J. Phys. Chem. A **2004,** *108,* 4194−4201

Ethylene. Experimental Evidence for New Assignments of Electronic Transitions in the $\pi \rightarrow \pi^*$ Energy Region. Absorption and Magnetic Circular Dichroism Measurements with Synchrotron Radiation

Patricia Ann Snyder* and Sylvia Atanasova

Department of Chemistry and Biochemistry, Florida Atlantic University, Boca Raton, Florida 33431

Roger W. C. Hansen

Synchrotron Radiation Center, University of Wisconsin—Madison, 3731 Schneider Drive,
Stoughton, Wisconsin 53589

Received: July 11, 2003; In Final Form: December 8, 2003

An exploration of the vacuum ultraviolet magnetic circular dichroism and absorption spectra of propylene and a comparison to ethylene spectra provides new information on the electronic structure of ethylene. Ethylene has three electronic transitions in the energy region previously assigned as two. The presently proposed assignments for these transitions are $\pi \rightarrow 3s(^1A_g \rightarrow {}^1B_{3u})$, $\pi \rightarrow \pi^*(^1A_g \rightarrow {}^1B_{1u})$, and $\pi \rightarrow 3p$. The lowest energy transition that was previously assigned as the beginning of the $\pi \rightarrow \pi^*$ is assigned as the $\pi \rightarrow 3s$ transition. The $\pi \rightarrow \pi^*$ and $\pi \rightarrow 3p$ transitions are accidentally degenerate in ethylene. The electronic transition with sharp structure doublets which was previously assigned as $\pi \rightarrow 3s$ is assigned as one of the $\pi \rightarrow 3p$ [$\pi \rightarrow 3p_\sigma$ ($^1A_g \rightarrow {}^1B_{2g}$), $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$), or $\pi \rightarrow 3p_x$ ($^1A_g \rightarrow {}^1A_{1g}$)] vibronically allowed electronic transitions. A case is presented that it is the $\pi \rightarrow 3p_\sigma$ ($^1A_g \rightarrow {}^1B_{2g}$) and/or the $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$) electronic transitions that are responsible for the sharp structured doublets in ethylene.

Introduction

A large number of molecules contain a carbon−carbon double bond and are often called olefins. Ethylene is the simplest olefin and serves as the basis for understanding the electronic structure of not only all molecules with one carbon−carbon double bond but also molecules with multiple double bonds. Electronic structure determines all the chemistry of a molecule. Consequently, the number of transitions, their energies, and their assignments in ethylene is an extremely important problem.

The assignment of transitions and their energy in ethylene has been generally agreed to for about 50 years.[1−7] The absorption spectrum of ethylene is shown in Figure 1. This accepted interpretation is that the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) starts at about 50 000 cm^{-1} (200 nm) with low intensity, and the transition continues gaining intensity and eventually reaches a maximum at about 160 nm (62 500 cm^{-1}). The vibrational peaks are separated by about 800 cm^{-1}. On top of the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) transition the $\pi \rightarrow 3s$ Rydberg ($^1A_g \rightarrow {}^1B_{3u}$) transition starts at about 57 336 cm^{-1} (174 nm) with a very sharp distinctive structure. The sharp absorption peaks occur in pairs and are often referred to as doublets. There are at least four doublets. The doublets are separated from each other by about 1300 cm^{-1} and the peaks within the doublet are separated by about 500 cm^{-1}.

This interpretation, while generally accepted, has always led to difficulties.[1,8−15] Obtaining agreement between theory and experiment for ethylene has proved to be difficult and illusive. Therefore, as soon as a new experimental method became available, it was utilized with the hope of furthering the understanding of the electronic structure of ethylene.[1,8,12−29] In addition, there have been innumerable theoretical calculations carried out to determine the electronic structure of ethylene and other simple olefins.[1,30−52]

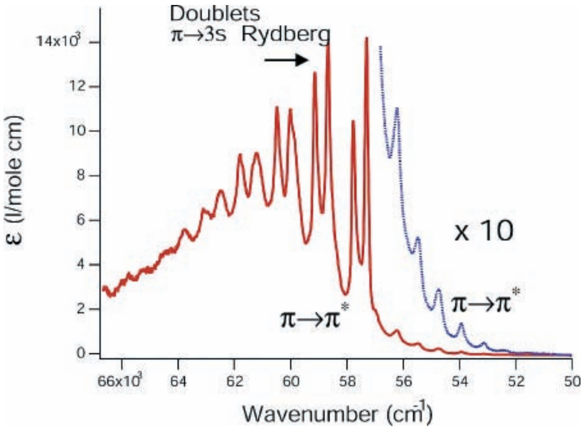


Figure 1. Absorption spectrum of ethylene. The generally accepted assignment is that the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) transition is the first transition observed. On top of the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) transition the $\pi \rightarrow 3s$ Rydberg ($^1A_g \rightarrow {}^1B_{3u}$) transition starting at about 57 336 cm^{-1} (174 nm) with a very sharp doublet structure.

Simple olefins such as propylene and other molecules with a single double bond absorb mainly in the vacuum ultraviolet region of the spectrum (below 200 nm or 50 000 cm^{-1}). This region is experimentally more challenging than the visible or ultraviolet regions of the spectrum. The capability has been developed to experimentally obtain the magnetic circular dichroism spectrum in the vacuum ultraviolet region through the use of synchrotron radiation at the Synchrotron Radiation Center, University of Wisconsin−Madison.[53−56] Magnetic circular dichroism measurements were carried out on the four meter normal incidence monochromator with an end station and superconducting magnet specifically designed for this purpose by Snyder et al.

10.1021/jp030837r CCC: $27.50

When molecules are in a strong magnetic field with the magnetic field parallel to the direction of propagation of the electromagnetic radiation, the absorption of left and right circularly polarized radiation is different. This is called magnetic circular dichroism. Magnetic circular dichroism spectroscopy measures the difference in molar extinction coefficient for left and right circularly polarized radiation, $\epsilon_L - \epsilon_R$, or the difference in absorbance for left and right circularly polarized radiation, $A_L - A_R$, as a function of wavelength or wavenumber. Because magnetic circular dichroism measures a difference, the peaks may be positive or negative. Since overlapping electronic transitions may have opposite signed magnetic circular dichroism (i.e., positive and negative peaks), a peak which appears to be one transition in the absorption spectrum can be shown to be more than one transition by the use of magnetic circular dichroism spectroscopy.

Application of magnetic circular dichroism gives new insights into the electronic structure of molecules. In discussion of magnetic circular dichroism there are three type of terms, the *A*, *B*, and *C* terms. *A* and *C* terms are only relevant for molecules which belong to a point group with degenerate ground or excited states. For molecules that do not belong to a point group with degenerate states, *B* terms are the only type of term observed in the magnetic circular dichroism spectrum. Both ethylene and propylene will exhibit only *B* terms in their magnetic circular dichroism spectrum. *B* terms have the same shape as the absorption but they may be positive or negative in sign. They are in general smaller and more difficult to measure than *A* and *C* terms. The *B* terms are more difficult to interpret theoretically since they arise from mixing of transitions. However, *B* terms are particularly useful for detecting hidden transitions.

The absorption spectrum is dominated by valence transitions which for ethylene and propylene would be the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) transition or N → V transition. That is to say, the allowed valence transitions are more intense than the Rydberg transitions such as $\pi \rightarrow 3s$ ($^1A_g \rightarrow {}^1B_{3u}$). In contrast to absorption, it has been experimentally observed in other polyatomic molecules that the magnetic circular dichroism spectrum is not dominated by the valence transitions. In fact, Rydberg transitions often exhibit a significant signal and dominate the magnetic circular dichroism spectrum.[11,57−59]

The magnetic circular dichroism and absorption spectra of propylene were obtained to gather information about the electronic structure of simple olefins, particularly ethylene.

Experimental Section

The magnetic circular dichroism and absorption spectra were measured using synchrotron radiation at the Synchrotron Radiation Center, University of Wisconsin−Madison. For the measurements on propylene the magnetic circular dichroism instrumentation was attached to the four-meter normal incidence monochromator. The monochromator had the 1200 groove per millimeter Al−MgF$_2$ grating (reciprocal linear dispersion 2.08 Å per mm) in place. With this grating, the monochromator has four times higher resolution than the aluminum Seya−Namioka monochromator used in previous experiments. The magnetic circular dichroism instrumentation has been described previously.[11,19,57−59] However, the instrument was upgraded when a new experimental chamber was constructed to accommodate a new sample cell and a new superconducting magnet. The new magnet was specifically designed for this experiment and constructed by Oxford Instruments. The new magnet is capable of generating stronger fields (8 and 10 T with pumping) than the previously used superconducting magnet. The slit width was 125 μm (i.e., a spectral bandwidth of 0.26 Å) in the higher energy region. The lower energy region of the spectrum was scanned with 500 μm slits (1.04 Å).

TABLE 1: Transition Notation for Ethylene, Point Group D_{2h} (*z* Axis along Double Bond; *x* Axis Perpendicular to the Molecular Plane)[a]

transition	orbital notation	state notation	polarization of orbitally allowed transition
$\pi \rightarrow \pi^*$	$1b_{3u} \rightarrow 1b_{2g}$	$^1A_g \rightarrow {}^1B_{1u}$	*z*
$\pi \rightarrow 3s$	$1b_{3u} \rightarrow 4a_g$	$^1A_g \rightarrow {}^1B_{3u}$	*x*
$\pi \rightarrow 3p_\sigma$	$1b_{3u} \rightarrow 3\ b_{1u}$	$^1A_g \rightarrow {}^1B_{2g}$	not orbitally allowed
$\pi \rightarrow 3p_y$	$1b_{3u} \rightarrow 2\ b_{2u}$	$^1A_g \rightarrow {}^1B_{1g}$	not orbitally allowed
$\pi \rightarrow 3p_x$	$1b_{3u} \rightarrow 2\ b_{3u}$	$^1A_g \rightarrow {}^1A_g$	not orbitally allowed

[a] An electronic transition is orbitally allowed if electric dipole transition moment integral has a value. The integral has a value if the triple direct product $\Gamma_{\text{electronic excited state}} \times \Gamma_{\text{dipole moment operator}} \times \Gamma_{\text{electronic ground state}}$ contains the totally symmetric irreducible representation, a_g.

For the magnetic circular dichroism measurements a time constant of 4 s was used on the lock-in amplifier. A computer averaged about six to eight readings for each point. The data were smoothed using a FORTRAN program written to smooth the high-frequency noise. The program smoothed the data by averaging each data point with its nearest neighbors. The system was calibrated using *d*-10-camphorsulfonic acid at 290 nm.[60]

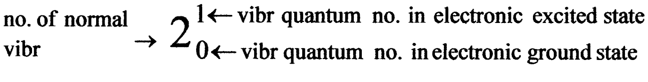
The absorption spectrum of ethylene was obtained on the 1 m Seya Namioka monochromator at the Synchrotron Radiation Center, University of Wisconsin, Madison. The spectral bandwidth for these measurements was 0.42 Å.

Results and Discussion

Coordinate System and Nomenclature. Ethylene belongs to the D_{2h} point group. Because of its high symmetry there are various conventions for the axes in the literature. In this paper the *z*-axis is taken to be along the double bond and the *x*-axis is perpendicular to the plane of the molecule. [This is the recommended convention for the ethylene coordinate system.][61] All symmetry designations are for this coordinate system. Table 1 provides the symmetry designations of the various electronic transitions for ethylene discussed in this paper. The table also gives the polarization for the orbitally allowed transitions.

It is important to know what coordinate system is used in a paper because choice of coordinates affects the symmetry labels. In the literature one can find papers that use all of the possible choices of coordinates. Often, particularly in vibrational spectroscopy, the *x*-axis is chosen along the double bond and the *z*-axis is perpendicular to the bond. This choice of axes interchanges 1 and 3 in the symmetry labels. Changing the axes changes the symmetry labels for both the electronic transitions and the normal modes of vibration.

In this paper, electronic excitations are being discussed. However, the observed vibrational structure will be used to help with this interpretation. For this purpose, the following notation for the normal modes of vibration involved in the electronic transition is used:



Therefore, 2_0^1 means one quanta of vibrational normal mode 2, (ν_2), in the electronic excited state from the electronic ground state and vibrational ground state with quantum number 0, (ν_0).

Propylene Spectra and Assignments. The magnetic circular dichroism and absorption spectra for propylene are presented

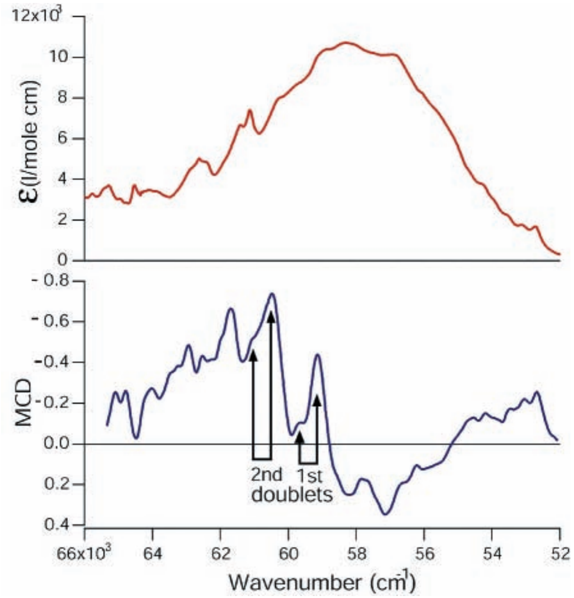


Figure 2. Absorption (top) and magnetic circular dichroism (bottom) spectra of propylene. The molar extinction coefficient, ϵ, has units of cm^{-1} L mol^{-1}. The magnetic circular dichroism [MCD] has units of $\Delta\epsilon$/T.

in Figure 2 for the 52 000−65 500 cm^{-1} energy region. The propylene absorption spectrum is at higher resolution than previous absorption spectra. The data shows the power of magnetic circular dichroism to uncover overlapping electronic transitions. The spectrum shows that there are at least three electronic transitions in this region of the spectrum. The first transition is negative, the second transition is positive, and the third transition is negative. The magnetic circular dichroism spectrum shows distinct and different vibrational structure for each electronic transition. The electronic excited states of propylene have been previously investigated using absorption spectroscopy, electron impact spectroscopy and theoretical calculations.[1,17,39,52,62−67] The magnetic circular dichroism results are consistent with what was expected from these previous results; however, it also gives new information about the electronic structure. The magnetic circular dichroism spectrum shows unequivocally that there are at least three electronic transitions in this energy region and also shows the energy of these transitions. The magnetic circular dichroism spectrum of propylene clearly shows the third electronic transition starts at a lower energy than previously believed. Also, since the absorption spectrum is at higher resolution than previous absorption spectra, it shows additional vibrational structure.

The first transition for propylene is from 52 000−55 080 cm^{-1}. This transition exhibits a vibrational progression in both the absorption and magnetic circular dichroism spectra of about 400 cm^{-1}. The magnetic circular dichroism is negative in this region. In the absorption spectrum the maximum molar extinction coefficient is approximately 1500 L mol^{-1} cm^{-1}, which is indicative of an orbitally allowed transition. The transitions that are orbitally allowed and expected to be in this energy region are $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) and $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$). The magnitude of the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) transition is expected to be larger than the $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) transition.[1] The energy and magnitude of the first transition is consistent with an assignment of $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$). [Ethylene symmetry notation for the transitions is used here.] This transition is often called the N → R(3s) Rydberg transition.

It is interesting to consider what type of vibration is responsible for the observed 400 cm^{-1} progression. Experimental values for the ground-state vibrations show vibrations with energies in the appropriate range.[67−70] A PM3 semiempirical calculation was carried out with Hyperchem software (version 6.0, by Hypercube) to obtain the normal modes and their energies. Comparison of experimental and theoretical values for various normal vibrations in propylene shows the vibrational progression of 400 cm^{-1} is most likely a wagging vibration. The 2a″ normal mode has a calculated energy of about 580 cm^{-1} in the ground state and an experimental value of 579 cm^{-1}. This 2a″ normal mode is expected to have a lower value in the excited state, and 400 cm^{-1} is a reasonable value for this wagging vibration in the $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) excited state.

The next electronic transition has an opposite sign from the first magnetic circular dichroism band and is positive. The transition is centered at about 57 000 cm^{-1} and extends from 55 080−58 760 cm^{-1}. This transition is much stronger in the absorption spectrum than the first transition. It has a molar extinction coefficient of about 9500 L mol^{-1} cm^{-1}, which indicates a strong transition that is orbitally allowed. There is no obvious vibrational progression in the magnetic circular dichroism spectrum for this transition. The absorption spectrum may have peaks separated by about 1350 cm^{-1}. This transition could be assigned as $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) or one of the $\pi \rightarrow$ 3p transitions. However, the magnitude of the molar extinction coefficient clearly shows that it is an allowed transition. The magnitude and energy indicate an assignment of $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$), often called the N → V valence transition.

The third transition is the same sign as the first transition (negative), and has sharp vibrational structure. The doublet structure observed in ethylene is clearly visible for this transition in the propylene magnetic circular dichroism spectrum. The propylene doublets are separated from each other by about 1300 cm^{-1}, and the second peak of the doublet is separated by about 560 cm^{-1} from the first peak. In ethylene, the doublets are separated from each other by about 1300 cm^{-1}, and the second peak of the doublet is separated by about 500 cm^{-1} from the first peak. The magnetic circular dichroism spectrum of propylene shows the connection of the third propylene transition to the sharp structured doublets in ethylene. The molar extinction coefficient for the third transition of propylene is less than the second transition. The assignment of the third transition is most likely one of the $\pi \rightarrow$ 3p (N → R(3p)) transitions. Regardless of the assignment of this transition, it is the same transition in ethylene and propylene.

One of the puzzles in the spectra of simple olefins has been the difference between the absorption spectra of ethylene and other olefins such as propylene. The first transition in ethylene has been traditionally assigned as $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) while in propylene and other monoolefins the first transition has been assigned as $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$). In addition the doublets in ethylene were not obvious in the propylene absorption spectra. For the first time the similarity of the spectra for ethylene and propylene becomes apparent. The magnetic circular dichroism spectrum of propylene clearly shows the doublet structure similar to the ethylene doublet structure for the third magnetic circular dichroism band in propylene.

Comparison to Ethylene. An important experiment was the measurement of the magnetic circular dichroism spectrum of ethylene in the 53 250−62 500 cm^{-1} region.[8] The results are presented in Figure 3 and discussed in the next few paragraphs.

First, the magnetic circular dichroism spectrum in the 55 000 cm^{-1} region shows a negative magnetic circular dichroism vibrational structure which matches the absorption spectrum. The vibrational peaks are separated by about 800 cm^{-1}. In the

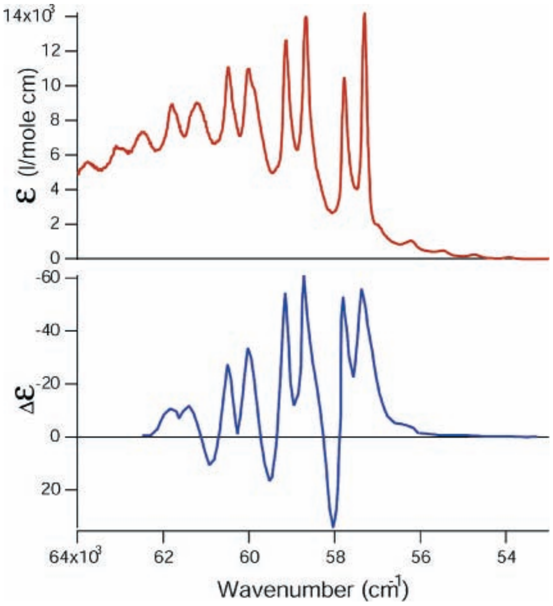


Figure 3. Absorption and magnetic circular dichroism spectra of ethylene. The molar extinction coefficient, ϵ, has units of cm^{-1} L mol^{-1}. The magnetic circular dichroism data plotted as $\Delta\epsilon = \epsilon_L - \epsilon_R$ (units of cm^{-1} L mol^{-1}) is from ref 8 (Brith-Linder and Allen). The magnetic circular dichroism was recorded with a magnetic field of 40kG. The data are plotted in terms of wavenumber for ease of comparison.

absorption spectrum this transition has been traditionally assigned as the beginning of the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$).

Next, there is the negative sharp doublet magnetic circular dichroism peaks connected to the doublet absorption peaks that start at about 57 400 cm^{-1}. These peaks are the same sign as the magnetic circular dichroism in the 55 000 cm^{-1} region. The sharp doublets are generally assigned as $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) in the absorption spectrum. Surprisingly, oppositely signed positive magnetic circular dichroism peaks were found between the sharp doublets. This is indicative of an additional electronic transition. It suggests that there are three electronic transitions in ethylene in a region formerly assigned to two electronic transitions. It was suggested that the transition with positive magnetic circular dichroism was one of the $\pi \rightarrow$ 3p transitions.[8]

Comparison to propylene results in a different interpretation for the electronic transitions in ethylene. The magnetic circular dichroism spectra show three transitions in a similar energy region, for both propylene and ethylene. These results support the fact that there are three electronic transitions in ethylene in this region. Given that there are three electronic transitions, the next question is the assignment of these transitions. Information obtained from the magnetic circular dichroism of propylene suggests new assignments for the ethylene spectrum. The suggested assignments are discussed below.

The first transition in propylene is in the energy range from 52 000 to 55 080 cm^{-1}. This transition has a vibrational progression in both the magnetic circular dichroism and absorption spectrum. The molar extinction coefficient in the absorption spectrum is 1500 L mol^{-1} cm^{-1}. All this is consistent with an assignment of $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$).

Now, consider the first region of the ethylene spectrum from 50 000 to about 57 000 cm^{-1}. This transition has a vibrational progression of 800 cm^{-1} in both the magnetic circular dichroism and absorption spectrum. The molar extinction coefficient in the absorption spectrum is 800 L mol^{-1} cm^{-1}. These observations are reminiscent of the observations for the first transition in propylene. This transition in ethylene has previously been assigned as the beginning of the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$). However, an assignment of $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) or N $\rightarrow$ R(3s) for this transition in ethylene would fit with the data and would agree with the assignment for propylene.

TABLE 2: Normal Vibrational Modes for Ethylene D_{2h} Point Group

no. of vibration	ground state[70] $\bar{\nu}$, cm^{-1}	symmetry
ν_1	3026	a_g CH_2 s-str
ν_2	1623	a_g C═C str
ν_3	1342	a_g CH_2 s-scis
ν_4	1023	a_u CH_2 twist
ν_5	2989	b_{1u} CH_2 s-str
ν_6	1444	b_{1u} CH_2 scis
ν_7	943	b_{2g} CH_2 wag
ν_8	3106	b_{2u} CH_2 as-str
ν_9	826	b_{2u} CH_2 rock
ν_{10}	3103	b_{3g} CH_2 as-str
ν_{11}	1236	b_{3g} CH_2 rock
ν_{12}	949	b_{3u} CH_2 wag

With an assignment of $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) for the electronic transition it is interesting to consider which vibration may be responsible for the 800 cm^{-1} vibrational progression. Table 2 lists all normal modes for the ground state, their vibrational energies, and the symmetry of each vibration for the coordinate system used in this paper.[70] On the basis of the ground state vibrational energies, the only normal modes with an energy in the appropriate range are the ν_7 [b_{2g}], ν_9 [b_{2u}], and ν_{12} [b_{3u}] vibrations. For an orbitally allowed electronic transition all the a_g vibrations, normal modes ν_1, $\nu_{2,}$ and ν_3, are allowed. To determine whether the ν_7 (b_{2g}) vibration is allowed for the ethylene $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) electronic transition the following direct product is evaluated using the D_{2h} point group.

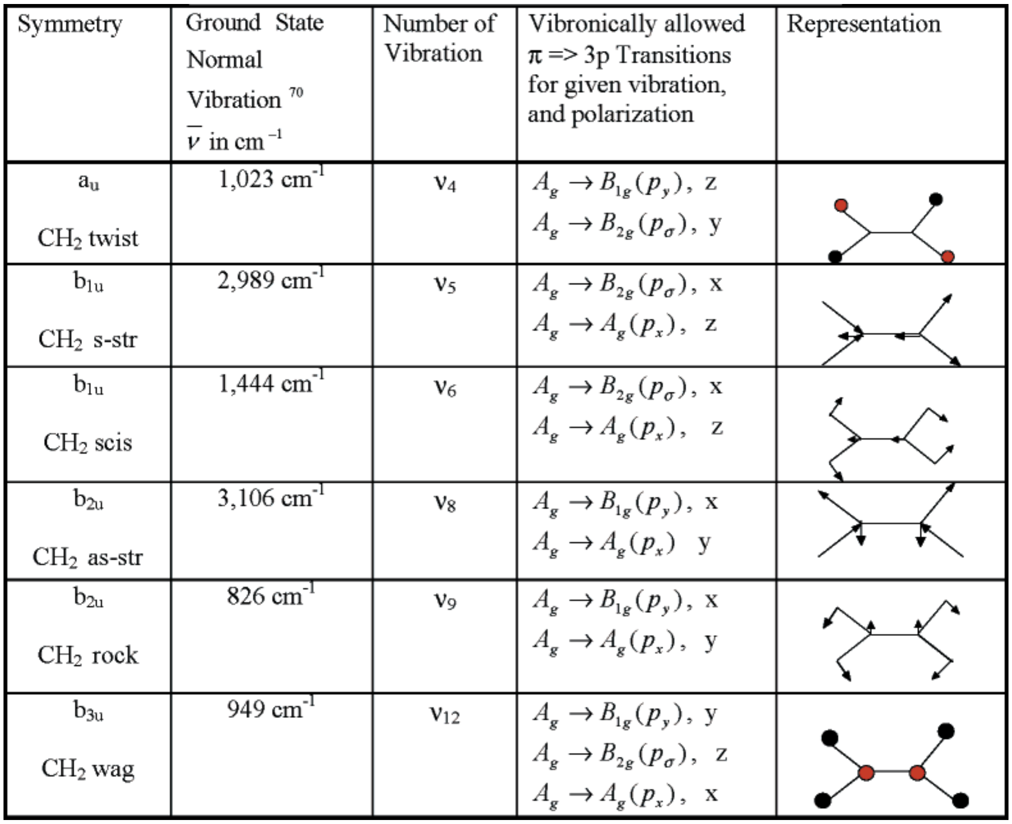
$$\Gamma_{\text{electronic excited state}} \times \Gamma_{\text{excit vibrational state}} \times \Gamma_{\text{dipole moment operator}} \times \Gamma_{\text{electronic ground state}} \times \Gamma_{\text{ground vibr state}}$$

$$B_{3u}b_{2g}\begin{pmatrix}b_{3u}\\ b_{2u}\\ b_{1u}\end{pmatrix}A_{1g}a_g = \begin{pmatrix}b_{2g}\\ b_{3g}\\ a_g\leftarrow\end{pmatrix}$$

Since the direct product contains the totally symmetric mode, a_g, the ν_7 (b_{2g}) normal mode is allowed for the $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) electronic transition. The vibrations, ν_9, and $\nu_{12,}$ are only allowed for the $\pi \rightarrow$ 3p vibronically allowed transitions. By elimination that leaves ν_7 (b_{2g}), a wagging vibration, which as shown above, is allowed for the $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) electronic transition and has a ground-state value of 943 cm^{-1}.

It is not unusual for the energy of vibration to be less in an excited electronic state than in the ground state. Thus, the experimentally observed value of 800 cm^{-1} is plausible for the ν_7 [b_{2g}] vibration in the 3s ($^1B_{3u}$) excited state. For the electronic transition $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) the transition moment integral is allowed for both even [$7^2_0 \sim a_g$] numbered vibrational levels and odd [$7^1_0 \sim b_{2g}$] numbered vibrational levels. That is because the $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) electronic transition is allowed

TABLE 3: Allowed Vibronic Origins for $\pi = 3p$ Transitions in Ethylene[a]



Symmetry	Ground State Normal Vibration [70] $\bar{\nu}$ in cm^{-1}	Number of Vibration	Vibronically allowed π => 3p Transitions for given vibration, and polarization	Representation
a_u CH_2 twist	1,023 cm^{-1}	ν_4	$A_g \rightarrow B_{1g}(p_y)$, z $A_g \rightarrow B_{2g}(p_\sigma)$, y	
b_{1u} CH_2 s-str	2,989 cm^{-1}	ν_5	$A_g \rightarrow B_{2g}(p_\sigma)$, x $A_g \rightarrow A_g(p_x)$, z	
b_{1u} CH_2 scis	1,444 cm^{-1}	ν_6	$A_g \rightarrow B_{2g}(p_\sigma)$, x $A_g \rightarrow A_g(p_x)$, z	
b_{2u} CH_2 as-str	3,106 cm^{-1}	ν_8	$A_g \rightarrow B_{1g}(p_y)$, x $A_g \rightarrow A_g(p_x)$ y	
b_{2u} CH_2 rock	826 cm^{-1}	ν_9	$A_g \rightarrow B_{1g}(p_y)$, x $A_g \rightarrow A_g(p_x)$, y	
b_{3u} CH_2 wag	949 cm^{-1}	ν_{12}	$A_g \rightarrow B_{1g}(p_y)$, y $A_g \rightarrow B_{2g}(p_\sigma)$, z $A_g \rightarrow A_g(p_x)$, x	

[a] To determine which vibrations can serve as a vibronic origin for the $\pi \rightarrow 3p$ transitions the following direct product is determined $\Gamma_{\text{electronic excited state}} \times \Gamma_{\text{excited vibrational}} \times \Gamma_{\text{dipole moment operator}} \times \Gamma_{\text{electronic ground}} \times \Gamma_{\text{ground vibrational}}$. If it contains the totally symmetric mode, a_g, it is vibronically allowed. [The ground electronic state and ground vibrational state both belong to the totally symmetric mode.]

for both vibrations of symmetry a_g and b_{2g}. If the electronic transition was not orbitally allowed this vibration would not be allowed for even numbered vibrational levels because ν_7 [b_{2g}] is not a totally symmetric mode. As a result, the transition is allowed for every vibrational level of υ_7. It is proposed that the ν_7 [b_{2g}] vibration is responsible for the observed vibrational progression. This vibration has been previously suggested as the mode responsible for this progression.[1,71] The ν_7 is a wagging vibration and is similar to the type of vibration involved in the vibrational progression observed for the $\pi \rightarrow 3s$ ($^1A_g \rightarrow {}^1B_{3u}$) transition in propylene.

The next two transitions are oppositely signed in the magnetic circular dichroism spectrum, and are degenerate in the 57 000−62 500 cm^{-1} region. The sharp structured doublets were previously assigned as $\pi \rightarrow 3s$ ($^1A_g \rightarrow {}^1B_{3u}$).[1,8] If the first transition in ethylene is assigned as $\pi \rightarrow 3s$ ($^1A_g \rightarrow {}^1B_{3u}$), then the next two transitions must be $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) and one of the $\pi \rightarrow 3p$ transitions. The sharp structured doublets should be the same transition in ethylene and propylene. Comparison with propylene leads to an assignment as one of the $\pi \rightarrow 3p$ (N $\rightarrow$ R(3p)) transitions. The fact that the doublets are so sharp in ethylene is consistent with an assignment of a vibronically allowed transition.

Now the question is, which one of the three possible $\pi \rightarrow 3p$ transitions is this? All of the $\pi \rightarrow 3p$ transitions are orbitally forbidden for ethylene. Coupling of an orbitally forbidden transition with an appropriate vibration results in a vibronically allowed transition. Table 3 lists all the vibrations which make the various $\pi \rightarrow 3p$ transitions vibronically allowed.

Since none of the $\pi \rightarrow 3p$ transitions are orbitally allowed in ethylene, the 0−0 band is not expected to be observed. The first peak of the first doublet is referred to as the vibronic origin. That leaves the question of the vibrational mode responsible for the vibronic origin. The normal modes which can couple with the various $\pi \rightarrow 3p$ transitions and make them vibronically allowed are ν_4[a_u, 1023 cm^{-1}], ν_5[b_{1u}, 2989 cm^{-1}], ν_6 [1444 cm^{-1}], ν_8 [3106 cm^{-1}], ν_9 [826 cm^{-1}], and ν_{12} [949 cm^{-1}]. Unfortunately the absorption or magnetic circular dichroism spectra do not provide any information to help choose what vibration is serving as the vibronic origin. We will refer to it as X^1 meaning that it is one quantum of normal mode X, and X could be any of the normal modes listed in Table 3.

The doublets are spaced from each other by 1300 cm^{-1} in ethylene. The vibrational spacing of 1300 cm^{-1} is the progression forming vibrational mode. Since progression forming modes are usually totally symmetric, the a_g vibrations are considered. The ground-state values for the a_g normal mode vibrations υ_2 [1623 cm^{-1}] and υ_3 [1342 cm^{-1}] of ethylene are in the correct energy range. The υ_2 vibration is the C=C stretching normal mode. The electronic excitation is from the π bonding orbital so the C=C stretching vibration in the excited state is expected to have a smaller value than the ground state. The value for υ_2 in the excited states is believed to be in the vicinity of 1350 cm^{-1} for ethylene[1] and is appropriate for the progression-forming mode. Also, the value of υ_2 is expected to be less affected by the substitution of H [ethylene] with CH_3 [propylene] since it is the C=C stretching vibration. This is consistent with the fact that in the ground states the C=C stretching vibration is 1623 cm^{-1} for ethylene, and 1652 cm^{-1} for propylene. Since the ground-state values are so close, it would not be unexpected that the excited-state values would be similar. Thus, the doublet structure would be expected to be similar in both molecules if the C═C stretching vibration is involved. This is consistent with the observation that the doublet spacing in both ethylene and propylene is about 1300 cm^{-1}. Thus, the progression-forming mode is assigned as v_2. The proposed assignment is X_0^1 (first peak first doublet), $2_0^1\,X_0^1$ (first peak second doublet), $2_0^2\,X_0^1$(first peak third doublet), $2_0^3\,X_0^1$ (first peak fourth doublet) where *X* is the normal mode involved in the vibronic origin. X is one of the normal modes listed in Table 3.

Data from resonance Raman spectra give a clue about what vibration maybe responsible for the vibronic origin. Resonance Raman spectra carried out in this region found activity in the v_2(C═C) stretching, v_3(CH$_2$) symmetric scissors, and the v_4 twisting mode.[15] Since this region has more than one electronic transition, the interpretation of which vibration is connected to which electronic transition is not completely clear. However, the v_4 twisting mode can serve to make the $\pi \rightarrow 3p_\sigma$ ($^1A_g \rightarrow {}^1B_{2g}$) and/or $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$) electronic transitions vibronically allowed. Assuming the vibration responsible for the vibronic origin is the v_4 CH$_2$ twisting mode, the vibrational assignment would be 4_0^1 (first peak first doublet), $2_0^1\,4_0^1$ (first peak second doublet), $2_0^2\,4_0^1$(first peak third doublet), $2_0^3\,4_0^1$ (first peak fourth doublet). This assignment is consistent with the v_2 and v_4 normal modes being observed in the resonance Raman spectra. It is proposed that the progression forming mode is the totally symmetric v_2(C═C) stretching mode adding on in multiples to the v_4(CH$_2$) twisting mode.

Using symmetry arguments, it can be shown that the $\pi \rightarrow 3p_x$ ($^1A_{1g} \rightarrow {}^1A_g$) electronic transition does not contribute to the magnetic circular dichroism spectrum in either the D_{2h} or D_2 point groups.[11,38] The D_2 point group is considered in addition to D_{2h} since it is believed that the equilibrium structure in the excited states of ethylene is twisted. In addition the v_4 (a$_u$) twisting vibration, which is observed in the resonance Raman spectrum of ethylene, cannot serve as the vibronic origin for $\pi \rightarrow 3p_x$ ($^1A1_g \rightarrow {}^1A_g$) electronic transition. The vibrations shown in Table 3 that could serve as vibronic origins for this transition would have a magnetic circular dichroism. However, these vibrational transitions were not observed in the resonance Raman spectrum. For these reasons the assignment of the $\pi \rightarrow 3p$ transition as $\pi \rightarrow 3p_x$ ($^1A_g \rightarrow {}^1A_g$) is considered unlikely.

The vibrational assignment with v_4 as the vibronic origin and v_2 as the progression-forming mode is consistent with both an assignment of the electronic transition as $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$) and $\pi \rightarrow 3p_\sigma$ ($^1A_g \rightarrow {}^1B_{2g}$). An assignment of the electronic transition as $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$) with v_4 serving as vibronic origin would be *z* polarized. It would gain intensity from the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) as well as any other *z* polarized transition. The $\pi \rightarrow 3p_\sigma$ ($^1A_g \rightarrow {}^1B_{2g}$) transition vibronically allowed by the v_4 transition would be *y* polarized. Both of these transitions can be shown to have a magnetic circular dichroism signal either in the D_2 point group or in the D_{2h} point group with v_4 serving as vibronic origin and v_2 as the progression-forming mode.

The next question is the assignment of the second peak in each doublet. Since the spacing of the second peaks in the doublet from each other is 1300 cm^{-1}, the vibrational progression forming mode would be the same as the progression forming mode for the first peaks, the v_2(C═C) stretching mode. Searching Table 3 for normal modes that have a value about 500 cm^{-1} larger than the v_4 [1023 cm^{-1}] twisting vibration and can serve as a vibronic origin shows that there does not appear to be an appropriate vibration for the $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$) electronic transition.

However, the v_6 b$_{1u}$ [CH$_2$ scissors, 1444 cm^{-1}] vibration is in the appropriate energy range to serve as a second vibronic origin for the $\pi \rightarrow 3p_\sigma$ ($^1A_g \rightarrow {}^1B_{2g}$) transition. Thus, the doublets could be due to the $\pi \rightarrow 3p_\sigma$ ($^1A_g \rightarrow {}^1B_{2g}$) electronic transition. The v_4 and v_6 normal modes would serve as vibronic origins for the first and second peak of the first doublet, and v_2 serves as the progression-forming mode.

There are two arguments against the above assignment. First v_6 was not observed in the resonance Raman spectra. Second the v_6 normal mode should be affected by the substitution of CH$_3$ for H in going from ethylene to propylene. The reason that it should be affected is that it is a scissors vibration involving the CH bonds in ethylene. Neither of these arguments is conclusive, but they indicate that other possibilities should be considered.

There is a possibility that has not been considered previously and is worth considering. The three $\pi \rightarrow 3p$ transitions in ethylene will not be degenerate, but they may not have very different energies. Perhaps the second peak in the doublets is a vibronic origin for another vibronically allowed $\pi \rightarrow 3p$ transition based on the v_4 twisting mode. That is to say the first peak in each doublet would belong to one of the $\pi \rightarrow 3p$ transitions and the second peak in each doublet would correspond to another $\pi \rightarrow 3p$ transition. The v_4 twisting vibration would serve as the vibronic origin for both electronic transitions and the v_2 normal mode would serve as the progression forming mode in both transitions. The two electronic transitions involved would be the $\pi \rightarrow 3p_\sigma$ ($^1A_g \rightarrow {}^1B_{2g}$) and $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$) transitions. This would solve the problem of finding one of the other $\pi \rightarrow 3p$ transitions. If this is the situation, whether the $\pi \rightarrow 3p_\sigma$ ($^1A_g \rightarrow {}^1B_{2g}$) or $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$) electronic transition is the first transition and which is the second transition would be an open question.

The arguments above provide two possible assignments of the sharp doublets. First, the sharp doublets could be one of the $\pi \rightarrow 3p$ [$\pi \rightarrow 3p_\sigma$ ($^1A_g \rightarrow {}^1B_{2g}$) or $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$)] transitions with two different vibronic origins and v_2 progression mode. Second, the sharp doublets would be assigned as two different $\pi \rightarrow 3p$ electronic transitions [$\pi \rightarrow 3p_\sigma$ ($^1A_g \rightarrow {}^1B_{2g}$) and $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$)] both with the same enabling vibrational mode and v_2 progression mode.

Other Considerations

The proposed assignments of the electronic transitions in ethylene are also consistent with other research observations. Three of these are discussed in the following paragraphs.

Multiphoton ionization measurements were carried out on ethylene with the goal of detecting the orbitally forbidden $\pi \rightarrow 3p$ transitions.[16] The orbitally allowed transitions, $\pi \rightarrow \pi^*$ and $\pi \rightarrow 3s$ are forbidden for two photons. The $\pi \rightarrow 3p$ transitions are orbitally forbidden for one photon absorption, but they are allowed for two photons. The surprising experimental result was as follows. Two photon resonances were found in the doublet region, which was assigned as $\pi \rightarrow 3s$. Since the $\pi \rightarrow 3s$ transition is not two photon allowed, one would not expect to observe it. The fact that it was observed has been explained. However, another explanation is that the assignment of the doublet structure in ethylene as $\pi \rightarrow 3s$ is not correct. This explanation supports the suggested assignment of the doublets to a $\pi \rightarrow 3p$ transition rather than the $\pi \rightarrow 3s$ transition.

Another problem has been the ability to theoretically calculate the oscillator strengths of the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) and $\pi \rightarrow 3s$ ($^1A_g \rightarrow {}^1B_{3u}$) transitions. The oscillator strength of the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) transition is expected to be larger than the $\pi \rightarrow 3s$ ($^1A_g \rightarrow {}^1B_{3u}$) transition. However, when calculations were carried out using the time-dependent wave packet method, the

TABLE 4: Summary of Assigned Electronic Transitions for Propylene and Ethylene

propylene		ethylene	
wavenumber	assignment (using ethylene notation)	wavenumber	assignment
52 000−55 080 cm^{-1} (190−182 nm) (190−182 nm)	$\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$)	50 000−57 000 cm^{-1} (200−175 nm)	$\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$)
55 080−58 760 cm^{-1} (182−170 nm)	$\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$)	57 000−62 500 cm^{-1} (175−160 nm), accidentally degenerate, with $\pi \rightarrow 3p_\sigma$ and/or $\pi \rightarrow 3p_y$	$\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$)
58 760−65 550 cm^{-1} (170−153 nm), doublets	$\pi \rightarrow 3p_\sigma$ ($^1A_g \rightarrow {}^1B_{2g}$) and/or $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$)	57 000−62 500 cm^{-1} (175−160) doublets, accidentally degenerate, with $\pi \rightarrow \pi^*$	$\pi \rightarrow 3p_\sigma$ ($^1A_g \rightarrow {}^1B_{2g}$) and/or $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$)

predicted oscillator strength of the $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) was much larger than the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$).[10] To resolve this problem the suggestion was made that the sharp structured doublets belong to the $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$) transition rather than the $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) transition. While the $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$) transition is orbitally forbidden for ethylene, it is suggested that it is vibronically coupled to the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$).[10] Table 3 shows that the $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$) transition is vibronically allowed with v_4 serving as the vibronic origin and that it would be z polarized. Since the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) transition is z polarized (see Table 2), it would couple to the $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$) transition. With this assignment of transitions the theoretical calculation is able to better predict the absorption spectrum and get a more realistic oscillator strength for the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) transition. This reference leaves the question of where the $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) transition is located open.[10] The results of these wave packet calculations are consistent with our experimental results, which assign the doublet structure to the $\pi \rightarrow 3p_\sigma$ ($^1A_g \rightarrow {}^1B_{2g}$) and/or $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$) vibronically allowed transition.

An interesting theoretical calculation is the first ab initio calculations of the magnetic circular dichroism for ethylene. These calculations were carried out at various levels of approximation.[38] The magnetic circular dichroism B terms were calculated for the $\pi \rightarrow \pi^*$($^1A_g \rightarrow {}^1B_{1u}$) and $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) transitions at the self-consistent field and MCSCF levels for ethylene. For the traditional electronic assignments in ethylene the experimental magnetic circular dichroism for the $\pi \rightarrow \pi^*$($^1A_g \rightarrow {}^1B_{1u}$) and $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) have the same sign. What is interesting about the theoretical calculations is that the $\pi \rightarrow \pi^*$($^1A_g \rightarrow {}^1B_{1u}$) and $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) transitions have oppositely signed magnetic circular dichroism for most levels of approximation. This result is consistent with the assignments proposed for ethylene in this paper. The $\pi \rightarrow \pi^*$($^1A_g \rightarrow {}^1B_{1u}$) and $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) electronic transitions have opposite signs in the magnetic circular dichroism spectra in both ethylene and propylene.

Conclusion

One of the puzzles in the spectra of simple olefins has been the difference between the absorption spectra of ethylene and other olefins such as propylene. The magnetic circular dichroism and absorption spectra of propylene and its comparison to the spectra of ethylene show three electronic transitions for both molecules in the $\pi \rightarrow \pi^*$ energy region. The comparison to propylene confirms that the oppositely signed magnetic circular dichroism between the sharp doublets in ethylene is due to another electronic transition. The first and most important result is that there are at least three electronic transitions in the $\pi \rightarrow \pi^*$ region of the spectrum for both ethylene and propylene. An equally important result is that the $\pi \rightarrow \pi^*$ is not the lowest energy transition.

The next result is the assignment of these three electronic transitions. The experimental results lead to new assignments for the electronic transitions in ethylene. These new assignments are summarized in Table 4 and are discussed briefly in the next few paragraphs. The new assignments for ethylene reveal a correspondence of the electronic structure for ethylene and propylene as well as other olefins.

The lowest energy orbitally allowed electronic transition is assigned as $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) in both ethylene and propylene. A wagging vibration appears to account for the vibrational progression in both molecules.

The second orbitally allowed transition in propylene is assigned as $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$). It is opposite in sign to the first transition in the magnetic circular dichroism spectrum, the $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) transition. The next transition in propylene is assigned as the vibronically allowed $\pi \rightarrow$ 3p transitions, most likely the $\pi \rightarrow 3p_\sigma$ ($^1A_g \rightarrow {}^1B_{2g}$) and/or $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$). The $\pi \rightarrow$ 3p transition is opposite in sign to the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) transition and it has the same type of sharp structured doublets observed in ethylene. The sharp structured doublets of propylene have the same sign as the $\pi \rightarrow$ 3s ($^1A_g \rightarrow {}^1B_{3u}$) transition in the magnetic circular dichroism spectrum of propylene.

In ethylene the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) electronic transition and the $\pi \rightarrow$ 3p vibronically allowed transition are accidentally degenerate. Since the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) and $\pi \rightarrow$ 3p transition have opposite signs in the magnetic circular dichroism spectrum, the $\pi \rightarrow \pi^*$ ($^1A_g \rightarrow {}^1B_{1u}$) transition is observed between the doublet structure of the $\pi \rightarrow$ 3p transition. It is argued that the sharp doublets are due to the $\pi \rightarrow 3p_\sigma$ ($^1A_g \rightarrow {}^1B_{2g}$) and/or $\pi \rightarrow 3p_y$ ($^1A_g \rightarrow {}^1B_{1g}$) transition. It appears that the v_4 twisting vibration serves as the vibronic origin making the $\pi \rightarrow$ 3p transition allowed. The v_2(C=C) stretching vibration serves as the progression-forming mode.

Figure 4 shows the absorption spectrum of ethylene with the new assignments of the electronic transitions indicated on the spectrum.

These experimental results demonstrate the power and necessity of vacuum ultraviolet magnetic circular dichroism measurements. For instance, examining the absorption spectra of propylene, it is not possible to tell that a third electronic transition occurs at 58 760 cm^{-1} or even that there is a third transition at this energy. The third transition is clearly revealed in the magnetic circular dichroism spectrum. Not only that but the connection of the electronic structure of ethylene and propylene is revealed by the use of magnetic circular dichroism spectroscopy. It is a powerful tool when applied to the problem of the electronic structure of molecules, even in molecules without degenerate states. The measurement of vacuum ultraviolet magnetic circular dichroism spectra of molecules is difficult and time-consuming even with the use of synchrotron

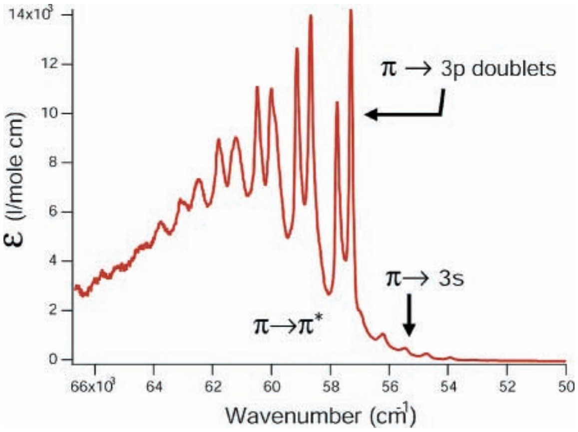


Figure 4. New assignments for the electronic transitions in ethylene.

radiation, but it gives unique information about the electronic structure of molecules.

Acknowledgment. We are particularly indebted to Ednor M. Rowe. It was his interest in encouraging high-risk experiments at the Synchrotron Radiation Center that was instrumental in these experimental measurements being successfully completed. We dedicate this paper to Ednor M. Rowe. We would also like to acknowledge the staff of the Synchrotron Radiation Center, University of Wisconsin—Madison where we carried out the experiments and National Science Foundation Grant DMR-0084402. We also acknowledge NSF Grant Number CHE 8416312. P.A.S. gratefully acknowledges Florida Atlantic University for the award of a sabbatical, which allowed the necessary time for this research. She is grateful to Kelly Taylor for proofreading the manuscript.

References and Notes

(1) Robin, M. B. *Higher Excited States of Polyatomic Molecules*, Academic Press: New York, 1985; Vols. 2 and 3.

(2) Mullikan, R. S. *Phys. Rev.* **1932**, *41*, 751.

(3) Wilkinson, P. G.; Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1895.

(4) Mullikan, R. S. *Phys. Rev.* **1933**, *43*, 279.

(5) Mullikan, R. S. *J. Chem. Phys.* **1977**, *66*, 2448.

(6) Mullikan, R. S. *J. Chem. Phys.* **1979**, *71*, 556.

(7) Merer, A. J.; Mulliken, R. S. *Chem. Rev.* **1969**, *69*, 639.

(8) Brith-Linder, M.; Allen, S. D. *Chem. Phys. Lett.* **1977**, *47*, 32.

(9) Ryu, J.; Hudson, B. S. *Chem. Phys. Lett.* **1995,** *454*, 448.

(10) Ryu, J.; Hudson, B. S. *J. Korean Phys. Soc.* **1997**, *31*, 282.

(11) Snyder, P. A.; Hansen, R. W. C.; Rowe, E. M. *J. Phys. Chem.* **1996**, *100*, 17756.

(12) Watson, F. H., Jr.; Nycum, M. W. *Spectrosc. Lett.* **1975**, *8*, 223.

(13) Snyder, P. A.; Clark, L. B. *J. Chem. Phys.* **1970**, *52*, 908.

(14) Drake, A. F.; Mason, S. F. *Tetrahedron* **1977**, *33*, 937.

(15) Sension, R. J.; Hudson, B. S. *J. Chem. Phys.* **1989**, *90*, 1377.

(16) Gedanken, A.; Kuebler, N. A.; Robin, M. B. *J. Chem. Phys.* **1982**, *76*, 46.

(17) Johnson, K. E.; Johnston, D. B.; Lipsky, S. *J. Chem. Phys.* **1979**, *70*, 3844.

(18) Williams, B. A.; Cool, T. A. *J. Chem. Phys.* **1991**, *94*, 6358.

(19) Snyder, P. A.; Schatz, P. N.; Rowe, E. M. *Chem. Phys. Lett.* **1984**, *110*, 508.

(20) Allan, M.; Robin, M. B.; Snyder, P. A. *J. Phys. Chem.* **1985**, *89*, 4900.

(21) Palmer, M. H.; Beveridge, A. J.; Walker, I. C.; Abuain, T. M. *Chem. Phys.* **1986**, *102*, 63.

(22) Foo, P. D.; Innes, K. K. *Chem. Phys.* **1974**, *60*, 4582.

(23) Mehaffy, D.; Keller, P. R.; Taylor, J. W.; Carlson, T. A.; Krause, M. O.; Grimm, F. A.; Allen, J. D., Jr. *J. Electron Spectrosc. Relat. Phenom.* **1982**, *26*, 213.

(24) Grimm, F. A.; Whitley, T. A.; Keller, P. R.; Taylor, J. W. *Chem. Phys.* **1991**, *154*, 303.

(25) Mintz, D. M.; Kuppermann, A. *J. Chem. Phys.* **1979**, *71*, 3499.

(26) Kempgens, B.; Kivimaki, A.; Itchkawitz, B. S.; Koppe, H. M.; Schmidbauer, M.; Neeb, M.; Maier, K.; Feldhaus, J.; Bradshaw, A. M. *J. Electron Spectrosc. Relat. Phenom.* **1998**, *93*, 39.

(27) Holland, D. M. P.; Shaw, D. A.; Hayes, M. A.; Shpinkova, L. G.; Rennie, E. E.; Karlsson, L.; Baltzer, P.; Wannberg, B. *J. Chem. Phys.* **1997**, *219*, 91.

(28) Chen, F. Z.; Wu, C. Y. R. *J. Phys. B.* **1999**, *32B*, 3283.

(29) Love, D. E.; Jordan, K. D. *J. Phys. Chem.* **1999**, *103*, 5667.

(30) Müller, T.; Dallos, M.; Lischka,H. *J. Chem. Phys.* **1999**, *110*, 7176.

(31) Wiberg, K. B.; Hadad, C. M.; Foresman, J. B.; Chupka, W. A. *J. Phys. Chem.* **1992**, *96*, 10756.

(32) Davidson, E. R. *J. Phys. Chem.* **1996**, *100*, 6161.

(33) Ben-Nun, M.; Martinez, T. J. *J. Phys. Chem.* **1999**, *103*, 10517.

(34) Ben-Nun, M.; Martinez, T. *J. Chem. Phys.* **2000**, *259*, 237.

(35) Bozek, J. D.; Carroll, T. X.; Hahne, J. A.; Saethre, L. J.; True, J. E.; Thomas, T. D. *Phys. Rev.* **1998**, *57 A*, 157.

(36) Danovich, D.; Marian, C. M.; Neuheuser, T.; Peyerimhoff, S. D.; Shaik, S. *J. Phys. Chem. A* **1998**, *102*, 5923.

(37) Watson, J. K. G.; Siebrand, W.; Zgierski, M. Z. *J. Chem. Phys.* **1996**, *105*, 1348.

(38) Coriani, S.; Jørgensen, P.; Rizzo, A.; Ruud, K.; Olsen, J. *Chem. Phys. Lett.* **1999**, *300*, 61.

(39) Serrano-Andres, L.; Merchan, M.; Nebot-Gil, I. *J. Chem. Phys.* **1993**, *98*, 3151.

(40) Bouman, T. D. *Chem. Phys. Lett.* **1985**, *117*, 461.

(41) Siebrand, W.; Zerbetto, F.; Zgierski, M. Z. *Chem. Phys. Lett.* **1990**, *174*, 119.

(42) Watts, D.; Gwaltney, S. R.; Bartlett, R. J. *J. Chem. Phys.* **1996**, *105*, 6979.

(43) Hattig, C.; Weigend,F. *J. Chem. Phys.* **2000**, *113*, 5154.

(44) Jensen, H. J. A.; Kock, H.; Jorgensen, P. *Chem. Phys.* **1988**, *119*, 297.

(45) Lindh, R.; Roos, B. O. *Int. J. Quantum Chem.* **1989**, *35*, 813.

(46) Mebel, A. H.; Hayashi, M.; Lin, S. H. *Chem. Phys. Lett.* **1997**, *274*, 281.

(47) Hayashi, M.; Mebel, A.; Liang, K. K.; Lin, S. H. *J. Chem. Phys.* **1998**, *108*, 2044.

(48) Dolgounitcheva, O.; Zakrzewski, V. G.; Ortiz, J. V. *J. Chem. Phys.* **2001**, *114*, 130.

(49) Quenneville, J.; Martinez, T. J. *J. Phys. Chem.* **2003**, *107A*, 829.

(50) Ben-Nun, M.; Quenneville, J.; Martinez, T. J. *J. Phys. Chem.* **2000**, *104A*, 5161.

(51) Bertsch, G. F.; Giansiracusa, J.; Yabana, K. *Isr. J. Chem.* **2002**, *42*, 151.

(52) Walker, I. C.; Abuain, T. M.; Palmer, M. H.; Beveridge, A. *J. Chem. Phys.* **1986**, *109*, 269.

(53) Snyder, P. A.; Rowe, E. M. *Nucl. Instrum. Methods* **1980**, *172*, 345.

(54) Snyder, P. A.; Schatz, P. N.; Rowe, E. M. *Ann. Israel Phys. Soc.* **1984**, *6*, 144.

(55) Snyder, P. A. *Photochem. Photobiol.* **1986**, *44*, 237.

(56) Snyder, P. A. *Nucl. Instrum. Methods* **1984**, *222*, 364.

(57) Allen, S. C.; Mason, M. G.; Schnepp, O.; Stephens, P. J. *Chem. Phys. Lett.* **1975**, *30*, 140.

(58) Snyder, P. A.; Lund, P.; Schatz, P.; Rowe, E. M. *Chem. Phys. Lett.* **1981**, *82*, 54.

(59) Snyder, P. A.; Munger, R.; Hansen, R. W. C.; Rowe, E. M. Production and Analysis of Polarized X-rays. *SPIE* **1991**, *1548*, 188.

(60) Chen, G. C.; Yang, J. T. *Anal. Lett.* **1977**, *10*, 1195.

(61) Joint Commission for Spectroscopy of the International Astronomical Union and the International Union of Pure and Applied Physics. Report on Notation for the Spectra of Polyatomic Molecules. *J. Chem. Phys.* **1955**, *23*, 1997.

(62) Price, W. C.; Tutte, W. T. *Proc. R. Soc. London* **1940**, *174A*, 207.

(63) Samson, J. A. R.; Marmo, F. F.; Watanabe, K. *J. Chem. Phys.* **1962**, *36*, 783.

(64) Watson, Jr., F. H.; Armstrong, A. T.; McGlynn, S. P. *Theor. Chim. Acta* **1970**, *16*, 75.

(65) Walker, D. F.; Walker, I. C. *J. Chem. Soc., Faraday Trans.* 2 **1975**, *71*, 1903.

(66) Watson, Jr., F. H.; McGlynn, S. P. *Theor. Chim. Acta* **1971**, *21*, 309.

(67) Iverson, A. A.; Russell, B. R.; Jones, P. R. *Chem. Phys. Lett.* **1972**, *17*, 98.

(68) Herzberg, G. *Molecular Spectra and Molecular Structure, III. Electronic Spectra and Electronic Structure of Polyatomic Molecules*; Van Nostrand Reinhold Company: New York, 1966.

(69) Barns, A. J.; Howells, J. D. R. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 532.

(70) Shimanouchi, T. *Tables of Molecular Vibration Frequencies*; National Bureau of Standards: Washington, DC, 1972; Volume I. Website: http://webbook.nist.gov/chemistry (accessed July 2001). This table assumes the *x*-axis of ethylene is along the double bond. Therefore the normal modes are corrected for the *z*-axis chosen along the double bond.

(71) Ogilvie, J. F. *J. Chem. Phys.* **1968**, *40*, 2095.