

Influence of the Structure of Azole and Aliphatic Alcohol Molecules on the Effectiveness of Van der Waals Interactions with Carbon Tetrachloride

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Annotation

The literature data on the frequencies of *N-H* vibrations of azole molecules and *O-H* vibrations of aliphatic alcohol molecules in the gas phase and in the CCl_4 medium are analyzed. It is shown that the relative spectral shifts β of the considered molecules in a condensed medium can vary by a factor of 3 depending on their structure. The difference in the values of β is explained by the difference in the efficiency of the Van der Waals interactions *VVI* between the CCl_4 molecule and the solute molecule. The effectiveness of the *VVI* is determined by the action of orientation, dispersion and induction forces. The action of these forces affects the structure of the electron shell of the solute molecule. The deformation of the electron shell of this molecule leads to a change in the force constants of the chemical bonds of the molecule and, accordingly, to a shift in the vibrational frequencies of these bonds. The degree of deformation of the electron shell of a solute molecule depends on its polarizability α and the magnitude of the dipole moment d . Thus, the established difference in the values of β is a consequence of the individuality of the values of α and d of the solute molecules. It was found that fluorination of alcohol molecules reduces the effect of *VVI*, which is explained by the increase in the size of alcohol molecules during fluorination.

Keywords: Carbon Tetrachloride; Frequency of NH; OH Vibrations of Azole and Alcohol Molecules, Van Der Waals Interaction



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Introduction

In vibrational spectroscopy of liquid solutions, carbon tetrachloride CCl_4 is widely used in the study of universal and specific interactions as a standard neutral solvent [1,2]. Apparently, the use of the CCl_4 molecule as a neutral solvent is due to the fact that the dipole moment of this molecule is $d_{\text{CCl}_4} = 0$. However, the partial dipole moment of the C-Cl bond dpCCl_4 is 1.87 D [2]. The presence of a dipole moment indicates that there is an electric charge on the chlorine atom of the C-Cl bond. As a result, the CCl_4

molecule, which has side chlorine atoms, creates a local electric field around itself, which, due to the Van der Waals interactions VVI , is able to influence the electronic shell of the solute molecule. The deformation of the electron shell of a molecule can lead to a change in the force constants of the chemical bonds of this molecule and, accordingly, to a shift in the vibrational frequencies of these bonds. VVI is caused by the electrostatic interaction, which has three components: orientation $E_{\text{d-d}}$ (1), induction E_{ind} (2) and dispersion E_{disp} (3) [2].

$$E_{\text{d-d}} = 2d_i^2 d_{\text{CCl}_4}^2 / 3kTr^6 \quad (1),$$

$$E_{\text{ind}} = 2\alpha_i d_{\text{CCl}_4}^2 / r^6 \quad (2),$$

$$E_{\text{disp}} = -3\alpha_i^2 I_i / 4r^6 \quad (3),$$

where d_i , d_{CCl_4} are the dipole moment of the i -th solute molecule, the partial dipole moment of the C-Cl bond in the CCl_4 molecule; k is the Boltzmann constant; T is the absolute temperature; α_i is the polarizability of the solute molecule; r is the distance between the dipoles of different molecules; I is the ionization potential of the i -th molecule. Thus, the change of the frequency of the chemical bond of a molecule of a substance dissolved in CCl_4 may depend on the individual electronic structure of the i -th molecule, and, accordingly, on the magnitude of the polarizability α_i and the intrinsic dipole moment d_i . The mechanism of shifts in vibrational frequencies as a result of the explosive force of a solute molecule with a dipole moment of a solvent molecule was discussed in detail earlier in [1-4].

Despite the long history of work on the spectroscopy of intermolecular interactions, in which CCl_4 was widely used as a neutral solvent, there is no quantitative systematic information on the effect of the CCl_4 medium itself on the change in the vibrational frequencies of solute molecules relative to the vibrational frequencies of molecules in the gas phase. A priori, it can be assumed that since solute molecules have individual electronic structures,

the magnitudes of changes in shift frequencies that are directly related to the structure in the CCl_4 medium will differ for different molecules.

The purpose of this report was to compare the previously obtained frequencies of valence N-H vibrations of azole molecules and O-H vibrations of aliphatic alcohols in the CCl_4 medium and the frequencies of vibrations of these molecules in the gas phase (IR spectra). The choice of the azole and alcohol molecules considered was due to the availability of data on the frequencies of N-H and O-H vibrations of these molecules in the CCl_4 medium and in the gas, since we did not have such information for other compounds. The study of the effect of VVI on the vibrational spectra of molecules of selected classes is of interest, since alcohols are widely used in organic chemistry as reagents and solvents [5], and molecules of the azole class are currently one of the most sought-after compounds in the synthesis of pharmaceutical products [6].

The effect of changes in the frequencies of N-H and O-H vibrations in the CCl_4 medium relative to the gas phase was studied in relative units. The value β_i , determined by (4), was taken as the value of the relative frequency shift of these vibrations.

$$\beta_i = (v_{\text{gas},i} - v_{\text{CCl}_4,i}) / v_{\text{gas},i} \quad (4).$$

In (4) $\nu_{\text{gas},i}$, $\nu_{\text{CCl}_4,i}$ frequency *N-H*, *O-H* vibrations of the *i*-th molecule azole or alcohol in the gas and in CCl_4 . Thus, the value β_i was a descriptor of the effectiveness of the VVI effect on the frequencies of N-H and O-H vibrations in

molecules of azoles and alcohols.

Results and Discussion

Table 1: Values of frequencies of N-H and O-H vibrations of molecules of azoles and alcohols in gas $\nu_{\text{gas},i}$ in CCl_4 $\nu_{\text{CCl}_4,i}$ and relative shifts of these frequencies β_i ;

i	Molecule	$\nu_{\text{gas},i}$	$\nu_{\text{CCl}_4,i}$	β_i
1	carbazole	3500 ^[8]	3483 ^[7]	0.00486
2	pyrrole	3530.8 ^[9]	3497 ^[7]	0.00957
3	imidazole	3514.3 ^[10,11]	3478 ^[7]	0.00883
4	indole	3526 ^[7]	3491 ^[7]	0.0099
5	benzimidazole	3509 ^[12]	3478 ^[7]	0.00883
6	benztriazole	3511 ^[13]	3462 ^[7]	0.01396
7	isatin	3500 ^[14]	3444 ^[7]	0.016
8	butanol	3646 ^[15]	3619 ^[15]	0.00741
9	ethanol	3675 ^[15]	3634 ^[15]	0.01116
10	methanol	3688 ^[15]	3644 ^[15]	0.01193
11	propanol	3683 ^[15]	3624 ^[15]	0.016
12	2,2,3,3-tetrafluoropropanol	3658 ^[15]	3622 ^[15]	0.00984
13	2,2,2-trifluoroethanol	3659 ^[15]	3622 ^[15]	0.01011

Table 1 shows the frequencies of *N-H* vibrations of azole and alcohol molecules in the gas $\nu_{\text{gas},i}$ in CCl_4 $\nu_{\text{CCl}_4,i}$ and the relative shifts of the frequencies of *N-H* and *O-H* vibrations of the *i*-th molecule in CCl_4 β_i . As can be seen from the above data, each *i*-th molecule of azole or alcohol has an individual value of β_i . The difference in values of β_i is more than 3 times. The difference in the values of β_i confirms the position that the effectiveness of the van der Waals interaction of the CCl_4 molecule with the electronic structure of azole and alcohol molecules individually affects the frequency of *N-H* and *O-H* vibrations of these molecules.

From the data in the Tab.1 it follows that fluorination of alcohols leads to a decrease in the effectiveness of VVI: $\beta_{13} < \beta_9 < \beta_{12} < \beta_{11}$. During fluorination, a hydrogen atom (radius 0.116 nm) is replaced by a fluorine atom (radius 0.14 nm) [16]. As a result, the Onsager distance H...Cl 0.297 nm becomes 0.326 nm for the distance F...Cl [16]. According to

(1) - (3), an increase in the value of *r* should lead to a decrease in the value of VVI, which is observed in the experiment. Thus, the decrease in the values of β_i during fluorination can be explained by an increase in the intermolecular distance between the dipoles of solute molecules and the partial dipole moment of the C-Cl bond of the CCl_4 molecule.

The results obtained on the difference in the relative shift frequencies of the solute molecules in CCl_4 relative to the gas mean that correlations such as "spectral parameters of a molecule in a CCl_4 medium – enthalpy of H-bond formation" [17-19] are not entirely correct. The approach is not correct, which is based on the fact that the data of the spectral frequency shift of the A-H vibration of the proton donor molecule in the H complex A-H...B relative to the frequency in CCl_4 are compared with the total value of the enthalpy of formation of the H bond obtained thermochemi-

cally. In this approach, part of the shift due to the VVI, which also determines the total frequency shift of the A-H vibration of the proton donor molecule in the H-complex, is ignored. The correlation "Spectral parameters of a molecule in a gas – enthalpy of H-bond formation" should be considered more correct.

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