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Absolute Intensities of CH Stretching Overtones in Alkenes

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We have measured the CH stretching vibrational spectrum of ethene gas in the regions corresponding to 1−5 quanta in the CH stretching vibration with Fourier transform infrared and conventional absorption spectroscopy and have determined the corresponding oscillator strengths. We have calculated the CH stretching vibrational oscillator strengths for a series of alkenes: ethene, propene, 1,3-butadiene, *cis*-2-butene, and *trans*-2-butene. The CH stretching intensities are calculated with a simple Morse oscillator local mode model for CH groups and with the harmonically coupled anharmonic oscillator local mode model for CH_2 and CH_3 groups. The local mode parameters, frequencies, and anharmonicities are obtained from experiments. The harmonic coupling coefficients and the dipole moment functions are calculated with a range of ab initio methods. These include self-consistent-field Hartree−Fock, density functional, correlated, and multireference theories, combined with basis sets ranging from double- to quadruple-ζ quality augmented with polarization and diffuse functions. Variation in calculated oscillator strengths with the choice of ab initio method is systematically studied and compared with observed intensities. From this comparison between the calculated and observed values, we can quantitatively understand the relative usefulness of various ab initio dipole moment functions in calculations of vibrational oscillator strength for alkenes.

Introduction

Local mode theory has been extensively applied in vibrational spectroscopy.[1−6] Initially the local mode model was successfully used to predict transition frequencies in high overtone spectra followed by predictions of relative intensities within a given overtone.[7,8] Later more complicated band profiles like the methyl band shape in molecules with low methyl rotational barriers were successfully simulated.[9−12] The relative intensities and spectral profiles within a given overtone could be calculated in good agreement with experiment with a relatively simple local mode model.

Calculation and measurement of absolute intensities are difficult. Transition frequencies can be measured very accurately; however, transition intensities rely on several experimental parameters and are difficult to measure accurately. Likewise, theoretically, transition frequencies can be calculated precisely solely from the molecular Hamiltonian, whereas transition intensities require both energies and wave functions from the molecular Hamiltonian as well as dipole moment functions.

Recently, there have been a number of studies that have compared calculated and measured absolute oscillator strengths of CH and OH stretching vibrational overtone transitions. These have mostly been based on anharmonic oscillator (AO) and harmonically coupled anharmonic oscillator (HCAO) local mode models combined with empirical or ab initio calculated dipole moment functions in the internal local coordinates.[13−20]

These previous studies have shown that electron correlation in the ab initio methods used to obtain the dipole moment function seems to have little effect on the intensities of CH and OH stretching overtones in most molecules. The exception is a few molecules that contain a triple bond to which the CH bond is attached.[16]

Calculated fundamental intensities were found to improve with the addition of electron correlation. Dipole moment functions calculated with density functional theory (DFT) produce improved fundamental intensities compared to those obtained with the Hartree−Fock (HF) method. Nonlocal and hybrid DFT methods give results that are similar to those obtained with third-order perturbative Møller−Plesset (MP3) and quadratic configuration interaction including single and double excitation (QCISD) methods.[15] The importance of electron correlation for fundamentals is perhaps related to the fact that fundamental intensities depend primarily on the first derivative of the dipole moment expansion. However, an anharmonic potential energy surface and a nonlinear dipole moment function are necessary for accurate prediction of even fundamental transition frequencies and intensities.[19] Takahashi et al.[19,20] found that for calculations of fundamental transitions the HCAO local mode model provided similar transition frequencies but improved intensities compared to the normal mode model. However, the result would depend on the number of vibrational modes included in the HCAO local mode model.

The intensities of first overtone transitions depend on both first- and higher-order derivatives in the dipole moment expansion. The intensities of these first overtone transitions are thus more difficult to predict both theoretically and intuitively as their intensities depend both on the choice of ab initio method and on the possibility of cancellation of terms. The OH stretching transitions associated with hydrogen bonding often

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show increased fundamental intensities but decreased first overtone intensities. For example, the hydrogen-bonded OH stretching transition in the water dimer is a factor of 5 more intense than the asymmetric stretch of the water monomer for the fundamental region, while it is about 2 orders of magnitude weaker than the corresponding water monomer transitions for the first overtone.[21−23]

Absolute CH and OH stretching overtone intensities calculated with HF/6-31G(d) dipole moment functions have been found to be larger than the observed values. The calculated intensities decrease as the basis set size increases beyond 6-31G-(d).[16] We have found that overtone intensities calculated with HF/6-311+G(d,p) and HF/6-311++G(2d,2p) dipole moment functions give absolute CH and OH stretching overtone intensities that are in reasonable agreement with observed intensities (usually within a factor of 2 of the experimental values).[14,15]

Previous calculations have often focused on the intensities of individual transitions. However, the experimental peaks of these individual transitions are often overlapped and peak intensities need to be obtained from deconvolutions, which can lead to significant errors for extensively overlapped peaks. Moreover, even for water, where the experimental values have been measured relatively accurately, the published intensities change between subsequent versions of the HITRAN database.

The extent to which the interactions between stretching modes, and between stretching and other vibrational modes, is included in the theoretical model can also affect the calculated results. However, inclusion of the HOH bending mode in water has only a small effect on the intensities of the dominant OH stretching bands.[13,14] These complications can be avoided if the total observed intensity of a CH stretching vibrational band rather than the intensity of individual transitions is compared to calculated values. This is the approach we have taken here.

Previously, the effect of the choice of anharmonic potential was investigated by comparing calculated intensities obtained with the Morse potential and a generalized Morse potential (Deng−Fan potential) for a series of molecules.[24] However, the Deng−Fan potential was not consistently better, and we have continued to use the Morse potential to model the CH stretching potential in the present paper. The Morse oscillator parameters, frequency and anharmonicity, are obtained from experimentally observed transitions. We assume that only the CH stretching vibration contributes to the total intensities of the observed transitions in the CH stretching region.

Our aim is to systematically monitor how the calculated intensity evolves when different ab initio theories and basis sets are used to obtain the dipole moment function. Initially, we calculate the dipole moment function of ethene with self-consistent-field Hartree−Fock, hybrid density functional, correlated, and multireference theories, combined with basis sets ranging from double- to quadruple-ζ quality augmented with polarization and diffuse functions, and compare the calculated oscillator strengths with experimental results. From this comprehensive set of results, we select a subset of ab initio methods to apply to propene, 1,3-butadiene, *cis*-2-butene, and *trans*-2-butene and again compare with available experimental results.

Experiment

Ethene (99.5+% Aldrich) was used without further purification. The fundamental CH stretching spectrum of ethene gas was recorded with a Nicolet 510 Fourier transform infrared spectrometer with a 10.05 cm glass cell fitted with sodium chloride windows. The spectrum was recorded at room temperature (21.8 °C) with a gas pressure of 51.3 Torr at a resolution of 1 cm^{-1} and was averaged over 400 scans. A Cary 5e UV−vis−NIR conventional absorption spectrometer fitted with a 20.25 m long path White cell was used to record room temperature (22.8 °C) CH stretching overtone spectra of ethene gas in the $\Delta v_{\text{CH}} = 2-5$ regions. In the spectra of the $\Delta v_{\text{CH}} = 2$ and 3 regions a pressure of 62.6 Torr was used, and for $\Delta v_{\text{CH}} = 4$ and 5 a pressure of 685.3 Torr was used. Background spectra of an evacuated cell with the same experimental conditions were recorded and subtracted from each of the sample spectra.

Theory

The oscillator strength of a vibrational transition from the ground state to an excited state is given by[25,26]

$$f = \frac{4\pi m_e}{3e^2\hbar}\tilde{\nu}_{\text{eg}}|\langle v|\vec{\mu}|0\rangle|^2 \tag{1}$$

where $\tilde{\nu}_{\text{eg}}$ is the transition frequency, $|0\rangle$ and $|v\rangle$ are the ground- and excited-state vibrational wave functions, $\vec{\mu}$ is the dipole moment function, $\hbar$ is the Planck constant divided by 2π, and m_e and e are the mass and the charge of an electron, respectively. The energies and wave functions are obtained from the molecular vibrational Hamiltonian, and the dipole moment functions are calculated ab initio.

Vibrational Hamiltonian. We use a simple Morse oscillator local mode model for an isolated CH group and the HCAO local mode model for coupled CH_2 and CH_3 groups. The Hamiltonians without zero-point energy of CH, CH_2, and CH_3 groups can be expressed in Morse oscillator wave function product basis sets ($|v_1\rangle$, $|v_1v_2\rangle$, and $|v_1v_2v_3\rangle$), respectively, as[27,28]

$$H_{\text{CH}}/hc = \tilde{\omega}_1 v_1 - \tilde{\omega}x_1({v_1}^2 + v_1) \tag{2}$$

$$H_{\text{CH}_2}/hc = \tilde{\omega}_1 v_1 + \tilde{\omega}_2 v_2 - \tilde{\omega}x_1({v_1}^2 + v_1) - \tilde{\omega}x_2({v_2}^2 + v_2) - \gamma'_{12}(a_1{a_2}^+ + {a_1}^+a_2) \tag{3}$$

$$H_{\text{CH}_3}/hc = \tilde{\omega}_1 v_1 + \tilde{\omega}_2 v_2 + \tilde{\omega}_3 v_3 - \tilde{\omega}x_1({v_1}^2 + v_1) - \tilde{\omega}x_2({v_2}^2 + v_2) - \tilde{\omega}x_3({v_3}^2 + v_3) - \gamma'_{12}(a_1{a_2}^+ + {a_1}^+a_2) - \gamma'_{13}(a_1{a_3}^+ + {a_1}^+a_3) - \gamma'_{23}(a_2{a_3}^+ + {a_2}^+a_3) \tag{4}$$

where $\tilde{\omega}$ and $\tilde{\omega}x$ are the frequency and anharmonicity in cm^{-1}, γ' is the effective stretching coupling coefficient in cm^{-1}, and v is the vibrational quantum number of the various oscillators. The frequency and anharmonicity are obtained from a Birge−Sponer-type fitting of the observed pure local mode transitions.[28] The stretching coupling coefficient is calculated ab initio as[7]

$$\gamma'_{12} = -\left(\frac{\mu\cos(\varphi)}{2m_C} + \frac{F_{12}}{2F_{11}}\right)(\omega_1\omega_2)^{1/2} \tag{5}$$

where m_C is the mass of the carbon atom, μ is the reduced mass of the CH oscillator, φ is the angle between the two oscillators, and F is the force constant. We have omitted the energy of the vibrational ground state, as it does not contribute to the intensity calculations.

We investigate the accuracy of intensity calculations with local mode models as changes are made to the ab initio dipole moment functions. We calculate the vibrational oscillator strengths of isolated CH groups, coupled CH_2 groups, and coupled CH_3 groups of the alkenes—ethene, propene, 1,3-butadiene, *cis*-2-butene, and *trans*-2-butene—and obtain the total

TABLE 1: Frequency, Anharmonicity, and Stretching Coupling Coefficient of CH Stretching Modes in Alkenes (cm^{-1})

molecule	bond	frequency	anharmonicity	coupling coefficient[e]
ethene[a]		3167 ± 3	58.6 ± 0.6	$\gamma' = 45.1 \pm 1.9$
1,3-butadiene[b]	nonterminal	3122 ± 4	58.3 ± 0.6	
	cis terminal	3150 ± 6	58.0 ± 0.9	$\gamma_{ct}' = 47.5 \pm 1.6$
	trans terminal	3171 ± 5	56.7 ± 0.7	
propene[c]	*cis* olefinic	3133 ± 14	57 ± 3	$\gamma_{ct}' = 46.3 \pm 1.5$
	trans olefinic	3142 ± 11	54 ± 2	
	nonterminal	3104 ± 7	57 ± 1	
	in-plane methyl	3058 ± 12	58 ± 3	$\gamma_{ipop}' = 24.6 \pm 1.7$
	out-of-plane methyl	3036 ± 12	60 ± 2	$\gamma_{opop}' = 16.7 \pm 1.6$
cis-2-butene[d]	methine	3129 ± 2	59.9 ± 0.3	
	in-plane methyl	3062 ± 5	57.1 ± 0.5	$\gamma_{ipop}' = 23.1 \pm 1.6$
	out-of-plane methyl	3061 ± 5	65.7 ± 0.6	$\gamma_{opop}' = 15.6 \pm 1.7$
trans-2-butene[d]	methine	3101 ± 1	59.3 ± 0.1	
	in-plane methyl	3076 ± 2	60.9 ± 0.2	$\gamma_{ipop}' = 23.8 \pm 1.7$
	out-of-plane methyl	3060 ± 4	64.8 ± 0.5	$\gamma_{opop}' = 15.1 \pm 1.8$

[a] From a Birge−Sponer fit of $\Delta v_{CH} = 4$ of ref 31 and $\Delta v_{CH} = 5{-}7$ of ref 32. [b] From ref 27. [c] From ref 33. [d] From ref 34. [e] Coupling coefficient is calculated ab initio and averaged with uncertainties corresponding to one standard deviation.

CH stretching oscillator strength for a given overtone by simple addition of the calculated intensities of the individual transitions. Coupling between CH stretching oscillators is only included for CH bonds that share a common carbon atom. The accurate value of this coupling coefficient, which is calculated ab initio, has a minimal effect on the absolute intensities.

Dipole Moment Function. The molecular dipole moment functions are vector quantities. The x component of the dipole moment functions of CH, CH_2, and CH_3 groups can be expressed as[27,28]

$$\mu_x = \sum_{i=1}^{6} a_{1i} q^i \tag{6}$$

$$\mu_x = \sum_{i=1}^{6} (a_{1i} q_1^{\,i} + a_{2i} q_2^{\,i}) + b_1 q_1 q_2 + c_1 q_1 q_2^{\,2} + c_2 q_1^{\,2} q_2 \tag{7}$$

$$\begin{aligned}\mu_x = \sum_{i=1}^{6} (a_{1i} q_1^{\,i} + a_{2i} q_2^{\,i} + a_{3i} q_3^{\,i}) + b_1 q_1 q_2 + b_2 q_1 q_3 + \\ b_3 q_2 q_3 + c_1 q_1^{\,2} q_2 + c_2 q_1 q_2^{\,2} + c_3 q_1^{\,2} q_3 + c_4 q_1 q_3^{\,2} + \\ c_5 q_2^{\,2} q_3 + c_6 q_2 q_3^{\,2}\end{aligned} \tag{8}$$

where a, b, and c are Taylor series expansion coefficients, which can be obtained from a series of ab initio calculations. We have omitted the permanent dipole, which does not contribute to the intensity. The expansion of the dipole moment function is limited to the sixth order for the diagonal and the third order for the cross-terms which depend on the two displacement coordinates. A one-dimensional 15-point grid with displacements from −0.3 to 0.4 Å in 0.05 Å steps is used to calculate the diagonal coefficients a and a two-dimensional 9 by 9 grid with displacements from −0.2 to 0.2 Å in 0.05 Å steps is used to calculate the mixed coefficients b and c. The one-dimensional grid is least-squares fitted with a sixth-order polynomial and the two-dimensional grids with polynomials to fourth order. We define the y and z components in a similar fashion. Use of symmetry somewhat reduces the number of grid points required for the CH_2 group of ethene and also reduces the numbers of grids required for the CH_3 groups in the other alkenes due to the plane of symmetry.

We calculate the dipole moment function of ethene with HF and Becke's three-parameter hybrid method with the Lee−Yang−Parr correction function (B3LYP) theories and the 6-31G(d), 6-31+G(d,p), 6-311+G(d,p), 6-311++G(2d,2p), 6-311++G(3d,3p), 6-311++G(3df,3pd), aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets. We label these basis sets I to IX. We do the same calculations with third-order perturbative Møller−Plesset (MP3) and quadratic configuration interaction including single- and double-excitation (QCISD) ab initio theories and the 6-31G(d), 6-31+G(d,p), 6-311+G(d,p), 6-311++G(2d,2p), and aug-cc-pVDZ basis sets. Finally, we use the multireference complete active space self-consistent-field (CASSCF) theory with the aug-cc-pVDZ, 6-311++G(2d,2p), and aug-cc-pVTZ basis sets. On the basis of these results, we selected a subset of ab initio methods to apply to propene, 1,3-butadiene, *cis*-2-butene, and *trans*-2-butene.

The CASSCF calculation on ethene was run with a full valence active space comprising 12 electrons distributed among the 12 valence molecular orbitals (4 from each C and 1 from each H). We have used Gaussian 98[29] for all ab initio calculations except the multireference calculations, which were performed with use of MOLPRO 2002.[30]

Results and Discussion

To calculate the total absolute oscillator strengths for the CH stretching vibrational spectra of the five alkenes—ethene, propene, 1,3-butadiene, *cis*-2-butene, and *trans*-2-butene—we require the local mode parameters, frequency and anharmonicity, of the CH stretching oscillators. Values for these parameters are obtained from experiment and are given in Table 1.[27,31−34] The calculated intensity depends linearly on the value of the local mode frequency (eq 1), and since the largest uncertainty in frequency is 14 cm^{-1}, this leads to a maximum change in intensity of less than 2%. The maximum standard deviation in anharmonicity is 3 cm^{-1} (Table 1), which leads to a maximum change in calculated oscillator strengths of 16% for transitions with $\Delta v_{CH} \leq 6$ in ethene, in good agreement with results from a previous study.[21]

The stretching−stretching coupling coefficients are calculated with all of the ab initio methods used to calculate the dipole moment functions and the average values are shown in Table 1. The coefficient varies more with the basis set than with the level of theory; however, the overall variation is small and has little effect on the intensities of the dominant transitions. Within the HCAO local mode model, the calculated total CH stretching overtone intensities are insensitive to the value of the coefficient, which mainly distributes the intensity among transitions within a given overtone. Our calculated coupling coefficients for 1,3-butadiene, *cis*-2-butene, and *trans*-2-butene are consistent with the previous calculated values.[27,34]

TABLE 2: Observed and Calculated Total Oscillator Strengths for Ethene[a]

	v	I	II	III	VII	IV	V	VI	VIII	IX	obs[b]
HF	1	1.5×10^{-5}	1.2×10^{-5}	1.1×10^{-5}	1.1×10^{-5}	1.1×10^{-5}	1.1×10^{-5}	1.1×10^{-5}	1.1×10^{-5}	1.1×10^{-5}	5.8×10^{-6}
	2	4.0×10^{-7}	4.6×10^{-7}	3.6×10^{-7}	3.8×10^{-7}	3.6×10^{-7}	3.7×10^{-7}	3.7×10^{-7}	3.6×10^{-7}	3.7×10^{-7}	2.1×10^{-7}
	3	7.8×10^{-8}	5.7×10^{-8}	4.1×10^{-8}	4.3×10^{-8}	3.6×10^{-8}	3.9×10^{-8}	3.6×10^{-8}	3.5×10^{-8}	3.6×10^{-8}	3.9×10^{-8}
	4	9.7×10^{-9}	5.2×10^{-9}	4.2×10^{-9}	4.1×10^{-9}	2.9×10^{-9}	3.2×10^{-9}	2.7×10^{-9}	2.7×10^{-9}	2.9×10^{-9}	3.5×10^{-9}
	5	1.3×10^{-9}	5.3×10^{-10}	5.6×10^{-10}	4.5×10^{-10}	3.1×10^{-10}	2.9×10^{-10}	2.3×10^{-10}	2.7×10^{-10}	2.9×10^{-10}	3.2×10^{-10}
	6	2.1×10^{-10}	7.2×10^{-11}	8.6×10^{-11}	6.2×10^{-11}	4.7×10^{-11}	3.4×10^{-11}	3.1×10^{-11}	3.9×10^{-11}	4.0×10^{-11}	5.5×10^{-11}
B3LYP	1	1.2×10^{-5}	1.1×10^{-5}	9.8×10^{-6}	8.9×10^{-6}	9.1×10^{-6}	8.7×10^{-6}	8.6×10^{-6}	8.7×10^{-6}	8.7×10^{-6}	
	2	3.6×10^{-7}	4.0×10^{-7}	2.8×10^{-7}	3.0×10^{-7}	2.8×10^{-7}	3.0×10^{-7}	3.0×10^{-7}	2.9×10^{-7}	3.0×10^{-7}	
	3	7.8×10^{-8}	6.2×10^{-8}	4.0×10^{-8}	4.1×10^{-8}	3.7×10^{-8}	3.9×10^{-8}	3.7×10^{-8}	3.5×10^{-8}	3.7×10^{-8}	
	4	8.9×10^{-9}	5.2×10^{-9}	4.0×10^{-9}	3.5×10^{-9}	3.1×10^{-9}	3.1×10^{-9}	2.6×10^{-9}	2.6×10^{-9}	2.8×10^{-9}	
	5	1.1×10^{-9}	4.3×10^{-10}	5.1×10^{-10}	3.1×10^{-10}	3.1×10^{-10}	2.7×10^{-10}	1.9×10^{-10}	2.3×10^{-10}	2.5×10^{-10}	
	6	1.6×10^{-10}	4.6×10^{-11}	7.9×10^{-11}	3.6×10^{-11}	4.2×10^{-11}	3.0×10^{-11}	2.3×10^{-11}	3.0×10^{-11}	3.2×10^{-11}	
MP3	1	9.3×10^{-6}	9.6×10^{-6}	8.0×10^{-6}	8.0×10^{-6}	7.6×10^{-6}					
	2	2.0×10^{-7}	2.3×10^{-7}	1.7×10^{-7}	1.6×10^{-7}	1.5×10^{-7}					
	3	5.9×10^{-8}	5.0×10^{-8}	3.3×10^{-8}	3.2×10^{-8}	2.8×10^{-8}					
	4	7.7×10^{-9}	4.7×10^{-9}	3.3×10^{-9}	3.1×10^{-9}	2.7×10^{-9}					
	5	1.1×10^{-9}	4.6×10^{-10}	4.3×10^{-10}	3.2×10^{-10}	3.1×10^{-10}					
	6	1.8×10^{-10}	5.9×10^{-11}	6.7×10^{-11}	3.9×10^{-11}	4.5×10^{-11}					
QCISD	1	1.1×10^{-5}	1.1×10^{-5}	9.0×10^{-6}	8.7×10^{-6}	8.4×10^{-6}					
	2	2.3×10^{-7}	2.5×10^{-7}	1.9×10^{-7}	1.8×10^{-7}	1.8×10^{-7}					
	3	6.2×10^{-8}	5.1×10^{-8}	3.4×10^{-8}	3.4×10^{-8}	2.9×10^{-8}					
	4	7.8×10^{-9}	4.8×10^{-9}	3.4×10^{-9}	3.3×10^{-9}	2.7×10^{-9}					
	5	1.1×10^{-9}	4.7×10^{-10}	4.2×10^{-10}	3.3×10^{-10}	3.0×10^{-10}					
	6	1.7×10^{-10}	5.9×10^{-11}	6.5×10^{-11}	4.0×10^{-11}	4.5×10^{-11}					
CASSCF	1				1.3×10^{-5}	1.2×10^{-5}			1.2×10^{-5}		5.8×10^{-6}
	2				1.8×10^{-7}	2.0×10^{-7}			2.0×10^{-7}		2.1×10^{-7}
	3				4.6×10^{-8}	4.8×10^{-8}			4.8×10^{-8}		3.9×10^{-8}
	4				5.1×10^{-9}	5.5×10^{-9}			4.9×10^{-9}		3.5×10^{-9}
	5				5.9×10^{-10}	6.7×10^{-10}			5.5×10^{-10}		3.2×10^{-10}
	6				9.3×10^{-11}	7.3×10^{-11}			5.7×10^{-11}		5.5×10^{-11}

[a] I: 6-31G(d), II: 6-31+G(d,p), III: 6-311+G(d,p), IV: 6-311++G(2d,2p), V: 6-311++G(3d,3p), VI: 6-311++G(3df,3pd), VII: aug-cc-pVDZ, VIII: aug-cc-pVTZ, IX: aug-cc-pVQZ. [b] The $\Delta \upsilon_{CH} = 5$ and 6 values are taken from ref 40.

In this work, we will focus on the quantitative effect of the ab initio dipole moment function on the calculated intensity. We investigate HF, B3LYP, MP3, QCISD, and CASSCF theories combined with Dunning and Pople type basis sets of double to quadruple zeta quality. The number of basis functions for ethene increases in the order 6-31G(d) < 6-31+G(d,p) < 6-311+G(d,p) < aug-cc-pVDZ < 6-311++G(2d,2p) < 6-311++G(3d,3p) < 6-311++G(3df,3pd) < aug-cc-pVTZ < aug-cc-pVQZ.

Ethene. The fundamental spectrum and the CH stretching intensities of ethene were first measured more than 50 years ago.[35−38] Converted into oscillator strengths, these early intensities are 7.2×10^{-6}, 7.7×10^{-6}, 7.9×10^{-6}, and 12×10^{-6}, which are slightly higher than our current measured oscillator strength of 5.8×10^{-6}. The intensities of the $\Delta \upsilon_{CH} = 2-4$ overtones have not been reported previously; however, there are a few previous measurements of the $\Delta \upsilon_{CH} = 5$ and 6 overtone intensities. The $\Delta \upsilon_{CH} = 5$ transition intensity was recorded with laser photoacoustic spectroscopy[39] and reported to have an intensity of 3.2×10^{-10}. Very recently, cavity ring-down and FT-VIS spectroscopy have been used to determine oscillator strengths of 3.22×10^{-10} and 3.20×10^{-10}, respectively.[40] Our conventional long path measured oscillator strength of 3.8×10^{-10} is in reasonable agreement with these recent values. The comparison with previous results for $\Delta \upsilon_{CH} = 1$ and 5 gives us some indication of the uncertainty in our measured oscillator strengths. The CH stretching overtone intensity in the $\Delta \upsilon_{CH} = 6$ region was recorded with laser photoacoustic spectroscopy[39,41] and reported to be 4.8×10^{-11} and 7.3×10^{-11}. Recently, phase shift cavity ring-down absorption spectroscopy[40,42] obtained a value of 5.5×10^{-11}. We have measured the CH stretching vibrational oscillator strengths of ethene in the regions corresponding to $\Delta \upsilon_{CH} = 1-5$. We compare our values for the $\Delta \upsilon_{CH} = 1-4$ regions and the recent phase shift cavity ring-down results for the $\Delta \mathrm{v}_{CH} = 5$ and 6 regions with our various calculated oscillator strengths in Table 2.

We have arranged the calculated oscillator strengths in Table 2 in order of increasing number of basis functions. Basis set I, II, and VII are of double-ζ quality, and basis sets VII, VIII, and IX are Dunning type basis sets of increasing angular momentum.

If we focus on the HF results, we find, in agreement with previous studies, that as the size of the basis set increases the calculated oscillator strengths in general decrease. The oscillator strengths of the $\Delta \upsilon_{CH} = 1$ and 2 transitions, and the $\Delta \upsilon_{CH} = 3-6$ transitions, display different trends in their change with basis set compared with the experimental values. The HF calculations overestimate the observed intensities for $\Delta \upsilon_{CH} = 1$ and 2 for all basis sets, whereas for the higher overtones $\Delta \upsilon_{CH} = 3-6$, the smaller basis sets significantly overestimate the intensities and the larger basis sets give reasonable agreement with the experimental values.

Electron correlation in the ab initio calculation of the dipole moment function is known to be important for the fundamental and can make a significant contribution at $\Delta \upsilon_{CH} = 2$. The latter is clearly shown in Figure 1, which illustrates the calculated to observed intensity ratio of the $\Delta \upsilon_{CH} = 2$ transition for the various methods. The $\Delta \upsilon_{CH} = 1$ and 2 intensities for B3LYP, MP3, and QCISD are smaller than the HF results as expected from the addition of electron correlation. We find that the intensities of the higher overtones $\Delta \upsilon_{CH} = 3-6$ change significantly less than the fundamental and first overtone intensities upon addition of electron correlation. Thus, the oscillator strengths calculated with B3LYP, MP3, and QCSID dipole moment functions are very close to each other and to the HF results for $\Delta \upsilon_{CH} = 3-6$. The $\Delta \upsilon_{CH} = 3-6$ oscillator strengths calculated with the MP3 and QCISD dipole moment

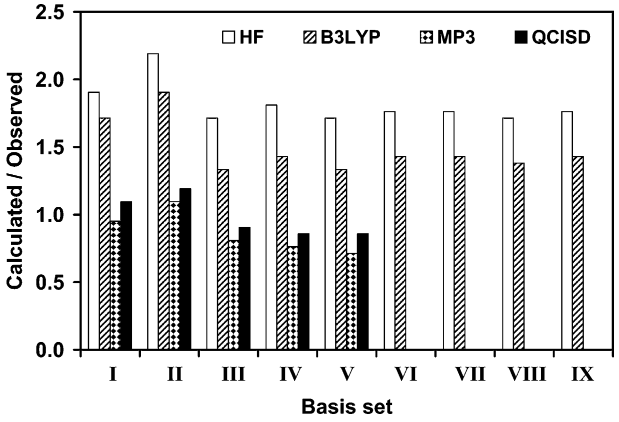

Figure 1. Calculated to observed total CH stretching intensity ratio of the first overtone transition in ethene. The intensities were calculated with the basis sets I to IX.

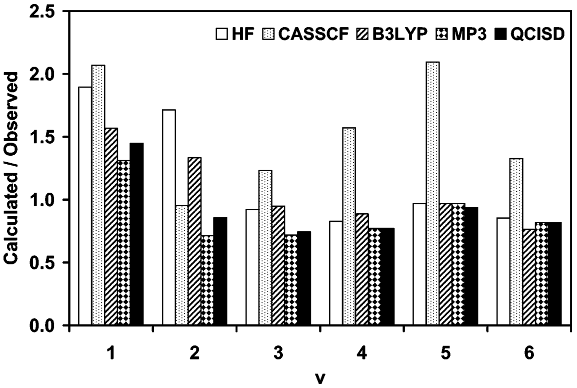

Figure 2. Calculated to observed total CH stretching intensity ratio of the $\Delta v_{CH} = 1-6$ transition in ethene. The intensities were calculated with the 6-311++G(2d,2p) basis set.

functions are within about 10% of each other. Comparison of the calculated and observed intensities for the different levels of theory with the 6-311++G(2d,2p) basis set is shown in Figure 2.

The lack of variation in the $\Delta v_{CH} = 2$ intensities with basis set is remarkable and not observed for the other overtones. Apart from the two smallest basis sets (I and II), the intensity of the first overtone shows very little variation to the basis set size at all levels of theory, as clearly shown in Figure 1. The overtone intensities calculated with the correlated methods generally decrease with basis set size to values slightly below the observed values.

To investigate the effect of multireference ab initio methods, we calculated intensities with CASSCF dipole moment functions for a few of the basis sets (VII, IV, and VIII).The variation in intensity with basis set for all but the two highest overtones is small. Compared to the HF results, the CASSCF results are similar for $\Delta v_{CH} = 1$ but differ for the overtones. Dynamical electron correlation is important for fundamental intensity which is something that CASSCF does not provide but MP3 and QCSID, etc., do. The CASSCF results are significantly better for $\Delta v_{CH} = 2$ but, somewhat surprisingly, are generally worse for the higher overtones. The only other good agreement with experiment that stands out is $\Delta v_{CH} = 5$ with basis set VIII, which is within 5% of the experimental value. It would appear that CASSCF methods do not do as well as the correlated methods as illustrated in Figure 2. Since we have chosen a full valence active space, we do not believe that choice of active space is the reason for this poorer performance of CASSCF.

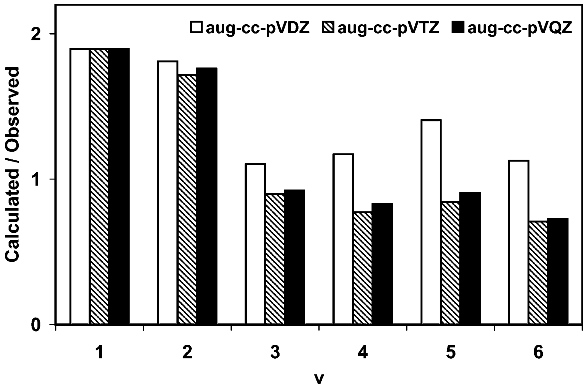

Figure 3. Calculated to observed total CH stretching intensity ratio of the $\Delta v_{CH} = 1-6$ transition in ethene. The intensities were calculated with the HF level of theory.

Comparison of the HF results with the three Dunning type basis sets shows essentially no change at $\Delta v_{CH} = 1$ and 2. For the overtones $\Delta v_{CH} = 3-6$ there is a change of up to 40% in HF intensities (30% for B3LYP) from basis set VII (aug-cc-pVDZ) to VIII (aug-cc-pVTZ) and a minimal difference of less than 10% between the basis set VIII and IX (aug-cc-pVQZ) results. The variation in HF calculated intensities with the three Dunning basis sets is shown in Figure 3, which clearly display the convergence with increasing basis set size. Comparison of the four triple-valence Pople type basis sets (III, IV, V, VI), which basically only differ in the number of polarized functions, shows larger variations than found between the double- to quadruple-ζ Dunning type basis sets. For the MP3 and QCSID correlated methods the results with the Dunning double-ζ (VII) and the 6-311++G(2d,2p) triple-ζ (IV) basis sets are similar and in overall good agreement with the observed absolute intensities.

Our best calculated value for the fundamental intensity is still about 30% higher than our experimental value; however, the previous experimental values were all higher than our present value. For the highest overtone our QCISD/IV intensity is within 20% of the recent accurate experimental value. For the $\Delta v_{CH} = 5$ overtone the agreement is even better (within 10%), and furthermore all levels of theory with basis set IV give similar intensities except for CASSCF. For $\Delta v_{CH} = 4$ our QCISD/IV intensity is about 25% lower than our experimental intensity. However, our experimental intensity at $\Delta v_{CH} = 5$ was 20% higher than the recent accurate result, and it is likely that our $\Delta v_{CH} = 4$ value is also too high as it uses the same method that we used to measure the $\Delta v_{CH} = 5$ intensity.

If we focus on the overtone intensities ($\Delta v_{CH} = 3-6$), basis sets III (6-311+G(d,p)), IV (6-311++G(2d,2p)), and VII (aug-cc-pVDZ) give good agreement with the experimental values and are basis sets for which it is feasible to do dipole grid calculations on larger systems. Thus, these ethene results would indicate that modest size basis sets are sufficient to obtain accurate absolute overtone intensities. On the basis of these results for ethene, we choose the 6-31+G(d,p), 6-311+G(d,p), 6-311++G(2d,2p), aug-cc-pVDZ, and aug-cc-pVTZ basis sets to calculate oscillator strengths with the HF and B3LYP theories and the 6-31+G(d,p) and 6-311+G(d,p) basis sets with the MP3 and QCISD theories for the other four alkenes.

1,3-Butadiene. The observed and calculated total CH stretching oscillator strengths of 1,3-butadiene are shown in Table 3.[27] Butadiene is similar to ethene in that it possesses only olefinic CH bonds, and as expected the local mode parameters are similar as can be seen in Table 1. Thus, we would expect to see similar intensity results to those for ethene. The experimental oscillator

TABLE 3: Observed and Calculated Total Oscillator Strengths for 1,3-Butadiene[a]

	v	II	III	VII	IV	VIII	obs[b]
HF	1	1.8×10^{-5}	1.7×10^{-5}	1.5×10^{-5}	1.6×10^{-5}	1.6×10^{-5}	1.1×10^{-5}
	2	7.5×10^{-7}	6.5×10^{-7}	7.1×10^{-7}	6.4×10^{-7}	6.3×10^{-7}	5.5×10^{-7}
	3	8.1×10^{-8}	6.7×10^{-8}	7.4×10^{-8}	5.7×10^{-8}	5.5×10^{-8}	6.0×10^{-8}
	4	7.2×10^{-9}	6.4×10^{-9}	6.6×10^{-9}	4.5×10^{-9}	4.1×10^{-9}	5.1×10^{-9}
	5	7.5×10^{-10}	8.0×10^{-10}	6.7×10^{-10}	4.6×10^{-10}	4.0×10^{-10}	5.3×10^{-10}
	6	1.0×10^{-10}	1.1×10^{-10}	8.6×10^{-11}	6.8×10^{-11}	6.0×10^{-11}	9.9×10^{-11}
B3LYP	1	1.6×10^{-5}	1.4×10^{-5}	1.3×10^{-5}	1.3×10^{-5}	1.3×10^{-5}	
	2	6.3×10^{-7}	4.9×10^{-7}	5.3×10^{-7}	4.9×10^{-7}	4.9×10^{-7}	
	3	8.6×10^{-8}	6.3×10^{-8}	6.8×10^{-8}	5.7×10^{-8}	5.3×10^{-8}	
	4	6.9×10^{-9}	5.8×10^{-9}	5.5×10^{-9}	4.5×10^{-9}	3.8×10^{-9}	
	5	5.8×10^{-10}	7.0×10^{-10}	4.6×10^{-10}	4.4×10^{-10}	3.3×10^{-10}	
	6	6.4×10^{-11}	1.0×10^{-10}	4.8×10^{-11}	5.9×10^{-11}	4.6×10^{-11}	
MP3	1	1.5×10^{-5}	1.2×10^{-5}				
	2	3.5×10^{-7}	2.9×10^{-7}				
	3	6.8×10^{-8}	4.9×10^{-8}				
	4	6.3×10^{-9}	4.7×10^{-9}				
	5	6.3×10^{-10}	5.6×10^{-10}				
	6	8.1×10^{-11}	8.4×10^{-11}				
QCISD	1	1.6×10^{-5}	1.3×10^{-5}				
	2	3.7×10^{-7}	3.3×10^{-7}				
	3	7.0×10^{-8}	5.4×10^{-8}				
	4	6.6×10^{-9}	5.4×10^{-9}				
	5	6.5×10^{-10}	6.7×10^{-10}				
	6	8.3×10^{-11}	8.2×10^{-11}				

[a] II: 6-31+G(d,p), III: 6-311+G(d,p), IV: 6-311++G(2d,2p), VII: aug-cc-pVDZ, VIII: aug-cc-pVTZ. [b] From ref 27.

strengths were recorded with FT-IR and long pass conventional spectroscopy, and the intensity of the highest overtone $\Delta v_{CH} = 6$ transition probably has substantial uncertainty.[27]

The oscillator strengths were previously calculated with a HF/6-31G(d) dipole moment function.[27] Our current HF/6-31+G(d,p) calculation is similar, but especially for the higher overtones, it is improved due to small differences in basis sets, a larger dipole moment grid, and a higher order dipole moment expansion.

The intensity patterns with the various ab initio methods are similar to what we found with the ethene results. The MP3 and QCISD calculated fundamental intensities with the 6-311+G(d,p) basis set are in good agreement with the observed oscillator strength as are the B3LYP results with basis sets larger than aug-cc-pVDZ.

The difference between the aug-cc-pVDZ and aug-cc-pVTZ calculated intensities for both HF and B3LYP theories is similar for 1,3-butadiene to that for ethene shown in Figure 3. The difference between the two basis sets is less in the B3LYP calculation than for the HF calculation.

Again, little variation between the MP3 and QCISD results are observed. Results with basis sets IV and VIII are similar for both HF and B3LYP theories as was also seen for ethene. The $\Delta v_{CH} = 2$ results do not show the same insensitivity to basis set size as was shown for ethene in Figure 1. However, for the higher overtones, the results show the same sensitivity to basis set size that we have noted for the other alkenes.

In general, the MP3 and QCISD calculations with basis set (III) give results very close to the observed values, as do the HF and B3LYP calculations with basis sets larger than VII. The exceptions are the fundamental transition intensity, which the HF results overestimate by more than 50%, and the $\Delta v_{CH} = 6$ intensity, which seems to be underestimated in most calculations, probably indicating that the experimental value is too high.

Propene. The calculated oscillator strengths of propene with different ab initio methods and basis sets are compared with the observed values in Table 4. The fundamental region was recorded with FT-IR and the first and second overtone with long pass conventional spectroscopy.[33] The intensities of the $\Delta v_{CH} = 4-6$ regions were determined from intracavity photoacoustic spectroscopy with the use of internal standards.[33,41] Propene has both olefinic CH bonds and a methyl group that need to be included in the total CH stretching intensity.

With the same basis set (III), the HF calculated fundamental intensity is higher than the correlated results as was the case for ethene and butadiene. For the first overtone both HF and B3LYP results are significantly higher than the MP3 and QCISD results. For the higher overtones, $\Delta v_{CH} = 3-6$, all theories give similar results with the HF and B3LYP results slightly larger.

In general, the MP3 and QCISD calculated results are again very similar. For basis set (III) the results are very close to the observed values. Results with basis sets IV and VIII are similar for both HF and B3LYP theories as was observed for ethene. The HF (B3LYP) calculated intensity of the first overtone is about a factor of 2 (1.5) higher than the experimental value, similar to the result for ethene but not that for 1,3-butadiene where the agreement was good.

***cis- and trans*-2-Butene.** The observed and calculated total oscillator strengths of *cis*- and *trans*-2-butene are shown in Tables 5 and 6. The fundamental region was recorded with FT-IR and the $\Delta v_{CH} = 2-6$ regions with long path length conventional spectroscopy.[34] Our HF/6-311+G(d,p) calculated oscillator strengths are comparable to those calculated previously with a HF/6-311+G(d,p) dipole moment function.[34] In addition to the two olefinic CH bonds, the 2-butenes have two methyl groups that need to be included in the total CH stretching intensity. The results for *cis*- and *trans*-2-butene are very similar as one might expect from the similar groups involved.

The fundamental intensities are overestimated with all methods for the 2-butenes. This is not observed for propene, and hence it is unlikely to be due to the presence of the methyl groups. The $\Delta v_{CH} = 2$ transition intensities are overestimated with the HF and B3LYP theories and significantly underestimated with the MP3 and QCISD theories. Similar results were observed for 1,3-butadiene and propene although the MP3 and QCISD results for propene were much closer to the observed values.

TABLE 4: Observed and Calculated Total Oscillator Strengths for Propene[a]

	v	II	III	VII	IV	VIII	obs[b]
HF	1	3.5×10^{-5}	3.4×10^{-5}	3.3×10^{-5}	3.2×10^{-5}	3.2×10^{-5}	2.9×10^{-5}
	2	7.2×10^{-7}	5.6×10^{-7}	6.0×10^{-7}	5.9×10^{-7}	6.0×10^{-7}	3.2×10^{-7}
	3	8.9×10^{-8}	6.2×10^{-8}	6.7×10^{-8}	6.0×10^{-8}	5.9×10^{-8}	5.5×10^{-8}
	4	7.7×10^{-9}	5.9×10^{-9}	5.7×10^{-9}	4.5×10^{-9}	4.2×10^{-9}	5.6×10^{-9}
	5	7.0×10^{-10}	7.6×10^{-10}	5.6×10^{-10}	4.2×10^{-10}	3.7×10^{-10}	5.1×10^{-10}
	6	8.2×10^{-11}	1.2×10^{-10}	7.2×10^{-11}	5.6×10^{-11}	4.9×10^{-11}	9.8×10^{-11}
B3LYP	1	2.8×10^{-5}	2.6×10^{-5}	2.5×10^{-5}	2.6×10^{-5}	2.4×10^{-5}	
	2	5.7×10^{-7}	4.1×10^{-7}	4.5×10^{-7}	5.0×10^{-7}	4.6×10^{-7}	
	3	9.3×10^{-8}	6.1×10^{-8}	6.4×10^{-8}	5.9×10^{-8}	5.8×10^{-8}	
	4	7.5×10^{-9}	5.7×10^{-9}	5.0×10^{-9}	4.6×10^{-9}	4.0×10^{-9}	
	5	5.9×10^{-10}	7.1×10^{-10}	4.1×10^{-10}	4.2×10^{-10}	3.2×10^{-10}	
	6	5.6×10^{-11}	1.1×10^{-10}	4.5×10^{-11}	5.3×10^{-11}	3.9×10^{-11}	
MP3	1	2.5×10^{-5}	2.3×10^{-5}				
	2	2.9×10^{-7}	2.0×10^{-7}				
	3	7.4×10^{-8}	4.9×10^{-8}				
	4	6.9×10^{-9}	4.8×10^{-9}				
	5	6.2×10^{-10}	5.8×10^{-10}				
	6	6.9×10^{-11}	9.1×10^{-11}				
QCISD	1	2.7×10^{-5}	2.5×10^{-5}				
	2	3.1×10^{-7}	2.3×10^{-7}				
	3	7.6×10^{-8}	5.0×10^{-8}				
	4	7.1×10^{-9}	4.8×10^{-9}				
	5	6.3×10^{-10}	5.8×10^{-10}				
	6	7.0×10^{-11}	8.9×10^{-11}				

[a] II: 6-31+G(d,p), III: 6-311+G(d,p), IV: 6-311++G(2d,2p), VII: aug-cc-pVDZ, VIII: aug-cc-pVTZ. [b] From ref 33.

TABLE 5: Observed and Calculated Total Oscillator Strengths for *cis*-2-Butene[a]

	v	II	III	VII	IV	VIII	obs[b]
HF	1	6.1×10^{-5}	6.0×10^{-5}	5.8×10^{-5}	5.6×10^{-5}	5.7×10^{-5}	3.1×10^{-5}
	2	9.6×10^{-7}	7.6×10^{-7}	8.2×10^{-7}	8.3×10^{-7}	8.4×10^{-7}	6.1×10^{-7}
	3	1.3×10^{-7}	9.3×10^{-8}	9.9×10^{-8}	9.3×10^{-8}	9.3×10^{-8}	8.7×10^{-8}
	4	1.2×10^{-8}	9.3×10^{-9}	8.9×10^{-9}	7.6×10^{-9}	7.2×10^{-9}	6.8×10^{-9}
	5	1.2×10^{-9}	1.2×10^{-9}	9.1×10^{-10}	7.3×10^{-10}	6.6×10^{-10}	6.1×10^{-10}
	6	1.4×10^{-10}	2.0×10^{-10}	1.2×10^{-10}	9.7×10^{-11}	8.5×10^{-11}	9.1×10^{-11}
B3LYP	1	4.9×10^{-5}	4.6×10^{-5}	4.5×10^{-5}	4.3×10^{-5}	4.3×10^{-5}	
	2	7.8×10^{-7}	5.8×10^{-7}	6.5×10^{-7}	6.6×10^{-7}	6.7×10^{-7}	
	3	1.4×10^{-7}	9.3×10^{-8}	9.7×10^{-8}	9.4×10^{-8}	9.3×10^{-8}	
	4	1.2×10^{-8}	9.2×10^{-9}	8.2×10^{-9}	7.8×10^{-9}	7.1×10^{-9}	
	5	1.1×10^{-9}	1.2×10^{-9}	7.3×10^{-10}	7.3×10^{-10}	6.0×10^{-10}	
	6	1.0×10^{-10}	1.9×10^{-10}	8.2×10^{-11}	8.8×10^{-11}	6.9×10^{-11}	
MP3	1	4.3×10^{-5}	3.9×10^{-5}				
	2	3.4×10^{-7}	2.4×10^{-7}				
	3	1.1×10^{-7}	7.1×10^{-8}				
	4	1.1×10^{-8}	7.5×10^{-9}				
	5	1.0×10^{-9}	9.5×10^{-10}				
	6	1.2×10^{-10}	1.5×10^{-10}				
QCISD	1	4.6×10^{-5}	4.3×10^{-5}				
	2	3.6×10^{-7}	2.7×10^{-7}				
	3	1.1×10^{-7}	7.3×10^{-8}				
	4	1.1×10^{-8}	7.6×10^{-9}				
	5	1.1×10^{-9}	9.4×10^{-10}				
	6	1.2×10^{-10}	1.5×10^{-10}				

[a] II: 6-31+G(d,p), III: 6-311+G(d,p), IV: 6-311++G(2d,2p), VII: aug-cc-pVDZ, VIII: aug-cc-pVTZ. [b] From ref 34.

The HF results with the basis sets VII, IV, and VIII are similar and in very good agreement with the experimental values for $\Delta v_{\mathrm{CH}} = 3-6$. For the B3LYP results, this agreement is extended to include also $\Delta v_{\mathrm{CH}} = 2$.

In Figure 4, we show the calculated to observed intensity ratios for the $\Delta v_{\mathrm{CH}} = 1-6$ regions for *cis*-2-butene for the four different ab initio theories with basis set III (6-311+G(d,p)). This figure is qualitatively similar to those of the four other molecules (not shown). For the $\Delta v_{\mathrm{CH}} = 3-6$ transitions HF and B3LYP on the one side and MP3 and QCISD on the other give similar results. The difference between the pairs is particularly large for $\Delta v_{\mathrm{CH}} = 2$. It is also clear that electron correlation does have an influence in all regions with this basis set. With the slightly larger basis set VII, correlation still matters for ethene. However, with the even larger basis set IV (6-311++G(2d,2p)) as shown in Figure 2, the $\Delta v_{\mathrm{CH}} = 3-6$ transition intensities for ethene are insensitive to electron correlation.

For ethene, propene, and 1,3-butadiene, the results obtained with the B3LYP/III method are quite good; however, for the 2-butenes, this method leads to somewhat larger disagreement with experiment for the two highest overtone transitions.

Conclusion

We have recorded the room temperature vapor phase CH stretching vibrational spectra of ethene corresponding to the $\Delta v_{\mathrm{CH}} = 1-5$ regions and determined the oscillator strengths.

We have calculated the absolute CH stretching oscillator strengths for a series of alkenes—ethene, propene, 1,3-butadiene,

TABLE 6: Observed and Calculated Total Oscillator Strengths for *trans*-2-Butene[a]

	v	II	III	VII	IV	VIII	obs[b]
HF	1	6.3×10^{-5}	6.2×10^{-5}	6.1×10^{-5}	5.9×10^{-5}	5.9×10^{-5}	3.5×10^{-5}
	2	9.4×10^{-7}	7.4×10^{-7}	7.9×10^{-7}	8.2×10^{-7}	8.2×10^{-7}	5.5×10^{-7}
	3	1.3×10^{-7}	9.0×10^{-8}	9.5×10^{-8}	9.1×10^{-8}	9.0×10^{-8}	7.6×10^{-8}
	4	1.2×10^{-8}	8.8×10^{-9}	8.5×10^{-9}	7.3×10^{-9}	7.0×10^{-9}	7.1×10^{-9}
	5	1.1×10^{-9}	1.2×10^{-9}	8.6×10^{-10}	7.0×10^{-10}	6.3×10^{-10}	6.3×10^{-10}
	6	1.3×10^{-10}	1.9×10^{-10}	1.1×10^{-10}	9.1×10^{-11}	8.0×10^{-11}	9.1×10^{-11}
B3LYP	1	5.2×10^{-5}	4.9×10^{-5}	4.8×10^{-5}	4.7×10^{-5}	4.6×10^{-5}	
	2	7.5×10^{-7}	5.6×10^{-7}	6.2×10^{-7}	6.4×10^{-7}	6.6×10^{-7}	
	3	1.3×10^{-7}	8.9×10^{-8}	9.3×10^{-8}	9.1×10^{-8}	9.0×10^{-8}	
	4	1.2×10^{-8}	8.6×10^{-9}	7.7×10^{-9}	7.5×10^{-9}	6.8×10^{-9}	
	5	9.9×10^{-10}	1.1×10^{-9}	6.7×10^{-10}	6.8×10^{-10}	5.5×10^{-10}	
	6	9.7×10^{-11}	1.8×10^{-10}	7.7×10^{-11}	8.2×10^{-11}	6.5×10^{-11}	
MP3	1	4.5×10^{-5}	4.1×10^{-5}				
	2	3.2×10^{-7}	2.3×10^{-7}				
	3	1.0×10^{-7}	6.7×10^{-8}				
	4	1.0×10^{-8}	7.2×10^{-9}				
	5	9.9×10^{-10}	9.1×10^{-10}				
	6	1.1×10^{-10}	1.5×10^{-10}				
QCISD	1	4.8×10^{-5}	4.5×10^{-5}				
	2	3.4×10^{-7}	2.6×10^{-7}				
	3	1.0×10^{-7}	6.9×10^{-8}				
	4	1.1×10^{-8}	7.2×10^{-9}				
	5	1.0×10^{-9}	9.0×10^{-10}				
	6	1.1×10^{-10}	1.5×10^{-10}				

[a] II: 6-31+G(d,p), III: 6-311+G(d,p), IV: 6-311++G(2d,2p), VII: aug-cc-pVDZ, VIII: aug-cc-pVTZ. [b] From ref 34.

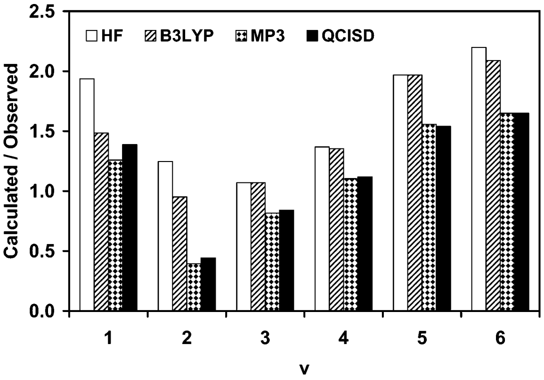

Figure 4. Calculated to observed total CH stretching intensity ratio of the $\Delta v_{CH} = 1-6$ transition in *cis*-2-butene. The intensities were calculated with the 6-311+G(d,p) basis set.

cis-2-butene, and *trans*-2-butene—with AO and HCAO local mode models combined with ab initio dipole moment functions. The local mode parameters, frequency and anharmonicity, were obtained from experiment and the stretching coupling coefficients from ab initio calculations.

Except for results obtained with the smallest 6-31G(d) basis set, the calculated oscillator strengths agree with the observed values to within a factor of 2. This agreement is remarkable given the absence of adjustable parameters and the spread of intensities from $\Delta v_{CH} = 1$ to 6 that spans 5 orders of magnitude.

The level of ab initio theory used to calculated the dipole moment function has an effect on the calculated fundamental and first overtone intensities irrespective of which basis set is used. However, the overtone intensities for the $\Delta v_{CH} = 3-6$ regions are relatively unaffected by electron correction and the level of theory chosen, provided a sufficiently large basis set is employed.

For the case of ethene, the CASSCF method provides no improvement on the results obtained with the HF treatment despite its much-increased computational complexity. It would be useful in the future to test the applicability of CASSCF for a molecule that is known to have significant multireference character in the ground electronic state.

Basis set size has a stronger effect on calculated intensities as v increases. In general, the oscillator strength decreases as the basis set size increases. With the Dunning basis sets we find basis set convergence with the aug-cc-pVTZ basis set. The aug-cc-p-VDZ calculations give results comparable to those obtained with the larger 6-311++G(2d,2p) basis set. For $\Delta v_{CH} = 2$, cancellation of terms makes results sensitive to both basis sets and level of theory.

In summary, we conclude that overtone intensities of useful accuracy for spectral comparison in the range $\Delta v_{CH} = 3-6$ can be obtained for alkenes with HF or B3LYP theory and a relatively modest basis set. For most transitions the 6-311+G-(d,p) basis set is sufficient. However, results with this basis set display some sensitivity to electron correlation that essentially disappears with a larger basis set like 6-311++G(2d,2p) or aug-cc-pVTZ.

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