

OBSERVATION OF X¹A₁ VINYLIDENE BY PHOTOELECTRON SPECTROSCOPY OF THE C₂H₂⁻ ION

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Photoelectron spectra of the vinylidene anion (C₂H₂⁻) show vibrational structure in X¹A₁ vinylidene up to 12 kcal/mol above the vibrational ground state. Analysis yields an EA(C₂H₂ X¹A₁) of 0.47 ± 0.02 eV, and frequencies for the CC stretch and HCH bend. Absence of the ³B₂ state in the photoelectron spectra indicates the ¹A₁–³B₂ splitting in vinylidene is ≥ 1.7 eV.

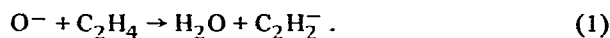
1. Introduction

The vinylidene radical (H₂C=C:) is the simplest unsaturated carbene and is postulated to be a reactive intermediate in a number of reactions [1,2], such as in the combination of two CH₂ radicals to produce acetylene. It is particularly interesting in that it rearranges by a 1,2 hydrogen shift, an important process in the chemistry of carbenes [3]. Extensive calculations have been done on the electronic structure of X¹A₁ vinylidene [4–12], which predict, among other things, a barrier to rearrangement of 4–8 kcal/mole [6,8], or even as low as 0.9 kcal/mole [11]. Dynamical calculations predict [4] a lifetime against tunneling of 0.1–10 ps, in agreement with indirect experiments [2,13]. There have been no direct observations of singlet vinylidene, and, indeed, the expected short lifetime has led to speculation that it may not be spectroscopically observable.

Calculations predict the lowest excited electronic state, ³B₂, to lie 30–50 kcal/mole above the singlet [5,8,14–17]. The triplet is predicted to have a much higher barrier to rearrangement, and might live sufficiently long to be experimentally observed. In fact, Laufer [18–20] has observed a transient absorption in both photolyzed acetylene and in ketene, which

is attributed to triplet vinylidene.

A negative ion of the composition C₂H₂⁻ is formed readily [21] by the reaction



Deuterium labeling experiments [22] indicate that the anion possesses the vinylidene structure. The observation [23] of electron transfer from C₂H₂⁻ to O₂ in a flow-drift apparatus indicates that EA(C₂H₂) ≈ EA(O₂), 0.44 eV. Photodetachment of this negative ion can be used to obtain information on the energetics of the neutral vinylidene, including the electron affinity (EA), vibrational frequencies, and perhaps clues regarding the potential surface and barrier to rearrangement. With an appropriately energetic photon, one could also access the lowest-lying triplet state (³B₂) and measure its energy relative to the ground state. In this paper we report the photoelectron spectra of C₂H₂⁻ and C₂D₂⁻, from which electron affinities and two vibrational frequencies are obtained for the corresponding neutral radicals.

2. Experimental

In the negative ion photoelectron spectrometer, a mass-selected negative ion beam is crossed with a laser beam, and the resulting photodetached electrons are energy analyzed and counted. The apparatus and tech-

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nique used in this experiment have been described in detail in previous papers [24–27], and will be just briefly outlined here. A gas discharge ion source produces the negative ions, which are extracted and accelerated into a beam. Ions of the desired mass are selected in a crossed electric and magnetic field region. The ion beam then intersects the 488 nm (2.54 eV) intracavity beam of an Ar II laser. Electrons photodetached into a cone of 5° half-angle (perpendicular to both beams) pass through a hemispherical energy analyzer. The energy-dispersed electrons are imaged onto a position-sensitive detector, which allows simultaneous collection of electrons in a 100–200 meV energy range [26, 27]. The analyzer resolution is ≈ 12 –20 meV for the conditions under which these data were obtained. Photodetachment of O^- , with a known [28] electron affinity, serves as a calibrant for an absolute electron energy scale.

A mixture of C_2H_4 and N_2O was used in the source (since O^- is easily made in this source from N_2O), in anticipation of making $C_2H_2^-$ by reaction (1). Using a LaB_6 -coated tantalum filament, we extract a several nanoampere beam of mass 26 ions, stable for several hours, and obtain the photoelectron spectrum. Using C_2D_4 in the ion source, a 10–100 pA beam of mass 28 ions produced a photoelectron spectrum similar to the mass 26 spectrum. Comparison of count rates shows that some 2% of the mass 26 ion current was $C_2H_2^-$. The remaining ion current is attributed to CN^- , which does not detach [29] with 2.54 eV photons.

3. Results and discussion

Fig. 1a shows the photoelectron spectrum of $C_2H_2^-$, obtained with 2.54 eV photons. The entire (0–2.54 eV) electron spectrum contains only the one group of peaks shown here, presumably all resulting from photodetachment to various levels of the ground electronic state of neutral vinylidene. To help with the identification of the peaks in the spectrum, the photoelectron spectrum of $C_2D_2^-$, also taken with 2.54 eV photons (fig. 1b) was obtained. The peaks labeled “B” shift significantly upon deuteration, indicating that they correspond to excited vibrations involving the H atoms; the peaks labeled “C” remain at nearly the same energy, and reflect a mode with little H atom motion. The peak labeled A in each spectrum is assigned as the

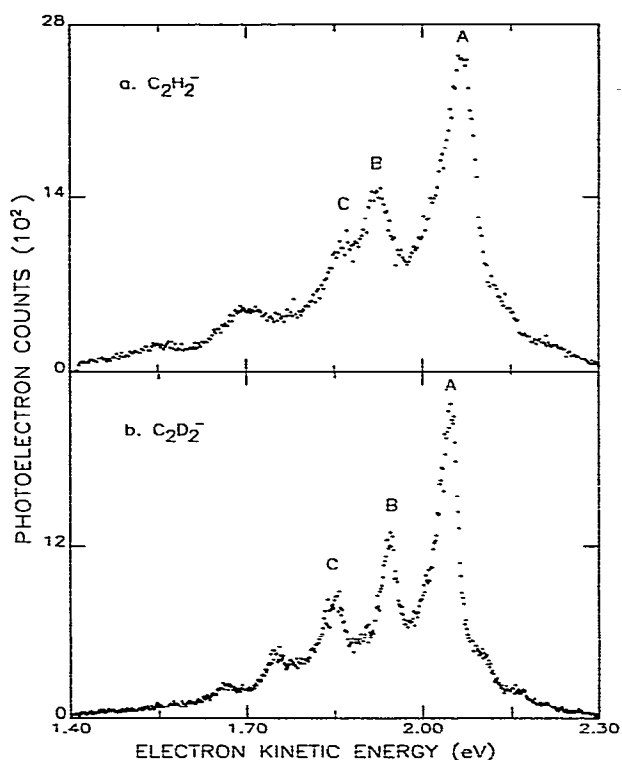


Fig. 1. Photoelectron spectra of $C_2H_2^-$ and $C_2D_2^-$, obtained with 2.54 eV photons.

(0–0) transition; this peak does not shift significantly upon deuteration, and peaks at higher electron kinetic energy have the appearance of anion hot bands.

To interpret the spectrum more quantitatively, we must consider the possible photodetachment transitions. The orbital occupancy for ground state (1A_1) vinylidene is $1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 1b_2^2 1b_1^2$. Calculations indicate [30, 31] that the extra electron in the anion is located in a $2b_2$ largely non-bonding orbital localized on the carbene carbon. Detachment of this electron results in production of ground-state 1A_1 vinylidene, while detachment of a $5a_1$ electron produces the lowest excited triplet state, 3B_2 . To assign the observed transitions to vibrational modes of the molecule, we use this orbital description to determine which modes are likely to be excited by the geometry changes involved in the photodetachment process.

Calculations indicate that both the anion [11, 30, 31] and neutral [5, 6, 32] are planar and of C_{2v} sym-

metry. Detachment of the $2b_2$ electron from the anion forms the ground state neutral, with the major geometry changes being a shortening of the carbon-carbon by 0.05 Å, and an increase in $\angle\text{HCH}$ of $\approx 7^\circ$ [5, 6, 30–32]. We thus expect that the photoelectron spectrum should predominantly consist of these two modes and combinations of them. In addition, peaks arising from the CH_2 scissors mode should shift considerably upon deuteration, while those due to the C–C stretch should not. We assign peak C as corresponding to a final state with $\nu = 1$ in the C–C stretch, since the A–C peak separation remains almost constant upon deuteration. Peak B is assigned to the scissors motion, as the A–B spacing decreases noticeably upon deuteration. All of the remaining peaks in the spectrum can be attributed to combinations or overtones of the two modes mentioned. There are no other large changes in geometry between the ion and the neutral; thus no other strong progressions are expected to be observed in the spectrum.

More quantitatively, the A–B peak splitting in the C_2H_2^- spectrum gives a frequency of $1120 \pm 100 \text{ cm}^{-1}$ for the CH_2 scissors bend, and the corresponding bend in C_2D_2^- is $840 \pm 100 \text{ cm}^{-1}$. The observed frequency of the C–C stretch is $1650 \pm 120 \text{ cm}^{-1}$ for C_2H_2^- and $1610 \pm 120 \text{ cm}^{-1}$ for C_2D_2^- . Table 1 compares the present results with predicted values for vibrational frequencies in vinylidene [4, 6]. Also included are known frequencies of the analogous modes in isostruc-

Table 2
Acetylene vibrational frequencies^{a)}

Mode	Frequency (cm^{-1})
CH symmetric stretch	3372.5
CH asymmetric stretch	3294.85
CC stretch	1973.5
cis bend	729.15
trans bend	611.70

^{a)} Ref. [33].

tural H_2CO and D_2CO ; these demonstrate that the CH_2 bend and the C–C stretch of vinylidene, upon deuteration, show shifts similar to the corresponding modes in formaldehyde. From an approximate Franck-Condon analysis [24] of the spectra, we find that Δr_c for the C–C bond length change between the ion and neutral is $0.05 \pm 0.01 \text{ Å}$, in good agreement with calculations [5, 6, 30, 31]. Table 2 lists the known vibrational frequencies of acetylene. The fact that none are near the two frequencies measured here serves as additional evidence that the neutral species produced in the photodetachment process is indeed the singlet diradical.

The electron affinity of vinylidene is obtained from the difference between the photon energy (2.54 eV) and the energy of peak A. Minor rotational corrections [24] to the electron affinities are estimated to be 0.005

Table 1
Vibrational frequencies of \tilde{X}^1A_1 vinylidene and formaldehyde

	Mode	Calculated frequency (cm^{-1})	Observed frequency (cm^{-1})
$^1A_1 \text{ C}_2\text{H}_2$	CH_2 scissors	1289 ^{d)}	1120 ^{b)}
	CC stretch	1719 ^{a)}	1650 ^{b)}
$^1A_1 \text{ C}_2\text{D}_2$	CD_2 scissors		840 ^{b)}
	CC stretch		1610 ^{b)}
H_2CO	CH_2 scissors		1501 ^{c)}
	CO stretch		1746 ^{c)}
D_2CO	CD_2 scissors		1105 ^{c)}
	CO stretch		1700 ^{c)}

^{d)} Double-zeta + polarization CI calculation [4]. These authors estimate the true ν_{1-0} energy difference to be $\approx 7\%$ less than these values.

^{b)} This work. ^{c)} Ref. [33].

eV for C_2H_2 and 0.002 eV for C_2D_2 . The electron affinities then, are 0.47 ± 0.02 eV for C_2H_2 (\tilde{X}^1A_1) and 0.49 ± 0.02 eV for C_2D_2 ; the substantial error limits are primarily due to uncertainty in the absolute energy scale calibration. The isotope shift of 20 meV in the electron affinities, as well as the vibrational frequencies, are more accurate than the EAs themselves, since they are relative quantities, not dependent on the absolute energy calibration. The reported EA is consistent with the earlier work of Lindinger et al. [23]. The direction of the isotope shift indicates that the ion has a higher zero point energy than the neutral.

Transitions to only one electronic state are visible in the photoelectron spectrum obtained in this experiment. That is, at electron kinetic energies below those of the singlet peaks, no peaks as large as 2% of the height of peak A are observed. This absence indicates that the lowest excited electronic state (3B_2) of C_2H_2 must lie at least 1.7 eV above the ground (1A_1) state.

An interesting feature of these spectra is that they show considerable vibrational structure as much as 12 kcal/mol above the vibrational ground state. While this quantity is considerably higher than the predicted barrier to rearrangement, the presence of structure alone indicates that the lifetime of 1A_1 vinylidene with 12 kcal/mol internal excitation is at least one vibrational period, $\approx 10^{-14}$ s. The width of peaks may shed further light on the lifetime of singlet vinylidene. The vibronic peaks in the spectra are broadened considerably over the 15 meV resolution of the analyzer, due to several factors. First, the analyzer does not resolve individual rotational transitions, so each vibronic peak in the spectrum is actually an envelope containing transitions from all populated rotational levels of the ion. In the present case, the rotational broadening is thought to be comparable to the observed 50 meV width. Second, there are underlying sequence bands from detachment from excited vibrational levels of the ion. Finally, in the case of a species such as 1A_1 vinylidene, there is a possibility of lifetime broadening. If we were to assume that the latter is entirely responsible for the peak widths in the $C_2H_2^-$ photoelectron spectrum, the observed 50 meV peak width (fwhm) would indicate a lifetime of $\approx 10^{-13}$ s. Since we do not know precisely which factors are responsible for these peak widths, it can only be said that 10^{-13} s is a lower limit on the lifetime of the vibrationless level of 1A_1 vinylidene. This result is consistent both with the tunneling calcu-

lations [6] using methods developed by Miller, and with experiment [2].

4. Conclusion

From the photoelectron spectra obtained in these experiments, the EA of \tilde{X}^1A_1 vinylidene is found to be 0.47 ± 0.02 eV and that of deuterated vinylidene 0.49 ± 0.02 eV. Vibrational structure in the spectrum yields frequencies for the scissors bend and C—C stretch in \tilde{X}^1A_1 C_2H_2 of 1120 ± 100 cm^{-1} and 1650 ± 120 cm^{-1} respectively, and 840 ± 100 cm^{-1} and 1610 ± 120 cm^{-1} for \tilde{X}^1A_1 C_2H_2 . Use of a new flowing afterglow [34] ion source should allow similar experiments to be done on a whole family of unsaturated carbenes which can be produced [21] by reactions analogous to reaction (1). In addition, it is expected that use of a higher-energy photon (3.4080 eV) in photodetachment of $C_2H_2^-$ should provide access to the 3B_2 state of neutral vinylidene, allowing direct measurement of the singlet—triplet splitting.

Acknowledgement

We are pleased to acknowledge support by grants CHE78-18424 and PHY82-00805 from the National Science Foundation. Acknowledgement is also made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research.

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