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Combined IR/NIR and Density Functional Theory Calculations Analysis of the Solvent Effects on Frequencies and Intensities of the Fundamental and Overtones of the C=O Stretching Vibrations of Acetone and 2-Hexanone

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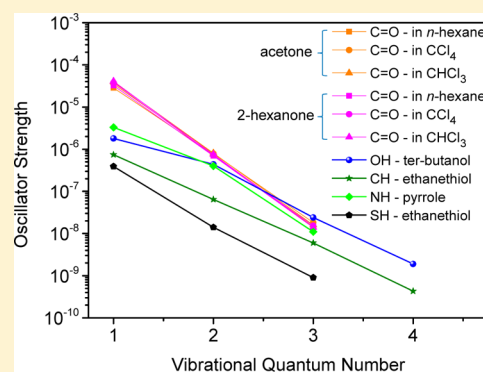
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Supporting Information

ABSTRACT: Vibrational overtone studies primarily focus on X—H stretching overtone transitions, where X is an atom like C, O, N, or S. In contrast, the studies on the C=O stretching overtones are very scattered. To advance the research in this field, we measured the fundamental, first, and second overtones of the C=O stretching vibration of acetone and 2-hexanone in *n*-hexane, CCl₄, and CHCl₃, as well as in the vapor phase using FT-IR/FT-NIR spectroscopy. Density functional theory (DFT) calculations have also been performed to help the assignment of the C=O stretching bands and to guide interpretation of the experimental results. It was found that the wavenumbers, absorption intensities, and oscillator strengths of the C=O stretching bands show marked solvent dependence. In the fundamental and the first overtone regions, the intensities of the C=O stretching vibration were found to be pronouncedly more intense than those of the C—H stretching vibration. In the second overtone region, the intensities of the C—H stretching vibration are comparable to those of the C=O stretching vibration. The theoretical and observed decrease in integrated intensity upon going from the fundamental to the first overtone of the C=O stretching vibration is around 50, which is significantly larger than those of the O—H, C—H, and S—H stretching vibration. Both the calculated and experimental results suggest that excessive weakness in the C=O stretching overtone was shown to be a result of both a low anharmonicity and a substantial reduction in the oscillator strength. These results provide new insight into our understanding of the C=O stretching vibration.



INTRODUCTION

The C=O stretching vibration bands are sensitive to both the physical and chemical environments of a chemical bond being probed. Effects of the inter- and intramolecular interactions appear clearly not only in the wavenumber shifts of the C=O stretching vibrational bands but also in their absorption intensity changes.^{1–3} As a consequence, the C=O stretching vibration bands have been studied extensively in the IR region.^{4–7}

In recent years, the rapid development of NIR spectrometers and progress in quantum chemical calculation studies of overtones, combinations, and anharmonicities have been attracted a great attention of numerous research group and permitted to achieve a lot of promising results.^{8–15} In the literature, the overtone studies primarily focus on the C—H and O—H stretching modes, less on N—H and very few on

S—H stretching vibrations. This results from increasing difficulty in recording of the overtone spectra. For the C—H and O—H stretching vibrations, the absorption intensities are the strongest for the fundamental transition and typically decrease by about 1 order of magnitude with each subsequent level of excitation.^{16–19} Miller et al. found that the intensities of the S—H stretching vibrations are significantly weaker than the equivalent C—H and O—H stretching vibrations in alcohols.²⁰ This reduction in intensity, at least partially, results from lower anharmonicity of the S—H stretching oscillator compared to the C—H and O—H stretching oscillators. However, in the literature there is a lack of the reliable information on the

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overtone, anharmonicity, and oscillator strengths of the C=O stretching vibration.

Recent spectroscopic and quantum chemical studies reveal that the presence of hydrogen bonding increases the oscillator strength of the O—H stretching fundamentals and leads to a substantial decrease in the intensity of its first overtone compared to that typically found for OH groups of non-hydrogen-bonded molecules.^{21–26} Futami et al. reported a similar result for the N—H stretching vibration mode of pyrrole–pyridine complex.²⁷ For C—H stretching vibrations, however, a hydrogen bonding has only subtle effects on the wavenumber shifts and absorption intensities of both the fundamental and the first overtone of the C—H stretching band.²⁸ Therefore, one can expect that the influence of hydrogen bonding on X—H stretching (where X is C, O, N, S, etc.) overtone intensities is different, depending on an X atom.

Futami et al. investigated the solvent dependence of the absorption intensities and wavenumbers in the fundamental and the first overtone spectra of the N—H stretching vibration of pyrrole in CCl₄, CHCl₃, and CH₂Cl₂.²⁹ The authors found that the wavenumbers of the N—H fundamental and its first overtone decrease in the order CCl₄, CHCl₃, and CH₂Cl₂, which is the increasing order of the dielectric constant. The absorption intensities of the N—H stretching modes increase in the same order. The solvent dependence observed for the N—H stretching vibration of pyrrole is quite different from a similar relationship for the hydrogen bonded N—H in the pyrrole–pyridine complex. The quantum chemical calculations of the wavenumbers and absorption intensities of the NH stretching bands elucidated that the decrease in wavenumbers of both the fundamental and overtone of the N—H stretching mode with the increase in the dielectric constant of the solvent results from the anharmonicity of vibrational potential. The intensity increase comes from the gradual increase in the slope of the dipole moment function. Gonjo et al. reported similar results for the O—H stretching mode of phenol and 2,6-dihalogenated phenol in *n*-hexane, CCl₄, CHCl₃, and CH₂Cl₂.³⁰ Moreover, they also found that the solvent shifts of phenol and 2,6-dihalogenated phenol change linearly with the vibrational quantum number. Thus, one can conclude that the effect of hydrogen bonding and the solvent effect induce different changes in the wavenumber shifts and absorption intensities of the fundamentals and first overtones of the X—H stretching vibrational modes.

Theoretical calculations like density functional theory (DFT) have enabled one to calculate the wavenumbers and absorption intensities of the fundamental and overtones.^{31–33} Preat et al. investigated dependence of the dielectric constant on the wavenumber and IR absorption intensity of the C=O stretching mode and electronic excitation energy of coumarin by using the Nancy continuum model (NCM) and the polarized continuum model (PCM).³⁴ They found that the wavenumber of the C=O stretching mode decreases, while its intensity increases with the increase of dielectric constant. A saturation of both wavenumbers and intensity of the C=O stretching vibration dependence was observed at the dielectric constant higher than 5. This study focused on the C=O stretching fundamental, whereas the information on the C=O stretching overtones is absent.

In the present work, we investigate the fundamental and overtones of the C=O stretching vibration of acetone and 2-hexanone in *n*-hexane, CCl₄, and CHCl₃, as well as in the vapor phase using IR/NIR spectroscopy and quantum chemical

calculation to elucidate the solvent dependence of the C=O stretching vibration. The dielectric constants of *n*-hexane, CCl₄, and CHCl₃ are 1.9, 2.2, and 4.8, respectively. Furthermore, the measurement of the C=O stretching band in solution will help us to overcome the uncertainties in the experimental oscillator strengths arising from inaccuracies in the sample vapor pressure.²⁰ The accurate values of the experimental oscillator strength will enable us to directly compare the C=O stretching oscillator strength with those of the O—H, C—H, N—H, and S—H stretching vibrations.

■ EXPERIMENTAL AND CALCULATION METHODS

Acetone (Wako, 99%) and 2-hexanone (Wako, 95%) were used without further purification, whereas *n*-hexane (Wako, 97.0%), CCl₄ (Wako 99.8%), and CHCl₃ (Wako 99.0%) were dried with molecular sieves (3, 4, and 5 Å) before use. The concentrations of acetone and 2-hexanone in *n*-hexane, CCl₄, and CHCl₃ were 0.1 mol·L^{−1}.

IR spectra of the solutions in the region 3000–400 cm^{−1} were measured with a Nicolet 6700 FTIR spectrometer, and NIR spectra in the region 10000–3000 cm^{−1} were recorded with a FT-NIR/IR spectrophotometer (Perkin-Elmer Spectrum One NTS FT-NIR spectrometer). Both spectrometers were purged with dry N₂ to minimize absorption from the atmosphere. The spectra in the fundamental and the first overtone regions were recorded at a resolution of 2 cm^{−1}, whereas that in the second overtone region was obtained at a resolution of 4 cm^{−1}. The BaF₂ liquid cell with a thickness of 0.2 mm and quartz cells with thicknesses of 2 and 10 mm were used. Gas spectra of acetone and 2-hexanone in the fundamentals were measured with a spectral resolution of 1 cm^{−1} using a gas cell with CaF₂ windows and those in the overtone region were measured using a white cell made by Yokogawa Co.

Analysis of the experimental spectra yielded the oscillator strength (*f*) calculated from the following equation:^{35,36}

$$f = 4.32 \times 10^{-11} (\text{mol} \cdot \text{L}^{-1} \text{ m cm}) \frac{1}{Cl} \int A(\tilde{\nu}) d(\tilde{\nu}) \quad (1)$$

where *A* is the absorbance, *C* is the concentration of the sample, and *l* is the path length.

DFT calculations were carried out by using Gaussian 09 program³⁷ with 6-311++G(3df,3pd) basis sets. Becke's three-parameter hybrid density function in combination with the Lee–Yang–Parr correlation functional (B3LYP) was used for the optimization of geometrical structures and the calculations of normal coordinates, vibrational potential curves, and dipole moment functions.^{29,36,38,39} Quantum chemical calculations based on a self-consistent reaction field (SCRF) and a isodensity surface polarized continuum model (IPCM) model were carried out by using the optimized structures in the gas phase.

In the present study, we solved the Schrödinger equation of one-dimensional C=O stretching vibration

$$H\psi_v(q) = \left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dq^2} + V(q) \right] \psi_v(q) = E_v \psi_v(q) \quad (2)$$

where *q*, *μ*, and *V*(*q*) are the normal coordinate, the reduced mass, and the potential energy function, respectively.

The oscillator strength *f*_{*v*0} of the C=O stretching transition was calculated as follows:

$$f_{\nu_0} = \frac{4m_e\pi}{3e^2\hbar} |\vec{\mu}_{\nu_0}|^2 \tilde{\nu}_{\nu_0} = 4.702 \times 10^{-7} (\text{cm D}^{-2}) |\vec{\mu}_{\nu_0}|^2 \tilde{\nu}_{\nu_0} \quad (3)$$

where $\tilde{\nu}_{\nu_0}$ is the transition energy in cm^{-1} and $|\vec{\mu}_{\nu_0}|^2$ is the sum of the squared transition dipole moments of the x , y , and z components in $(\text{debye})^2$ units.⁴⁰ $|\vec{\mu}_{\nu_0}|^2$ is given by

$$\begin{aligned} |\vec{\mu}_{\nu_0}|^2 &= |\vec{\mu}_{\nu_0}^x|^2 + |\vec{\mu}_{\nu_0}^y|^2 + |\vec{\mu}_{\nu_0}^z|^2 \\ &= \left| \int \psi_{\nu}(q) \vec{\mu}_{\nu_0}^x \psi_0(q) dq \right|^2 + \left| \int \psi_{\nu}(q) \vec{\mu}_{\nu_0}^y \psi_0(q) dq \right|^2 \\ &\quad + \left| \int \psi_{\nu}(q) \vec{\mu}_{\nu_0}^z \psi_0(q) dq \right|^2 \end{aligned} \quad (4)$$

Here, $|\vec{\mu}_{\nu_0}^x|^2 = 0$ and $|\vec{\mu}_{\nu_0}^y|^2 = 0$, because these are the A_1 symmetry.

We obtained the numerical results for the energy levels and the wave functions using the method given by Johnson.⁴¹ Potential energy curves used for the calculations cover the range from -0.7 to $+1.0$ q_0 in 0.02 q_0 steps around the equilibrium position, where q_0 is the unit for the normal coordinate corresponding to the C=O stretching mode (Figure 1); they are represented by the displacement vectors

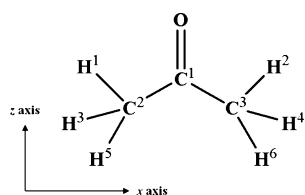


Figure 1. Optimized structure of acetone at the DFT//B3LYP/6-311++G(3df,3pd) level.

of atoms in Å unit as follows: $q_0 = \{\text{O}(0.00, 0.00, -0.46), \text{C}^1(0.00, 0.00, 0.71), \text{C}^2(0.00, 0.00, -0.04), \text{C}^3(0.00, 0.00, -0.04), \text{H}^1(0.01, -0.16, 0.20), \text{H}^2(-0.01, 0.16, 0.20), \text{H}^3(0.09,$

$0.07, -0.15), \text{H}^4(-0.09, -0.07, -0.15), \text{H}^5(-0.11, 0.09, -0.15), \text{H}^6(0.11, -0.09, -0.15)\}$

The number of calculation points is sufficient for the numerical calculations without such assumption like the Morse function. This ensures converged energy levels with precision higher than 0.001 cm^{-1} . This calculation method reproduced very well the solvent dependence of the NH stretching mode of pyrrole and of the OH stretching mode of phenol and 2,6-dihalogenated phenols.^{29,30}

RESULTS AND DISCUSSION

IR/NIR Spectra of C=O Stretching Vibrations of Acetone and 2-Hexanone in n -Hexane, CCl_4 , and CHCl_3 . Parts a–c of Figure 2 show absorption spectra of acetone and 2-hexanone in n -hexane, CCl_4 , and CHCl_3 in the region 1600 – 1850 , 3300 – 3600 , and 4900 – 5300 cm^{-1} , respectively. The second derivative spectra (Figure S1, Supporting Information) do not reveal the presence of the dimeric species under the given experimental conditions. The bottom parts of Figure 2a–c show the fundamental, the first, and second overtone of the C=O stretching modes of 2-hexanone in n -hexane, CCl_4 , and CHCl_3 , respectively. However, it can be seen from the top parts of Figure 2 that the spectra of acetone are more complex as compared with those of 2-hexanone. The lower frequency bands at 1722 , 1718 , 1711 cm^{-1} in the top parts of Figure 2a and at 3431 , 3420 , 3407 cm^{-1} in the top parts of Figure 2b are assigned to the fundamental and the first overtone of the C=O stretching vibration of acetone in n -hexane, CCl_4 , and CHCl_3 , respectively. The higher frequency bands at 1744 , 1746 , 1751 cm^{-1} and at 3453 , 3452 , 3454 cm^{-1} are respectively attributed to the combination band and their overtone in n -hexane, CCl_4 , and CHCl_3 , due to asymmetric stretching of the molecular skeleton and the CCO deformation. The observed wave-numbers of the absorption bands of the asymmetric stretching of molecular skeleton and the CCO deformation of acetone in Figure S2 and Table S1 (Supporting Information) indicate that the combination bands are correctly assigned.^{1,7} According to

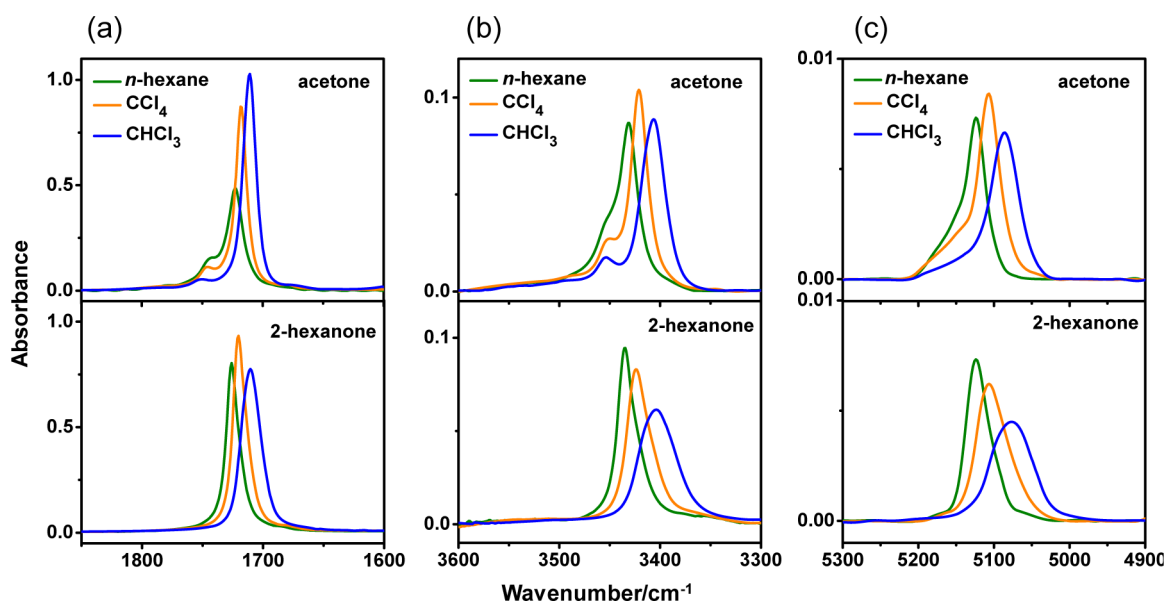


Figure 2. Spectra of acetone and 2-hexanone in n -hexane, CCl_4 , and CHCl_3 : (a) fundamental region; (b) first overtone region; (c) second overtone region.

the anharmonicity constant, the combination band of acetone in *n*-hexane, CCl_4 , and CHCl_3 in the $\nu_{\text{C=O}} = 3$ region should appear at ~ 5126 , 5121 , and 5109 cm^{-1} , respectively. However, the corresponding peaks were not observed in the second derivative spectra (Figure S1, Supporting Information). Therefore, we suggest that the combination bands become significantly weak in the $\nu_{\text{C=O}} = 3$ region. The bands in the top parts of Figure 2c are assigned to the second overtone of the C=O stretching vibration of acetone.

Figure 3 depicts the gas spectra of acetone and 2-hexanone in the $10000\text{--}3200 \text{ cm}^{-1}$ ($\Delta\nu_{\text{C=O}} = 2\text{--}4$) region along with the

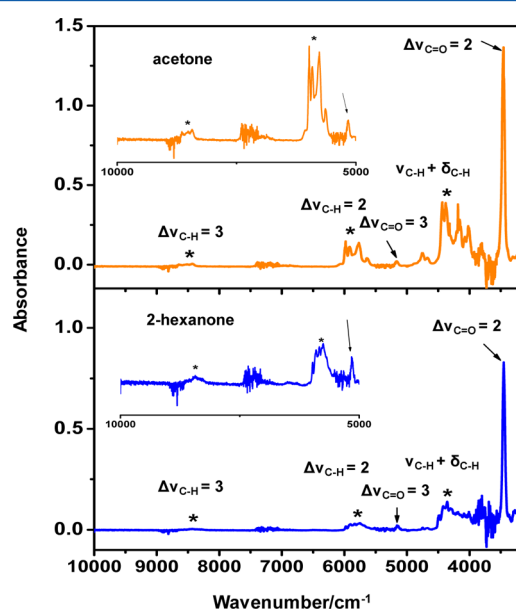


Figure 3. Room temperature vapor phase overtone spectra of acetone (top) and 2-hexanone (bottom) in the $10000\text{--}3200 \text{ cm}^{-1}$ ($\Delta\nu_{\text{C=O}} = 2\text{--}4$) region. The arrows show the C=O stretching overtone and the asterisks indicate the CH stretching overtone.

spectral assignment. In this way one can easily compare the relative intensities and frequencies of the C=O and C—H stretching vibration. It can be seen from Figure 3 that the intensities of the C=O stretching band are much more intense than those of the C—H stretching vibration in the first overtone region. In the second overtone region, the intensities of the C—H stretching band are similar to those of the C=O stretching. Further examination of Figure 3 also reveals that the intensity of the second overtone is much weaker than that of

the first overtone, reflecting that the intensity of the C=O stretching vibration drops profoundly in going from the first to the second overtone.

Table 1 summarizes the wavenumbers and the integrated mole absorption coefficients of the C=O stretching vibrations of acetone and 2-hexanone in a gas phase and in *n*-hexane, CCl_4 , and CHCl_3 . The wavenumbers were determined from the second derivative of the corresponding IR/NIR spectra. The band area was evaluated by the integration of the area under the absorption band and then converted to the integrated mole absorption coefficient. One should note that the combination bands were included in the integrated intensity, because the combination band borrows intensity from the C=O stretching band. Next, the integrated mole absorption coefficients were employed for calculation of the oscillator strength of the C=O stretching mode accordingly with eq 1. The corresponding values were collected in Table 2.

To explore more deeply the properties of the C=O stretching vibration, we calculated the wavenumbers and absorption intensities of the fundamental and overtones of the C=O stretching vibration by B3LPY/6-311++G-(3df,3pd)//IPCM. Because both acetone and 2-hexanone are the straight-chain ketones, one can expect that the calculated solvent dependence of wavenumbers and intensities of the fundamental and overtones of the C=O stretching vibration should be similar. Thus, in the present study we only show the results of calculations for acetone, the simplest straight-chain ketone (Table 3). It can be seen from Tables 1–3 that the calculated absorption intensities of the acetone C=O stretching vibration are in reasonable agreement with the observed values, whereas the calculated wavenumbers are considerably higher than the observed ones. Probably, this results from the fact that the SCRF/IPCM model yields larger deviations of the wavenumbers. In spite of this, the solvent dependences on wavenumbers and intensities are clearly reproduced by DFT calculations.

As is evident from Figure 2 and Table 1, for all the investigated compounds the C=O stretching vibration bands undergo a red shift and become broader in the order *n*-hexane, CCl_4 , and CHCl_3 , which is the increasing order of dielectric constant of the solvents. This is consistent with the solvent dependence of the N—H and O—H stretching vibrations.^{29,30} Furthermore, the bands due to the fundamentals and the first and second overtones in the gas state appear at higher frequencies than those in the solution because of the lack of the solvent effect in the gas state, which is responsible for the frequency shift. Futami et al. have confirmed that the solvent

Table 1. Observed Wavenumbers (cm^{-1}) and Integrated Mole Absorption Coefficient ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-2}$) of the Fundamental, First, and Second Overtones of the C=O Stretching Modes of Acetone and 2-Hexanone in a Gas State and in *n*-Hexane, CCl_4 , and CHCl_3

investigated compounds	solvent	fundamental		first overtone		second overtone	
		1ν	ϵ	2ν	ϵ	3ν	ϵ
acetone	gas	1739		3460		5163	
	<i>n</i> -hexane	1722	6585	3431	175.0	5122	3.336
	CCl_4	1718	8175	3420	181.3	5107	4.213
	CHCl_3	1711	9230	3407	185.5	5085	3.697
2-hexanone	gas	1736		3452		5149	
	<i>n</i> -hexane	1726	7505	3434	160.6	5124	3.213
	CCl_4	1720	8775	3424	165.3	5107	3.550
	CHCl_3	1711	9490	3404	174.0	5076	3.258

Table 2. Observed C=O Stretching Oscillator Strengths (f) of Acetone and 2-Hexanone

$\Delta\nu_{\text{C=O}}$	acetone			2-hexanone		
	<i>n</i> -hexane	CCl ₄	CHCl ₃	<i>n</i> -hexane	CCl ₄	CHCl ₃
1	2.84×10^{-5}	3.53×10^{-5}	3.99×10^{-5}	3.24×10^{-5}	3.79×10^{-5}	4.10×10^{-5}
2	7.56×10^{-7}	7.83×10^{-7}	8.01×10^{-7}	6.94×10^{-7}	7.14×10^{-7}	7.52×10^{-7}
3	1.44×10^{-8}	1.82×10^{-8}	1.60×10^{-8}	1.39×10^{-8}	1.53×10^{-8}	1.41×10^{-8}

Table 3. Calculated Wavenumbers (cm^{-1}) and the Oscillator Strengths of the Fundamental, First, and Second Overtones of the C=O Stretching Mode of Acetone in a Gas State and in *n*-Hexane, CCl₄, and CHCl₃^a

investigated compounds	solvent	dielectric constant	fundamental		first overtone		second overtone	
			1ν	f	2ν	f	3ν	f
acetone	gas	1.0	1775	3.6×10^{-5}	3533	5.7×10^{-7}	5272	1.7×10^{-8}
	<i>n</i> -hexane	1.9	1758	4.8×10^{-5}	3498	7.0×10^{-7}	5220	2.2×10^{-8}
	CCl ₄	2.2	1753	5.1×10^{-5}	3489	7.3×10^{-7}	5206	2.4×10^{-8}
	CHCl ₃	4.8	1736	6.4×10^{-5}	3455	8.4×10^{-7}	5155	2.9×10^{-8}

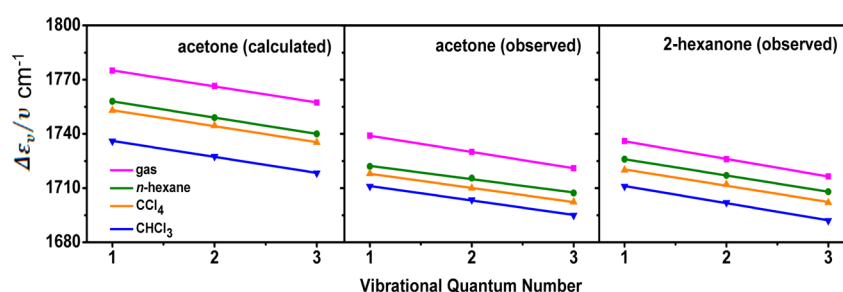
^aB3LPY/6-311++G(3df,3pd)//IPCM.

Figure 4. Birge–Sponer plot for the C=O stretching vibrations of acetone and 2-hexanone.

Table 4. Calculated and Observed Harmonic Frequency ω_e (cm^{-1}) and Anharmonicity Constant $\omega_e x_e$ (cm^{-1}) for the C=O Stretching Vibration of Acetone and 2-Hexanone

investigated compounds		solvent	ω_e	$\omega_e x_e$
acetone	calculated	gas	1784.0 ± 0.4	-8.9 ± 0.2
		<i>n</i> -hexane	1767 ± 0	-9 ± 0
		CCl ₄	1762.0 ± 0.4	-8.9 ± 0.2
		CHCl ₃	1745 ± 0.4	-8.9 ± 0.2
	observed	gas	1757.0 ± 0	-9.0 ± 0
		<i>n</i> -hexane	1737.0 ± 3.0	-7.4 ± 0.9
		CCl ₄	1733.7 ± 0.6	-7.9 ± 0.2
		CHCl ₃	1727.2 ± 1.8	-8.0 ± 0.6
2-hexanone	observed	gas	1755.5 ± 0.9	-9.8 ± 0.3
		<i>n</i> -hexane	1744.0 ± 0	-9.0 ± 0
		CCl ₄	1738.5 ± 3.5	-9.0 ± 1.1
		CHCl ₃	1730.2 ± 1.8	-9.5 ± 0.6

dependence of wavenumbers of N—H stretching vibration arises from the anharmonicity of vibrational potential and the solvent dependence of intensities results from the gradual increase in the slope of the dipole moment function.²⁹ In the present study, acetone or 2-hexanone did not form any complex with the solvents; however, the charge densities on the C=O stretching vibration was changed by the surrounding solvent and this leads to the changes in the dipole moment.^{1,7} This effect is proportional to the dielectric constant of the solvent (not more than 5).³⁴ It is clear from Tables 2 and 3 that the observed and calculated C=O stretching oscillator strength increases with the increase in the dielectric constant of the solvents in the fundamental and the first overtone region. The oscillator strength increase is more pronounced in the fundamentals region than those in the overtones region. As

for the second overtone region, the observed oscillator strengths of the C=O stretching of the acetone and 2-hexanone in CHCl₃ are smaller than those in CCl₄. In theory, however, the observed oscillator strengths of the C=O stretching of the acetone and 2-hexanone in CHCl₃ should be higher than those in CCl₄. The experimental errors possibly arise from the baseline correction and subsequent subtraction of the solvent absorption. Tables 1–3 demonstrate that the wavenumbers, absorption intensities and oscillator strength of the C=O stretching vibration show significant solvent dependence.

Effect of the Vibrational Quantum Number on the Anharmonicity and Intensity of the C=O Stretching Vibration. The experimental data in the fundamental, the first, and second overtone regions enable us to obtain the harmonic

frequency ω_e and anharmonicity constant $\omega_e x_e$ for the C=O stretching vibration from a Birge–Sponer plot,^{10,11,42}

$$\Delta\varepsilon_v/v = \omega_e - \omega_e x_e (v + 1) \quad (5)$$

where $\Delta\varepsilon_v$ is the wavenumber at vibrational quantum number v . Figure 4 shows Birge–Sponer plot of $\Delta\varepsilon_v$ versus $v + 1$ for the C=O stretching vibration of acetone and 2-hexanone. From the slope and intercepts of these plots, we obtain the harmonic frequency ω_e and the anharmonicity constant $\omega_e x_e$ for the C=O stretching vibration, which are given in Table 4.

The excellent fit to eq 5, which is clear from Figure 4 and from the standard errors given in Table 4, provide further support for our assignment of the spectra (Figures 2 and 3 and Table 1). Table 4 reveals that the experimental harmonic frequency and anharmonicity constant for the C=O stretching vibration of acetone are in accord with the theoretical results. Moreover, we did not observe a significant solvent dependence of anharmonicity constant. Further analysis of Table 4 indicates that the anharmonicity constant ($\omega_e x_e$) of the C=O stretching is about -9 cm^{-1} , which magnitude is significantly smaller than the typical anharmonicities of the O–H, N–H, and C–H stretching, as well as the S–H stretching vibration. Hence, one can conclude that the C=O stretching vibration is more harmonic than the O–H, N–H, and C–H stretching modes. On the basis of the anharmonicity arguments, one would expect that the C=O stretching intensities become increasingly weaker in the overtone region. This is consistent with what we observe in Figures 2 and 3.

In Figure 5 is displayed the C=O stretching oscillator strength for acetone and 2-hexanone in *n*-hexane, CCl₄, and

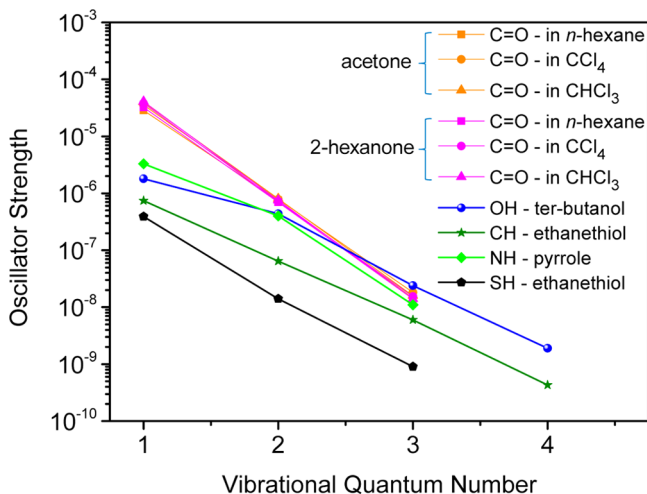


Figure 5. Experimental C=O stretching oscillator strength of acetone and 2-hexanone in *n*-hexane, CCl₄, and CHCl₃, along with the O–H, C–H, N–H, and S–H stretching oscillator strength.

CHCl₃ versus vibrational quantum number. Moreover, the oscillator strength of the O–H, C–H, N–H, and S–H stretching vibrations were added in the same figure to enable direct comparison of these values with those for the C=O stretching mode. Oscillator strength of the O–H, C–H, and S–H stretching vibrations were taken from ref 20, whereas the N–H oscillator strength came from ref 15. It is obvious from Figure 5 that the C=O stretching oscillator strength is the strongest in the fundamental region, followed by the O–H, N–H, C–H, and S–H oscillators. In the second overtone

region, however, the C=O stretching oscillator strength is close to those of the O–H and N–H oscillators, whereas it is a little stronger than that of the C–H oscillator and significantly stronger compared to the S–H oscillator. Analysis of the slope of the lines in Figure 5 suggests that the diminution of the C=O stretching oscillator strength with the vibrational quantum number is more distinct than that for the O–H, C–H, N–H, and S–H stretching modes. On this basis, one would anticipate that the C=O stretching oscillator strength in the higher overtone region should be weaker than the O–H, C–H, N–H, and S–H stretching oscillator strength, and hence the C=O stretching overtone will become barely visible.

Figure 6 displays the normalized intensities of the C=O stretching vibrations versus the vibrational quantum number. The intensities of the C=O stretching vibration at each vibrational quantum number were normalized by the corresponding fundamental intensities. In general, vibrational overtone intensities decrease by about 1 order of magnitude with each subsequent level of excitation. However, it can be seen from Figure 6 that both the theoretical and experimental overtone intensities of the C=O stretching vibration drop by about 2 orders of magnitude in going from the fundamental to the first overtone and about 4 orders of magnitude in going from the fundamental to the second overtone. Trends observed in all solvents are very similar. Therefore, Figure 6 demonstrates that the intensity reduction of the C=O stretching band along with the vibrational quantum number occurs rapidly.

We determined the theoretical and observed decrease in integrated intensity of the C=O stretching vibration of acetone and 2-hexanone. It was found that the intensity of the C=O stretching vibration drops by a factor of 50 in going from the fundamental to the first overtone. Almost the same reduction factor was obtained in going from the first to the second overtone. Yet, the intensity of the O–H, C–H, and N–H stretching modes drop only by a factor of about 10–20 and that of the S–H stretching mode decreases by a factor of 30.^{18–20} Thus, compared with the C–H, O–H, and S–H stretching bands, the intensity of the C=O stretching band tends to drop more rapidly. We suppose that the same reduction factor appears in the higher overtone region and hence the intensity of the C=O stretching vibration of acetone and 2-hexanone is weaker than that of the C–H stretching transition. As a consequence, the overtones higher than $\Delta v = 4$ would become hardly detected.

To record the fourth overtone spectra of the C=O stretching mode, we used a cell of 100 mm path length. In spite of this, we could not observe this band. On the other hand, under the same conditions, the fourth overtone of O–H stretching was still perceptible.³¹ On this basis, we infer that a large reduction factor and a low oscillator strength of the C=O stretching vibration are responsible for the weakening of its overtone intensity.

CONCLUSION

Solvent dependence of the wavenumbers and absorption intensities of the C=O stretching vibration in the fundamental and overtone regions for acetone and 2-hexanone in *n*-hexane, CCl₄, and CHCl₃, as well as in the vapor phase, have been explored by IR/NIR spectroscopy and DFT calculations. We observed that the wavenumbers, absorption intensities and oscillator strength of the C=O stretching vibration show significant solvent dependence. Calculated and experimental

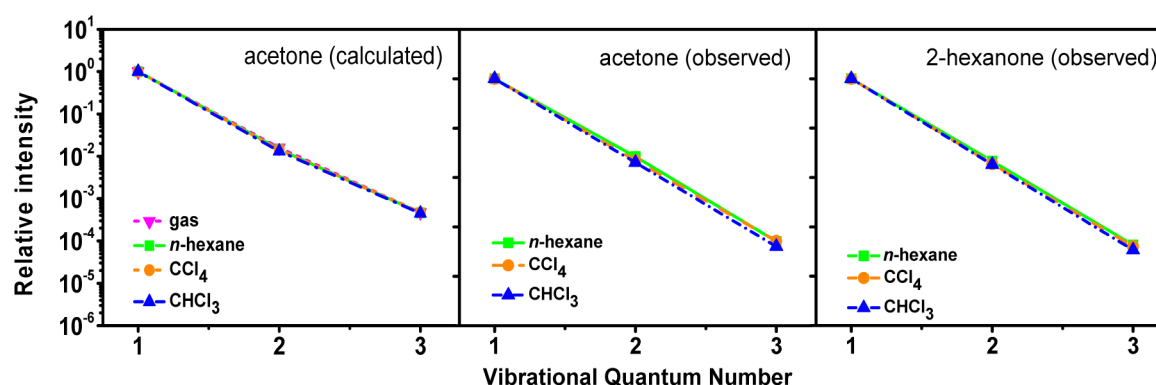


Figure 6. Normalized intensities of the C=O stretching vibration of acetone and 2-hexanone in *n*-hexane, CCl₄, and CHCl₃ versus the vibrational quantum number. The intensities of the C=O stretching vibration at each vibrational quantum number were normalized by the corresponding fundamental intensities.

values of the C=O stretching anharmonicity constant suggest that the C=O stretching mode is significantly more harmonic than the O—H, N—H, and C—H stretching modes. In addition, the theoretical and experimental intensity of the C=O stretching vibration drops by a factor of 50 in going from the fundamental to the first overtone, as well as from the first overtone to the second overtone. This decrease is much faster than that observed for the C—H, O—H, and S—H stretching vibrations. Both the calculated and experimental results suggest that the lower anharmonicity and a fast reduction of the oscillator strength are responsible for the excessive weakness of the overtones of the C=O stretching mode.

■ ASSOCIATED CONTENT

● Supporting Information

The second derivative spectra of acetone and 2-hexanone. The absorption bands and observed wavenumbers of the asymmetric stretching of molecular skeleton and the CCO deformation of acetone. Complete ref 37. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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