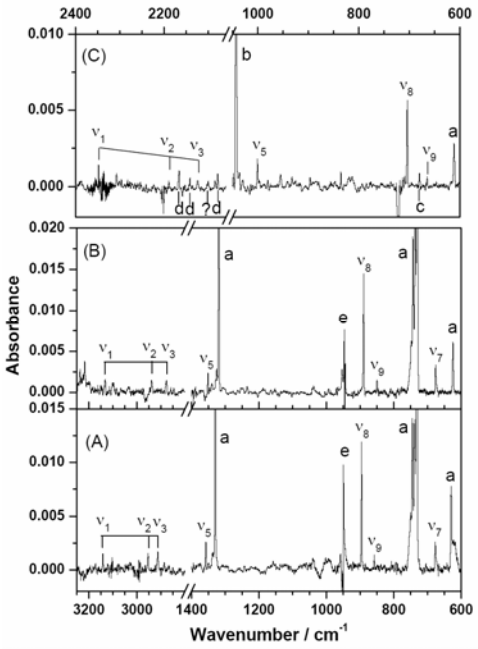

Figure 1. is a stripped spectrum recorded after irradiation of the matrix sample at 120 nm for 1.5 h. The stripped spectrum was derived on subtracting the spectrum of C_2H_4, reduced by a factor from that recorded after irradiation so that most lines due to C_2H_4 are diminished. As shown in Fig. 1, 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 is marked as e, and vinyl is marked according to the assigned vibrational modes.

mode	EOMIP -CCSD[a]	this work PW91PW91	this work B3LYP	Ref. 12 gas	Ref. 9 Ar matrix	this work Ne matrix
$\nu_1(a')$	3298 (1.4)[b]	3181 (0.5)[b]	3239 (0.5)[b]	3235 (7)		3141.0 (2.0)
$\nu_2(a')$	3222 (6.1)	3072 (2.7)	3138 (4.2)	3164 (11)		2953.6 (3.0)
$\nu_3(a')$	3118 (6.0)	2976 (6.8)	3044 (7.1)	3103 (0.5)		2911.5 (2.6)
$\nu_4(a')$	1689 (1.4)	1616 (2.7)	1650 (2.9)	1700 (0.1)		
$\nu_5(a')$	1419 (10.6)	1346 (12)	1395 (11)	1277 (100)	1356.7[c]	1357.4 (24)
$\nu_6(a')$	1077 (12.5)	1006 (11)	1047 (11)	1099 (43)		
$\nu_7(a')$	730 (29.8)	678 (32)	708 (31)	758 (11)[d]	c	677.1 (32)
$\nu_8(a'')$	965 (100)	886 (100)	928 (100)	955 (32)[e]	900.8[c]	895.3 (100)
$\nu_9(a'')$	850 (13.7)	787 (18)	820 (28)	895 (93)		857.0 (9.6)

Table I compares vibrational wavenumbers (in cm^{-1}) and relative intensities (listed in parentheses) of C_2H_3 predicted with various theoretical methods. Table I also lists previous experimental results for comparison. The vibrational wavenumbers of theoretical predictions are shown to agree satisfactorily with previous experimental values except ν_5 of the gaseous C_2H_3 reported by Letendre *et al*. In contrast, predicted relative infrared intensities vary greatly from those reported by Letendre *et al*., as shown in Table I. The three known vibrational wavenumbers of matrix-isolated C_2H_3, ν_5, ν_7, and ν_8, also deviate greatly from those reported by Letendre *et al*.

We irradiated matrix samples of C_2H_4/Ne near 3.0 K with synchrotron radiation at 120 nm and observed new IR absorption lines corresponding to vibrational modes of vinyl radical. These 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.