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ARTICLE *in* CHEMICAL PHYSICS · JUNE 2014

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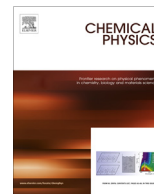


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On the unusual IR spectra of the acetic acid–trimethylamine complex in low temperature matrices



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ARTICLE INFO

Article history:

Received 20 January 2014

In final form 21 March 2014

Available online 1 April 2014

Keywords:

Hydrogen bond

Strong anharmonic coupling

Infrared spectra

B3LYP

ABSTRACT

Usually the stretching vibration of the A–H group in hydrogen-bonded complexes gives an intense, broad absorption in the IR spectrum. However in a few complexes it has proved difficult to detect this absorption in low temperature matrices. In this work the Ratajczak–Yaremko vibrational model of the hydrogen bond has been applied to simulate the IR spectrum obtained for one such complex: the acetic acid–trimethylamine, ACA–TMA, hydrogen bonded complex isolated in an argon matrix.

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1. Introduction

IR spectra of hydrogen-bonded complexes isolated in low temperature matrices were widely studied in different laboratories e.g. by Pimentel [1,2], Barnes [3,4], Mielke and Ratajczak [5,6], Perchard [7], Person and Szczepaniak [8], Andrews [9] and others. Analysis of IR spectra based on the Pimentel vibrational correlation diagram [2] strongly suggests that in the studied complexes the proton is “completely” or “partly” shared between two heavy sub-units, A···B. The degree of proton transfer continuously increases on moving to the stronger acid or to the stronger base. The potential energy curve of the hydrogen bond may be described by a single minimum. The position of the energy minimum depends systematically upon the difference between the proton affinities of the base (B) and the conjugate base (A[−]). More advanced quantum chemical calculations carried out for those systems are in general agreement with conclusions concerning the mechanism of proton transfer drawn from IR spectra [9–11]. Similar situations appear in the gas phase for the amine–hydrogen halide complexes, which were extensively studied by Legon et al. [12] and others [13].

However in a few hydrogen-bonded complexes (trimethylamine–acetic acid [5], trimethylamine–phenols [6], pyridine–hydrogen bromide [8], ammonia–nitric acid [14]) it was difficult to detect their IR spectra in the stretching vibration region of the A–H group in low temperature matrices. One rather observes a

very weak and very broad absorption in the range of ~ 3500 – 400 cm^{-1} . Or perhaps is better to say that one observes a little increased background of the spectrum.

The purpose of this work is to apply the Ratajczak–Yaremko vibrational model of the hydrogen bond [15] to simulate the IR spectrum obtained for the acetic acid–trimethylamine, ACA–TMA, hydrogen bonded complex isolated in an argon matrix [5].

2. Computational details

All calculations were performed with the Gaussian 09 program package [16]. The B3LYP level of theory [17] with the 6-311++G(2d,2p) basis set was used to optimize the structures of the trimethylamine (TMA) and acetic acid (ACA) monomers and the ACA–TMA complex. The obtained interaction energy of the complexes was corrected for basis set superposition error by the Boys–Bernardi full counterpoise method [18] as implemented in Gaussian 09. The B3LYP/6-311++G(2d,2p) harmonic vibrational frequencies and intensities were calculated at the optimized geometries both for the monomers and for the complex. The vibrational spectra were simulated using SYNSPEC program [19].

3. Results and discussion

3.1. Quantum chemical calculations of the vibrational spectra of TMA, ACA and the ACA–TMA complex

The B3LYP/6-311++G(2d,2p) optimized structure of the 1:1 complex formed between acetic acid and trimethylamine

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(ACA–TMA) is presented in Fig. 1 while selected geometric parameters are listed in Table 1. The ACA–TMA complex possesses C_s symmetry with the acid molecule coplanar with one of the N–C bonds of the amine subunit. The structure involves an O–H...N type of interaction with ACA acting as a proton donor to the N-atom of the TMA molecule. According to the performed calculations the hydrogen bond formed is relatively strong with an O...N distance of 2.729 Å and it is close to linearity with the O–H...N angle equal to 178.3°.

The harmonic frequency calculations predict a large perturbation of the OH stretching vibration of ACA upon complex formation ($\Delta\nu = 944 \text{ cm}^{-1}$) and a huge increase of the intensity of this mode (from 63 to 2593 km mol^{-1}). The calculated spectra of the ACA and TMA monomers and ACA–TMA complex are presented in Fig. 2.

3.2. Application of the Ratajczak–Yaremko model

The theory of profiles of hydrogen stretching infrared bands of hydrogen-bonded systems developed by Ratajczak and Yaremko took into account a strong anharmonic coupling between the high-frequency hydrogen stretching vibration $\nu(\text{A–H})$ and low-frequency phonons and the Fermi resonance interaction between a fundamental vibration of $\nu(\text{A–H})$ and an overtone or a combination tone of intramolecular vibrations. The theory was developed [15] in the framework of the extended Davydov molecular exciton approach [20,21].

So far this model was successful applied to different hydrogen-bonded solids, e.g. NaHF_2 , HCrO_2 , HCoO_2 and their deuterated species [15,22]. In the present paper for the first time this model has been applied to a molecular hydrogen-bonded complex trapped in a low temperature matrix.

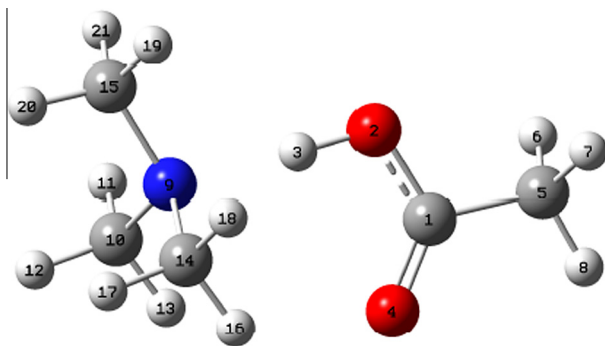


Fig. 1. B3LYP/6-311++G(2d,2p) optimized structure of the ACA–TMA complex.

Table 1
Selected bond lengths (Å), angles (°) and torsion angles (°) of the ACA–TMA complex calculated at the B3LYP/6-311++G(2d,2p) level.

Parameter	ACA–TMA	Parameter	ACA–TMA
<i>Bond lengths</i>		<i>Bond angles</i>	
C1–O2	1.334	C1–O2–H3	109.8
C1–O4	1.214	O2–C1–O4	123.6
O2–H3	1.015	O2–C1–C5	112.4
C1–C5	1.508	O4–C1–C5	124.0
C5–H6	1.090	C10–N9–C14	110.8
N9–C10	1.466	C14–N9–C15	111.4
C10–H11	1.089	<i>Torsion angles</i>	
		H3–O2–C1–O4	0.0
		H3–O2–C1–C5	180.0
<i>Hydrogen bond</i>			
O2...N9	2.729		
H3–N9	1.714		
O2–H3–N9	178.3		

3.3. Brief theory of the shape of the $\nu(\text{O–H})$ band

The intensity of light absorption in crystals with strong coupling between high frequency excitations and lattice phonons was considered in detail in works [15,22]. It was shown that the spectral dependence of intensity can be expressed by the Fourier-component of the retarded Green function. In hydrogen-bonded crystals, where the high frequency excitation is the $\nu(\text{O–H})$ vibration, two important factors arise: (i) the possibility of Fermi resonance between the O–H stretching and bending vibrations, (ii) strong interaction between the (high) $\nu(\text{O–H})$ vibration and low frequency vibrations of the lattice. For complexes with a strong enough H-bond we have a similar situation because, due to the low symmetry of the complex, we have to take into consideration the possibility of the Fermi resonance effect and coupling with the low frequency vibrations of the complex itself. Large distances between complexes and correspondingly very weak interaction between them reduce lattice phonons to low frequency intramolecular vibrations of the complex. Therefore we use the relations obtained in [15] as a qualitative approach to understand the spectral features observed for the studied ACA–TMA system.

Taking into account both the Fermi resonance between the fundamental and combination tone, and the interaction of these vibrations with the low frequency ones, the corresponding spectral profiles were described in [15] and expressed by the following relation:

$$I(\omega) \approx \text{Im} \left[-\sum_{\nu, \mu} d_{n\nu} d_{n\mu}^* G_n^{\nu\mu}(\omega) \right], \quad (1)$$

where

$$d_{n\nu} = \sum_f d_n^f \alpha_{n\nu}^f, d_n^f = \mu_f d_n^0, \quad (f = 1, 2), \quad \mu_f = [(\delta \pm \delta_0)/2\delta]^{\frac{1}{2}} \quad (2)$$

Index f marks the components of the Fermi doublet; values, μ_f and $\alpha_{n\nu}^f$ depend on the conditions of Fermi resonance (FR) and $\alpha_{n\nu}^f$ are expressed by values $D_n^f(0) = \mu_f \mu_g D_0$ [15]; d_n^0 is the dipole moment transition of the fundamental vibration participating in FR; $\delta_0 = \omega_f - 2\omega_2$, $\delta = (\delta_0^2 + 4\Gamma^2)^{\frac{1}{2}}$; ω_f is a fundamental mode frequency, $2\omega_2$ is an overtone frequency and Γ is the anharmonic constant responsible for the Fermi resonance interaction; $G_n^{\nu\mu}(\omega) = \delta_{\nu\mu} G_n^{\nu}(\omega)$ are the Fourier components of retarded Green function;

$$G_n^{\nu\nu}(\omega) = G_n^{\nu}(\omega) = -i \int_0^{\infty} dt \exp[i(\omega - \varepsilon_{n\nu} + i\gamma_{\nu}) + g_{n\nu}(t)] \quad (3)$$

G_n^{ν} is a Fourier component of the correlation function depending only on parameters of low frequency vibrations of the molecular complex and because all complexes are identical the index “ n ” in Eq. (3) can be omitted. The last parameters are the following: positive value γ_{ν} characterizes a natural damping of $\varepsilon_{n\nu}$ level of n th molecular complex; it is clear that interaction of the complex with the matrix will give rise to significant increase of the damping constant γ_{ν} in comparison with the crystal value; the function $g_{n\nu}(t)$ has a complicated dependence on the low frequencies Ω_s of the studied complex as well as on the coupling constants, χ_{qs}^{ν} , between the H-bond and low frequency vibrations and looks as follows (s is the number the low frequencies)

$$g_{n\nu}(t) = g_{\nu}(t) = \sum_s |\chi_{qs}^{\nu}|^2 \Omega_s^{-2} \{ [n_s + 1] \exp(-i\Omega_s t) + n_s \exp(i\Omega_s t) - [2n_s + 1] \}, \quad (4)$$

n_s is the filling number of the vibration with frequency Ω_s .

Eqs. (3) and (4) describe the features of the spectral dependence of light absorption at FR and strong interaction of the H-bond with the intramolecular vibrations which are numbered by indexes s .

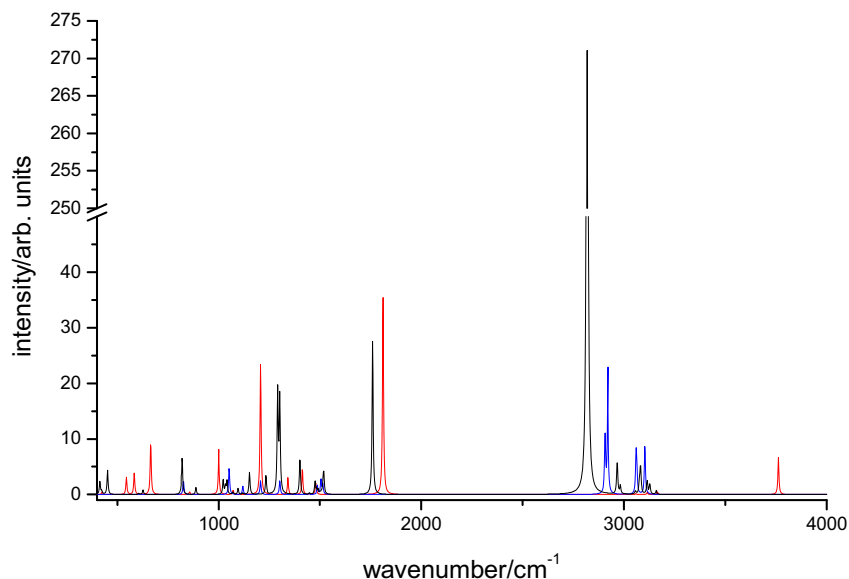


Fig. 2. B3LYP/6-311++G(2d,2p) simulated spectra of ACA (red trace), TMA (blue trace) and ACA–TMA complex (black trace). The theoretical spectra were created using Lorentzian functions centered at the calculated harmonic frequencies with the bandwidth at half-height equal to 6 cm^{-1} . Note the break in the intensity axis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

It should be noted that Eqs. (3) and (4) in work [15] were obtained for the crystal and the low frequencies are phonons which are characterized by two indexes $\Omega_{s,q}$, where q is the wave vector and s is the number of a phonon branch having some dispersion. But if the space between molecules (molecular complexes) becomes great the dispersion of the phonon branch significantly decreases and the phonon frequencies $\Omega_{s,q}$ reduces simply to those of intramolecular vibrations, $\Omega_{s,q} \rightarrow \Omega_s$.

Therefore for numerical analysis we use Eqs. (1)–(4) where the dependence on the wave vector q is neglected for both the lattice phonon frequencies by supposing $\Omega_{s,q} = \Omega_s$ and the coupling constants $\chi_{sq}^{nv} = \chi_s^v$. These equations show that the spectrum has a quite complicated dependence on the noted parameters and frequency.

By using the expressions (1)–(4) it is possible to calculate the absorption intensity, $I(\omega)$, as a function of the Fermi resonance coupling, Γ , the high frequency, $\nu(\text{XH})$, coupling with the low frequency phonons, χ_s^v , the lattice frequencies, Ω_s , damping constant, γ_v , and the temperature, T .

3.4. Model calculations

Variation of the absorption spectrum connected with the H-bond vibration as a function of the coupling constant χ_s^v is presented by several theoretical dependences in Fig. 3.

Fig. 3 shows that effect of strong interaction of the $\nu(\text{O-H})$ hydrogen bonded vibration with low frequency ones and the large damping constant γ^v principally change the character of spectrum of the $\nu(\text{O-H})$ band. It allows one to obtain a theoretical spectrum similar to the experimental one by proper use of the parameters of the theory. In Fig. 3 the simulation of spectra was made by using the parameters obtained from numerical calculations in which (in arbitrary units) $\delta_0 = -0.5$, $\Omega_1 = 2.1$, $\Gamma = 0.01$, $\gamma = 0.3$. If $\chi_1^v \approx 0$ we observe a very strong narrow band, curve 1, but with increasing coupling constant χ_1^v the number of components grows, all bands of the spectrum are shifted to low frequency and there is a redistribution of intensities between components, curves 2–4. If the damping constant becomes great enough, $\gamma = 0.8$, the curve 4 is transformed into very smooth curve 5 which, as it will be shown below, is similar to the experimental one in the region of the

$\nu(\text{O-H})$ vibration. More detailed fitting to experiments showed also that the calculated high frequencies, because of anharmonicity in potential energy, are somewhat overestimated and that FR effect in some cases is rather weak.

3.5. Results obtained for the ACA–TMA complex

According to the performed B3LYP calculations the intensities of the bands of both components (ACA, TMA) are relatively small (see Fig. 2 and Table S1 in Supporting Information) but the intensity of the stretching $\nu(\text{O-H})$ absorption in the ACA–TMA complex is predicted to be very large (2593 km mol^{-1}). In the experimental spectrum, however (Fig. 4) such a feature is not observed. We suppose therefore that there is such a transformation of the spectrum as was considered in the model simulation in Fig. 3.

The calculated IR spectrum of the acetic acid–trimethylamine complex in an argon matrix is presented in Fig. 4 and compared with the experimental one [5]. The general features observed in the experimental dependence in the region $1500\text{--}2500\text{ cm}^{-1}$ for the $\nu(\text{O-H})$ mode are in good correlation with the theoretical curve (two intense bands observed at ca. 1750 cm^{-1} are due to the C=O group stretching). The parameters obtained from the fit are given in Table 2. Two low frequency vibrations were chosen for the fitting procedure, namely $\Omega_1 = 169\text{ cm}^{-1}$ and $\Omega_2 = 121\text{ cm}^{-1}$. These vibrations are, according to the B3LYP calculations, characterized by the greatest contribution of the H-atom movement in the hydrogen bond bridge. For the $\nu(\text{O-H})$ stretching vibration of the complex the calculated value of 2818 cm^{-1} was used.

According to the quantum chemical calculations the change of energy due to the complex formation between acetic acid with trimethylamine is $-9.96\text{ kcal mol}^{-1}$ (corrected for basis set superposition error) or $-8.73\text{ kcal mol}^{-1}$ (corrected also for zero-point vibrational energy), the red shift of the $\nu(\text{O-H})$ band is equal to 944 cm^{-1} and the bond distance is 2.729 \AA . The calculations have shown that we are dealing with a relatively strongly hydrogen-bonded system of the $\text{O-H}\cdots\text{N}$ type.

As one can see from the Fig. 4 we can reproduce the experimental spectrum of the studied complex by the parameters close to those obtained from the model calculations shown in Fig. 3, curve 5. It means that two parameters play an important role in the

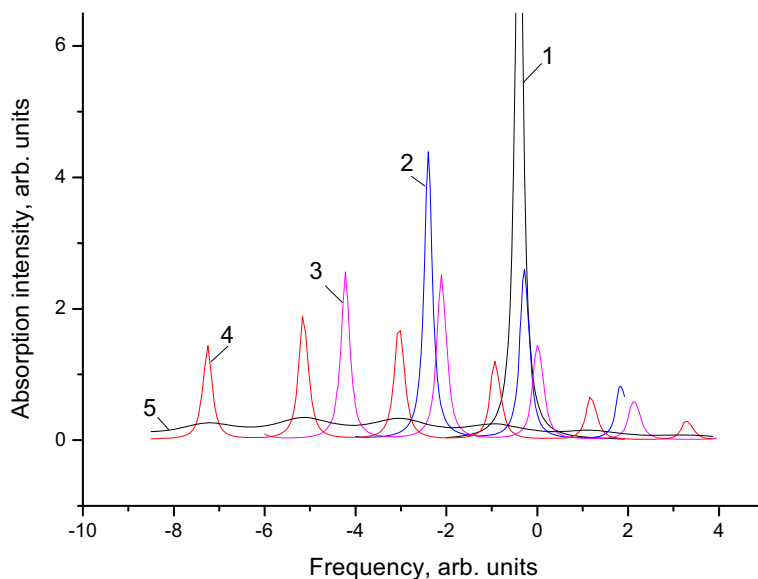


Fig. 3. Evaluation of absorption spectrum of $\nu(\text{O-H})$ hydrogen-bonded vibration with increasing of coupling constant χ_v^v , ($s = 1$, $\Omega = 2.1$, $\gamma^v = 0.3$): curve 1, $\chi_1^v = 0.01$; curve 2, $\chi_1^v = 2.5$; curve 3, $\chi_1^v = 3.5$; curve 4, $\chi_1^v = 5$; curve 5, $\chi_1^v = 5$, $\gamma^v = 0.8$; in theoretical analysis it is convenient to use arbitrary values: $\varepsilon = (\omega - 2\omega_2)/M_0$, (at $\omega = 2\omega_2$, $\varepsilon = 0$), $\chi_1^v \rightarrow \chi_1^v/M_0$, $\Omega_1 \rightarrow \Omega_1/M_0$, $M_0 = 100 \text{ cm}^{-1}$. For comparison with experiment one can obtain the traditional frequency ω according to the relation given above for ε .

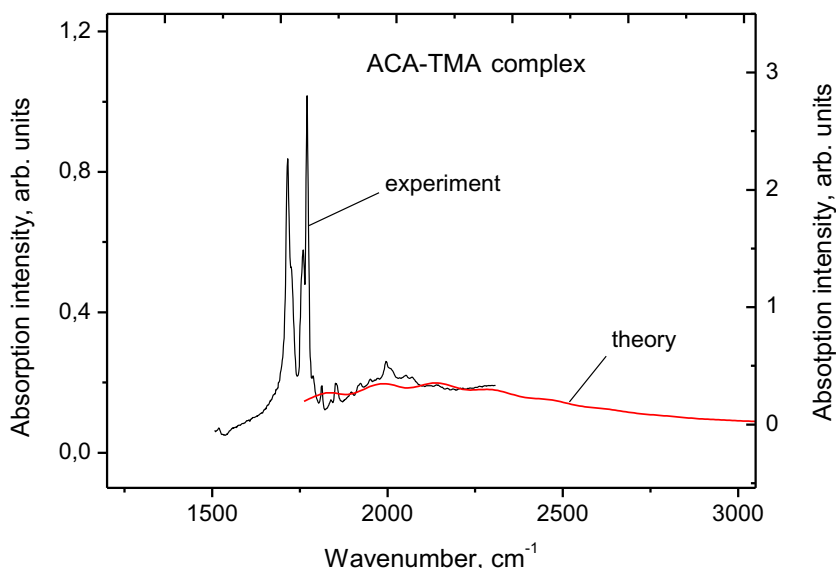


Fig. 4. Comparison between the theoretical and experimental IR spectrum of the ACA-TMA complex in the range of 1500–2500 cm^{-1} . Note that the $\nu(\text{O-H})$ absorption in the experimental spectrum is partly overlapped with $\nu(\text{C=O})$ bands while the theoretical one is limited to the $\nu(\text{O-H})$ contribution.

Table 2

Parameters obtained from fit of theoretical spectrum to experimental in Fig. 4 using B3LYP calculated frequencies. All energetic parameters are expressed in relative units, i.e. $\chi_1^v \rightarrow \chi_1^v/M_0$, $\Omega_1 \rightarrow \Omega_1/M_0$, $M_0 = 100 \text{ cm}^{-1}$.

Parameter	Ω_1	Ω_2	χ_1	χ_2	γ
$\nu(\text{OH})$	1.69	1.21	6	2.5	0.6

reproduction of the spectrum: coupling constants between high and low frequencies of the hydrogen bond and damping constant.

Acknowledgement

A grant of computer time from the Wrocław Center for Networking and Supercomputing is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemphys.2014.03.009>.

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