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Adsorption and Polymerization of Aniline on Cu(II)-Montmorillonite: Vibrational Spectroscopy and ab Initio Calculation[†]

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Batch adsorption experiments in the presence of oxygen were performed to study the interlayer reactions of aniline on Cu(II)-montmorillonite in aqueous solutions. At concentrations below a critical value of C_C = 2.6 mmol dm^{-3} only a colored Cu(II)–aniline complex is formed, characterized by a stability constant of $\log(K_{assoc}/dm^3\ mol^{-1})$ = 1.5. At concentrations beyond C_c aniline polymerizes yielding a dark brown product, which is identified by two vibrational spectroscopy techniques, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and FT-Raman spectroscopy. Vibrational assignment of aniline, polyaniline, and the interlayer reaction products of aniline at Cu(II)-montmorillonite was achieved by a comparison of the band position and intensity observed in the ATR and FT-Raman spectra with wavenumbers and intensities (IR and Raman) from ab initio quantum-mechanical calculations. Density functional theory (DFT, B3LYP/6-31G*) has been used to calculate the geometry, frequencies, and intensities (IR and Raman) of aniline. The geometry and vibrational calculations of a four-ring unit (emeraldine base, EB) are believed to be a good representation of the polyaniline at Cu(II)-montmorillonite. The geometry of EB was fully optimized at the Hartree–Fock level of theory. The data of polyaniline presented suggest that IR and Raman data calculated ab initio on relatively short oligomers (quantum-mechanical oligomer approach) may provide valuable information regarding the interpretation of vibrational spectra of polymers. From the comparison of experiments and calculations, it is concluded that a catalytic/intercalation polymerization of aniline to polyaniline took place inside the interlayer of the Cu(II)-montmorillonite clay mineral.

Introduction

Montmorillonites belong to the group of layer silicates. Their reactivity is mainly controlled by their large internal specific surface, the mean specific charge, and the nature of the interlayer-exchangeable cations.[1–4] Numerous publications have investigated the interaction of aniline and Cu(II) ions [5–11] proving the existence of labile weak complexes in aqueous solution. On the other hand, the interaction of aniline with montmorillonites at the gas–solid interface and in nonaqueous solutions is the subject of several publications. The group of Yariv and Heller[12–14] found that aniline may form complexes with transition metal ions in the montmorillonite interlayer by coordination of the free electron pair of the amino group to the metal ions. Moreale et al.[15,16] have investigated the adsorption at Cu(II)-montmorillonite in diluted aqueous suspension with the result that aniline forms a coordination complex beyond a defined concentration. Employing electron spin resonance (ESR) and thin dry film IR spectroscopy with empirical vibrational band assignment, they assume that at higher concentrations aniline is oxidized with Cu(II) ions as the catalyzer and is finally radically polymerized. However, the question remained open whether the nature of the product was affected by the drying procedure necessary for their IR experiments. Therefore, in this work we employ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and Raman spectroscopy, which allow vibrational spectra in aqueous suspension to be measured, and the nature of the product will not be affected by drying.

To identify interlayer reactions, techniques that appear to be promising for answering some basic questions regarding organic chemicals adsorption on clay minerals are attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy and near-infrared Fourier transform Raman spectroscopy (NIR-FT-Raman). For utilizing ATR-FTIR and NIR-FT-Raman spectra to study the polymerization of aniline by using Cu(II)-montmorillonite, we need precise assignments of vibrational wavenumbers. This is achieved by a comparison of the band positions and intensities observed in IR and Raman spectra with wavenumbers and intensities from quantum-chemical ab initio calculations of aniline and polyaniline.

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Therefore, in this work, we report on the adsorption of aniline on colloidal Cu(II)-montmorillonite in aqueous suspension. Adsorption isotherms, ATR-FTIR and NIR-FT-Raman spectroscopic measurements of aniline are presented, and the characteristic vibrational signals are interpreted by theoretical ab initio quantum-chemical calculations.

Experimental Part

Materials. Cu(II)-montmorillonite was prepared from Ca-bentonite (Süd Chemie AG, Germany) by separating the fraction <2 μm,[17] subsequent ion exchange with 1 N Cu(NO$_3$)$_2$ solution, and final dialysis to remove the excess salt. The product was centrifuged, lyophilized, and ground. The exchange efficiency is >95%, the cation exchange capacity is 0.91 mmol g^{-1}, and the pH of a 40 g dm^{-3} aqueous stock suspension is 5.5. Aniline was purchased as p.a. grade from Merck AG, Germany; the purity and a possible contamination by polymerization products were checked by UV spectroscopy.

Adsorption Experiments. For the determination of the adsorbed amount of aniline at Cu-montmorillonite, increasing amounts were added to a suspension of 13 g dm^{-3} and equilibrated for 24 h. Afterward, the suspension was centrifuged and the supernatant was analyzed spectroscopically using the absorption band of aniline at 280 nm. The adsorbed amount is calculated by

$$[aniline]_{sorbed} = ([aniline]_{total} - [aniline]_{sol})V/m \quad (1)$$

where V is the volume of the solution and m the content of Cu-montmorillonite.

ATR-FTIR Spectroscopy. Spectra were recorded interferometrically with a Brucker Equinox-55 spectrometer equipped with a DLATGS detector. Single-beam IR spectra were the result of about 1000 co-added interferograms and ranged from 400 to 2000 cm^{-1} with a spectral resolution of 0.5 cm^{-1}. A ZnSe ATR optical accessory set at 45° was used as a reflectance medium.

NIR-FT-Raman Spectroscopy. The instrument used was a Bruker FT-Raman system RFS 100 and a cooled Ge diode detector. A Nd:YAG laser was used as the excitation source (λ_{ex} = 1064 nm; 250 mW of power at the sample) in the backscattering configuration. All spectra were recorded at 4 cm^{-1} resolution.

Calculation Details. All calculations are performed with the Gaussian 98 suite of programs[18] on a Cray supercomputer (T90 or J90). Density functional theory (DFT) using the 6-31g* basis set and the three-parameter compound function of Becke (B3LYP) is used to calculate the geometry, frequencies, and intensities (IR and Raman) of aniline. The geometry and vibrational calculations of a four-ring unit (emeraldine base, EB, see below) are believed to be a good representation of polyaniline. The geometry of EB is fully optimized without imposing external symmetry constraints using the 6-31g* basis set at the Hartree–Fock level of theory. In the notation HF/6-31g* HF symbolizes the Hartree–Fock approximation and each atomic orbital is described by six Gaussian functions with the valence orbital split into sets of three and one Gaussian.

The geometry is optimized until the individual gradients were less than 10^{-4} hartree bohr^{-1} and the root-mean-square force was less than 10^{-5} hartree bohr^{-1}.

The configuration interaction singles (CSI) method was used to calculate the electronic states in order to interpret the UV–vis spectra.

A force constant calculation was then performed to obtain the vibrational frequencies and the corresponding infrared intensities. Since normally the errors within this type of calculation (including a significant part of anharmonicity correction) are
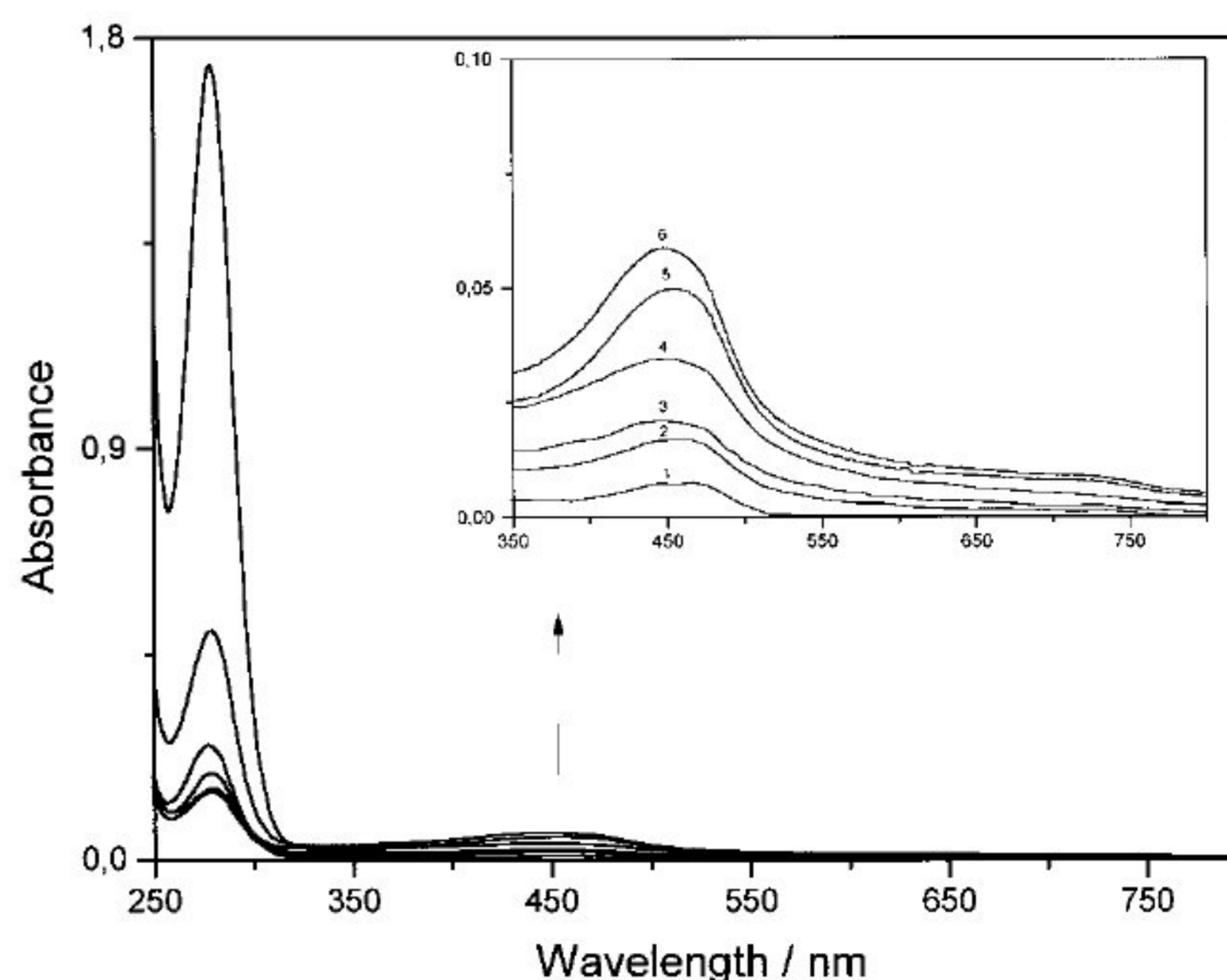
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Figure 1. UV–VIS absorption spectra of the supernatants of centrifuged suspensions of Cu(II)-montmorillonite (13 g dm^{-3}, pH = 6.0) in the presence of increasing concentrations of aniline: (1) 4; (2) 5.3; (3) 6.6; (4) 13; (5) 26; (6) 40 mmol/dm^3.
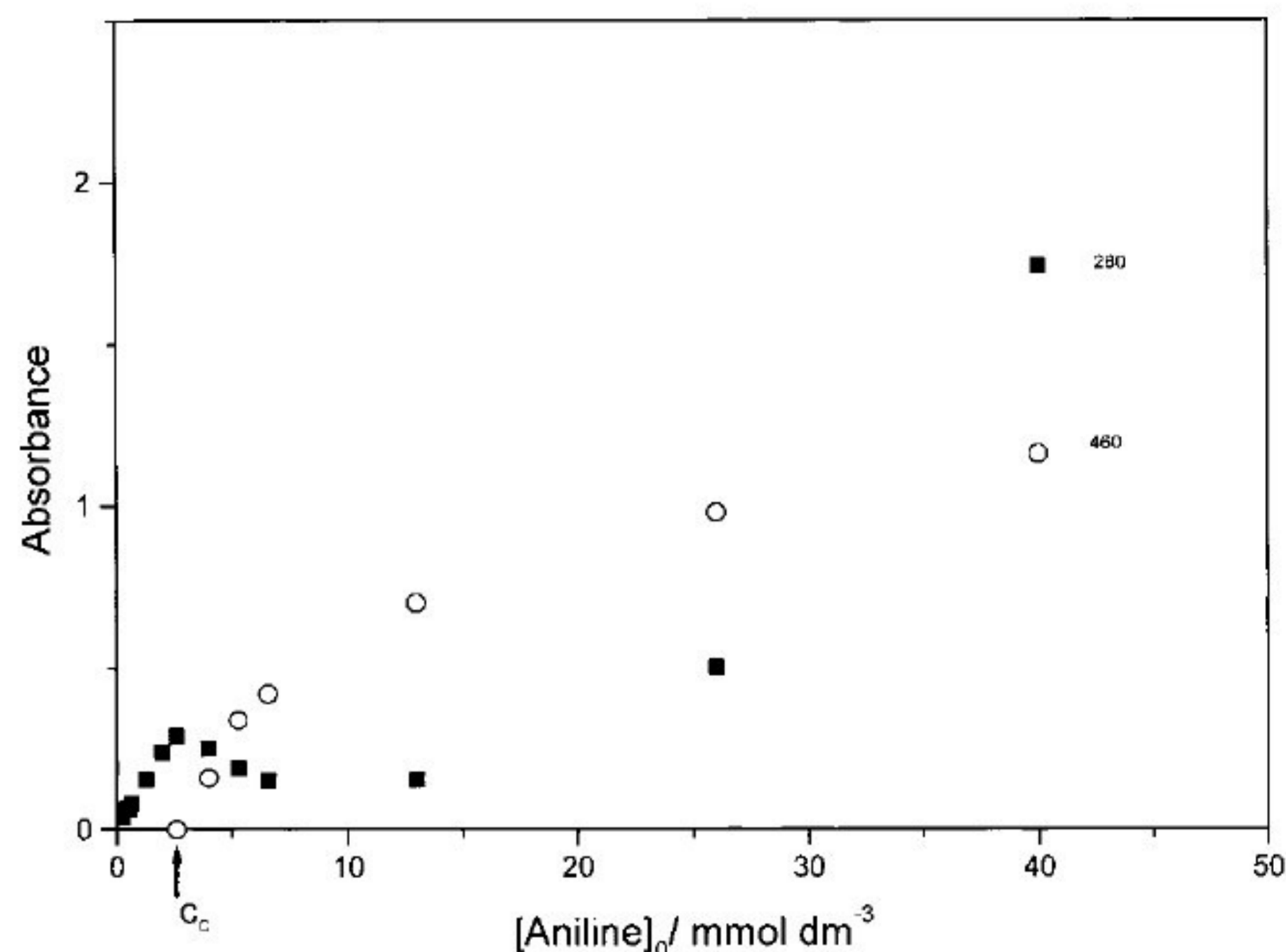

Figure 2. UV–VIS absorption at 280 nm (■) and at 460 nm (○ ×20) of aniline in the supernatants of centrifuged suspensions of Cu(II)-montmorillonite (13 g dm^{-3}, pH = 6.0) at different concentrations of aniline.

systematic, it is common practice to use empirical correction factors. In this study a unique scale factor of 0.89 was employed for the final frequencies.

Results and Discussion

Adsorption Measurements. In Figure 1 the UV spectra of the supernatant of the Cu(II)-montmorillonite/aniline system are plotted showing two characteristic bands at 280 and 460 nm. The band at 280 nm is characteristic of free aniline and is used for the photometric determination of its concentration. Beyond a certain total aniline concentration of 2.6 mmol dm^{-3} the occurrence of a second broad band at 460 nm is observed which may be associated to polyaniline according to Toshima et al.[19] In Figure 2 the absorbances at 280 and 460 nm are presented as a function of the total concentration of aniline. The polyaniline band occurs beyond a critical concentration of 2.6 mmol dm^{-3}, accompanied by a sharp decrease of the band of free aniline. One may qualitatively conclude that above this concentration aniline polymerizes, induced by the Cu-montmorillonite.

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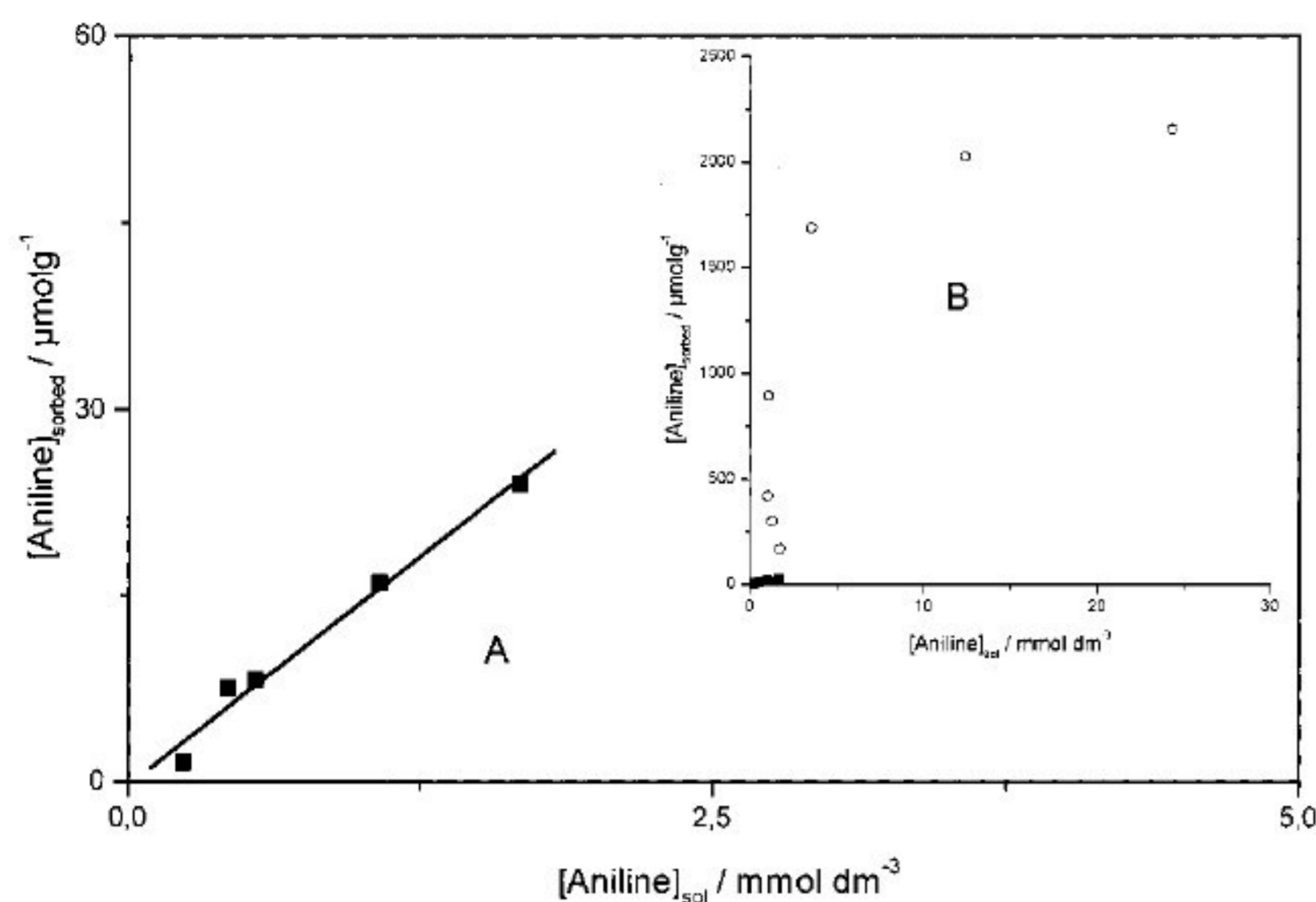
Figure 3. Adsorbed amount of aniline and polymerization products at Cu(II)-montmorillonite, calculated according eq 1: A, at low concentrations; B, for all concentrations.
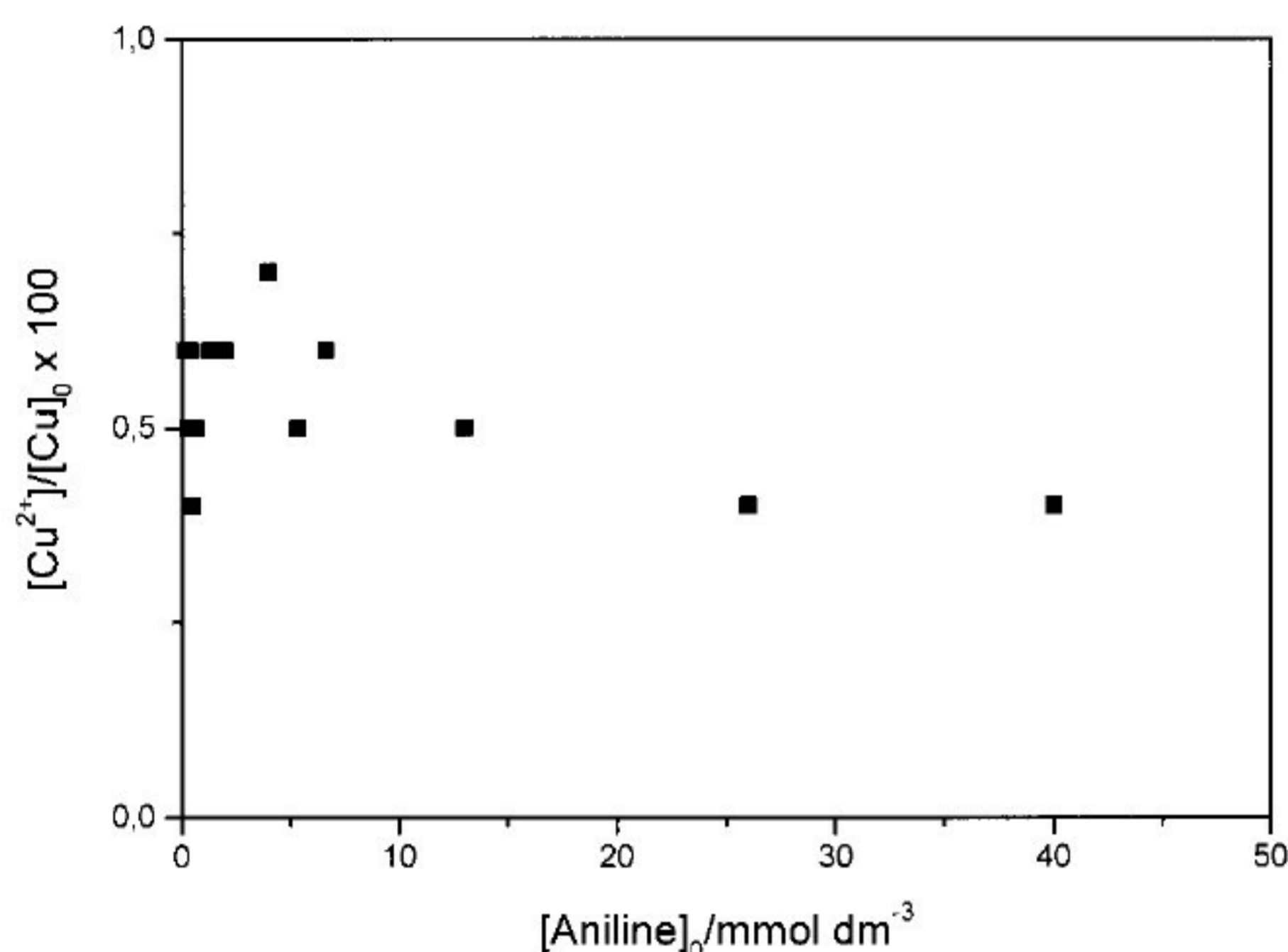

Figure 4. Ratio between Cu^{2+} ions in the supernatant and total Cu^{2+} content of the system Cu(II)-montmorillonite/aniline as a function of the initial aniline concentration.

This conclusion is supported by the observation of the occurrence of a dark brown color of the centrifugate, characteristic of polyaniline and by the spectroscopic data and calculations as shown below. At concentrations lower than 2.6 mmol dm^{-3} the suspension is slightly green, indicating the formation of a charge-transfer complex[5,6,9,10] between Cu(II) and aniline. This concentration is termed in the following the critical polymerization concentration, C_c. According to this observation the adsorbed amount is calculated first for total aniline concentrations lower than C_c and presented as a function of the free aniline concentration in Figure 3A. Figure 3B will be discussed below. Figure 4 shows that the amount of released Cu^{2+} ions as a function of the total aniline concentration is negligibly small; nearly all Cu^{2+} ions remain in the montmorillonite interlayer. This allows a calculation of the association constant of the [Cu-aniline]$^{2+}$ complex in the interlayer defined by

$$K_{assoc} = [\text{Cu-montm}-\text{aniline}]^{2+}/[\text{Cu}^{2+}{}_{montm.}][\text{aniline}] \tag{2}$$

The formation of complexes higher than the 1:1 complex is rather impossible due to the great surplus of copper ions in the montmorillonite interlayer. The isotherm in Figure 3A is nearly linear and $K_{assoc} = 10^{1.5}$ dm^3 mol^{-1} is obtained from the slope and the cation exchange capacity. The order of magnitude is similar to that obtained by Ablov and Nazarova[10] for the Ni^{2+}−aniline complex in
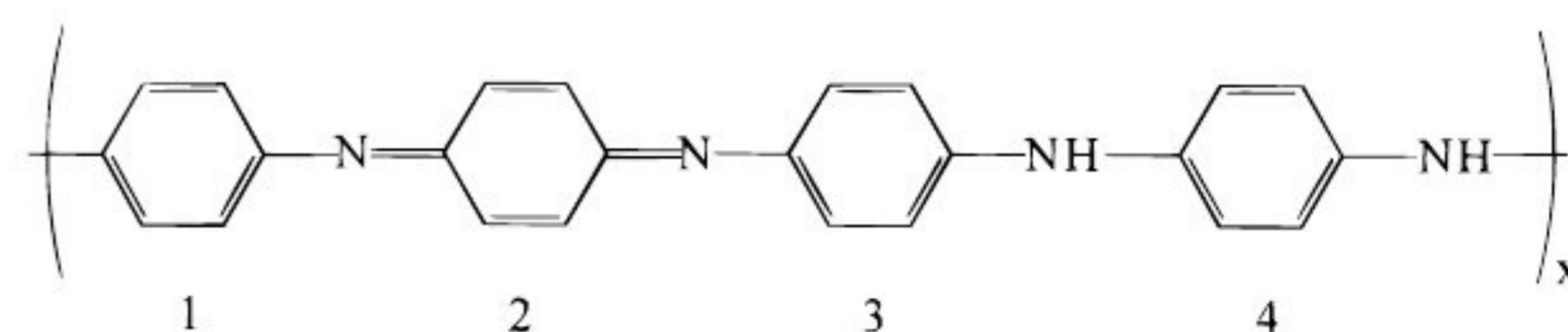

Figure 5. General formula for the base (unprotonated) form of polyaniline.

aqueous solution and further proves that the complex stability is weak compared, e.g., with the stability of Cu^{2+}−carboxylate complexes.[20]

The inset in Figure 3B shows the amount of bound aniline plus polymerization products calculated according to eq 1. It is obvious that above the critical concentration C_c of 2.6 mmol dm^{-3} the interpretation of this plot in terms of an adsorption isotherm is meaningless. The reason is that beyond C_c aniline polymerizes irreversibly in the montmorillonite interlayer. The consequence is a decrease of the free aniline concentration in the solution, which can be seen from Figure 2. Simultaneously, a very small part of the polymerization product vanishes from the interlayer and goes into solution.

The polymerization of aniline in aqueous solution was already observed by Tochima et al.[19] They propose a Cu^{2+}-catalyzed mechanism by which aniline is oxidized by oxygen and subsequently polymerizes radically. The structure of the final product is given in Figure 5. The polymerization in very diluted suspensions of Cu^{2+}- and Fe^{3+}-montmorillonites was also a topic of the investigations of Moreale at al.[15,16] who additionally employed ESR and dry thin film IR spectroscopy for the characterization. They confirmed the mechanism of Cu-catalyzed, oxidative radical polymerization for this system. As already emphasized in the Introduction, our approach goes beyond their work by employing the vibrational spectroscopy techniques applicable in aqueous suspension in combination with quantum-chemical calculations, which allows a secure assignment of the structure of the polymerization product.

ATR-FTIR and NIR-FT-Raman Spectroscopy. Aniline. To utilize ATR-FTIR and FT-Raman spectra to study the adsorption process of aniline on Cu(II)-montmorillonite, we need precise assignments of vibrational wavenumbers of the free aniline molecule for a comparative purpose. Figure 6 shows the ATR-FTIR spectrum of aniline in the liquid phase. The NIR-FT Raman spectrum in the liquid phase is represented in Figure 7. The vibrational frequencies obtained are included in Table 1. The vibrational assignment of the characteristic IR modes may be conveniently considered in two parts: phenyl-ring modes sensitive to the substituent and the modes of the NH$_2$ group. The IR fingerprint bands are located at 1626, 1604, 1498, and 1265 cm^{-1}. The NH$_2$ bending or scissors mode is attributed to 1626 cm^{-1}, and the band at 1604 cm^{-1} is the characteristic ring stretching vibration with a contribution of the NH$_2$ scissoring vibration. A typical ring stretching vibration is assigned to the band at 1498 cm^{-1}, and the band at 1265 cm^{-1} is assigned partly to the C−N stretching mode and partly to the ring stretching vibration.

The liquid FT-Raman spectrum is characterized by three specific scattering modes at 1603, 1020, 997, and 803 cm^{-1}. The most intense feature appears at 997 cm^{-1} and is attributed to the ring-breathing mode. The band observed at 1603 cm^{-1} is assigned to a ring mode and involves an in-plane deformation of the NH$_2$ group. The

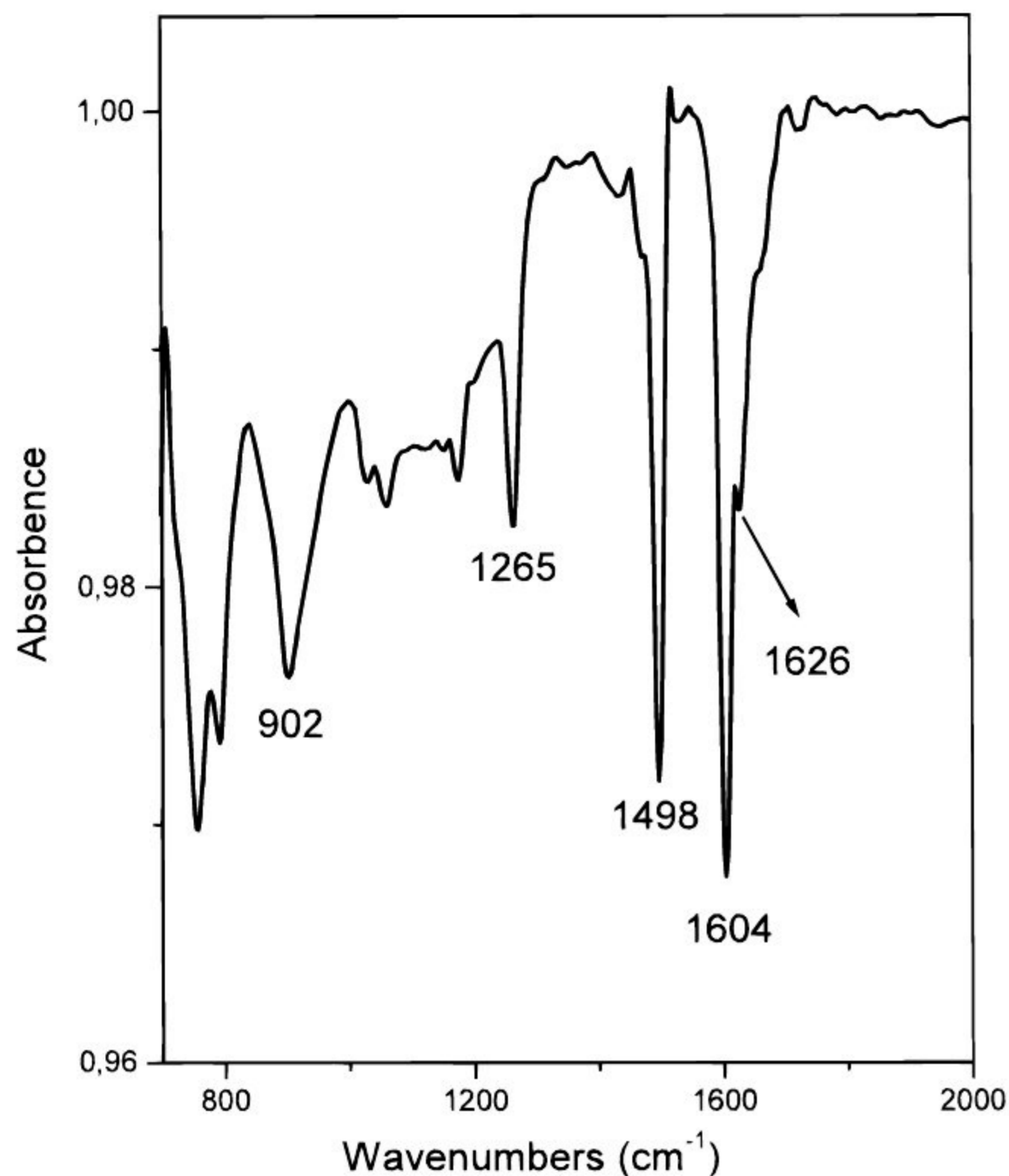(20) Martell, A. E.; Smith, R. M. *Critial stability constants*; New York 1975−1989.

Figure 6. ATR-FTIR spectrum of aniline in the liquid phase.
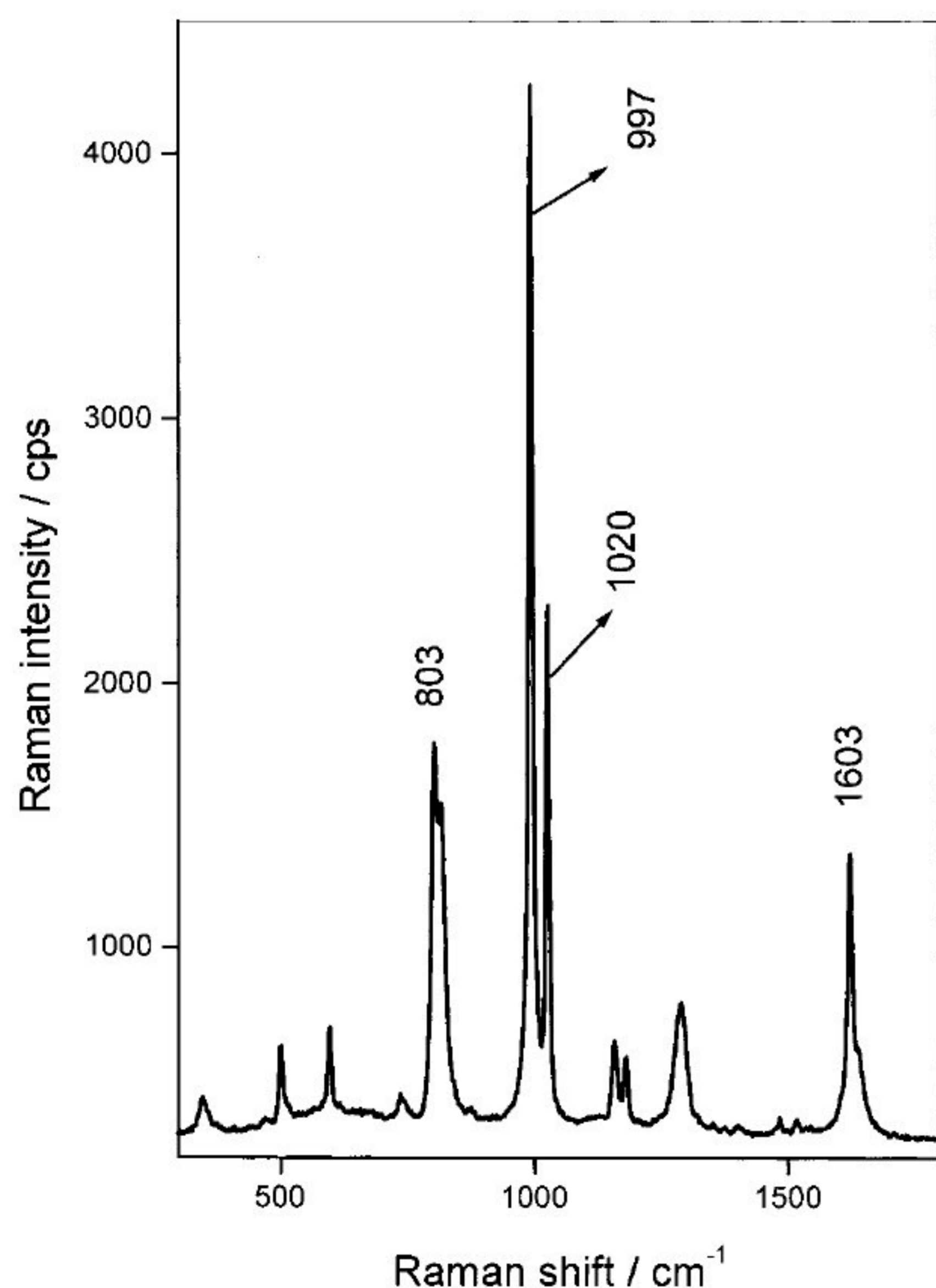

Figure 7. NIR-FT Raman spectrum of aniline in the 300–1800 cm^{-1} region: laser power, 250 mW; number of scans, 100.

low wavenumber band at 803 cm^{-1} involves the C–N stretching vibration and a ring stretching mode.

Cu(II)-montmorillonite/Aniline. Figure 8 presents the ATR-FTIR spectrum of the polymerization product in Cu(II)-montmorillonite at a concentration of sorbed aniline of 2 mmol g^{-1}. As model substance for the interpretation by ab initio calculation of the polyaniline, the

Table 1. Calculated (B3LYP) Vibrational Frequencies (cm^{-1}) and Infrared (km/mol) and Raman (Å^4/AMU) Intensities of Aniline

scaled freqs	intensities		experiment			assignment
	IR	Raman	Raman	IR^a	IR^b	
1627	106.9	23.9	1628	1626	1618	NH$_2$ sciss, ring str
1608	37.9	19.0	1603	1604	1603	ring str, NH$_2$ sciss
1503	54.9	0.9	1512	1497	1503	CH bend, ring str
1271	**55.0**	**7.3**	**1279**	**1264**	**1278**	**CN str, ring str**
1176	7.4	5.8	1176	1175	1173	CH bend ip
1156	1.8	5.4	1155	1153	1152	CH bend
1020	1.9	12.7	1029	1030	1020	ring def, ip
994	**0.6**	**20.4**	**997**		**996**	**ring breathing**
810	2.4	17.6	803	792	809	CN str, ring str

^{a} Experimental liquid-phase IR spectrum. ^{b} Experimental gas-phase IR spectrum (ref 12).
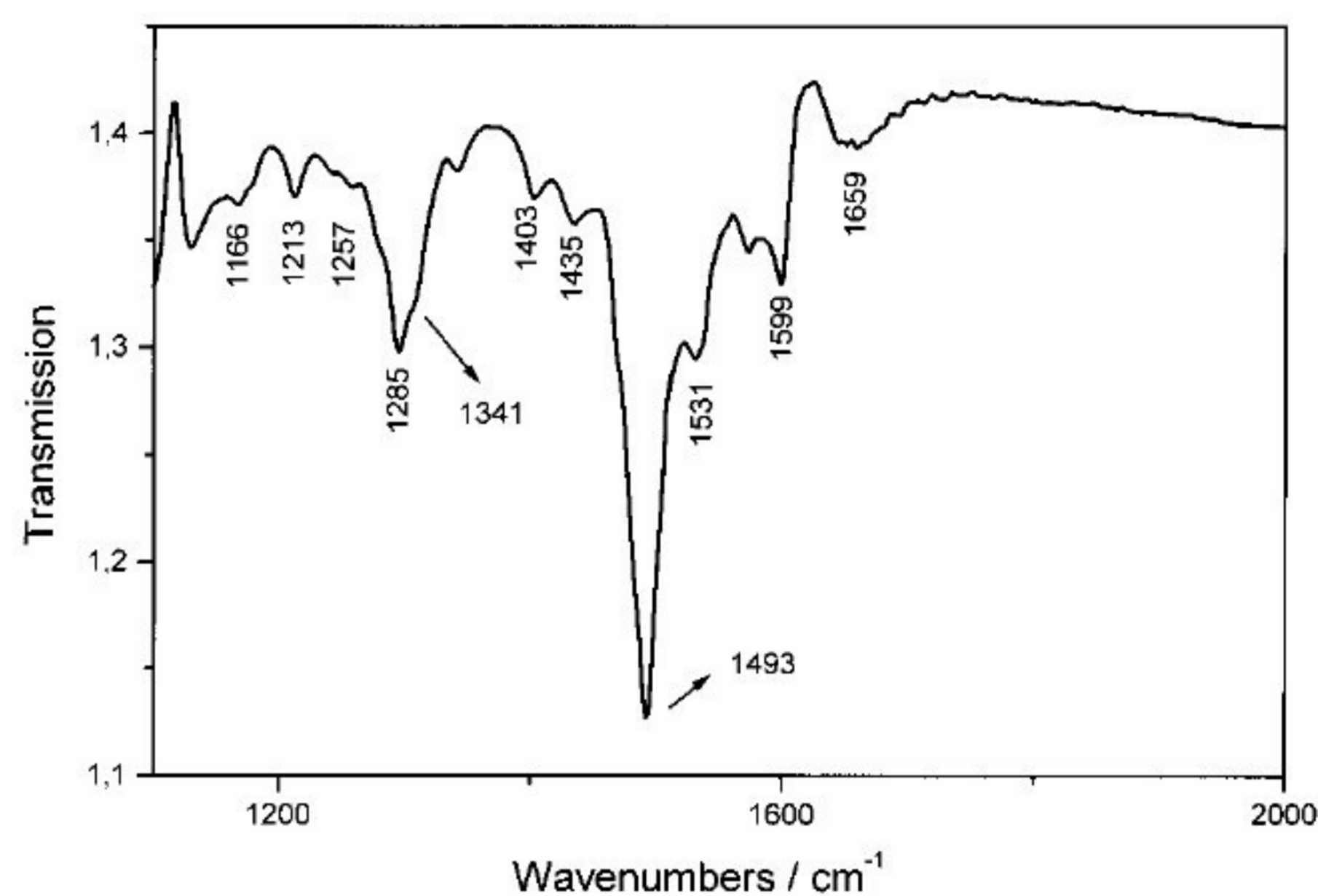

Figure 8. ATR-FTIR spectrum of adsorbed aniline (2.0 mmol g^{-1}) on Cu(II) montmorillonite.
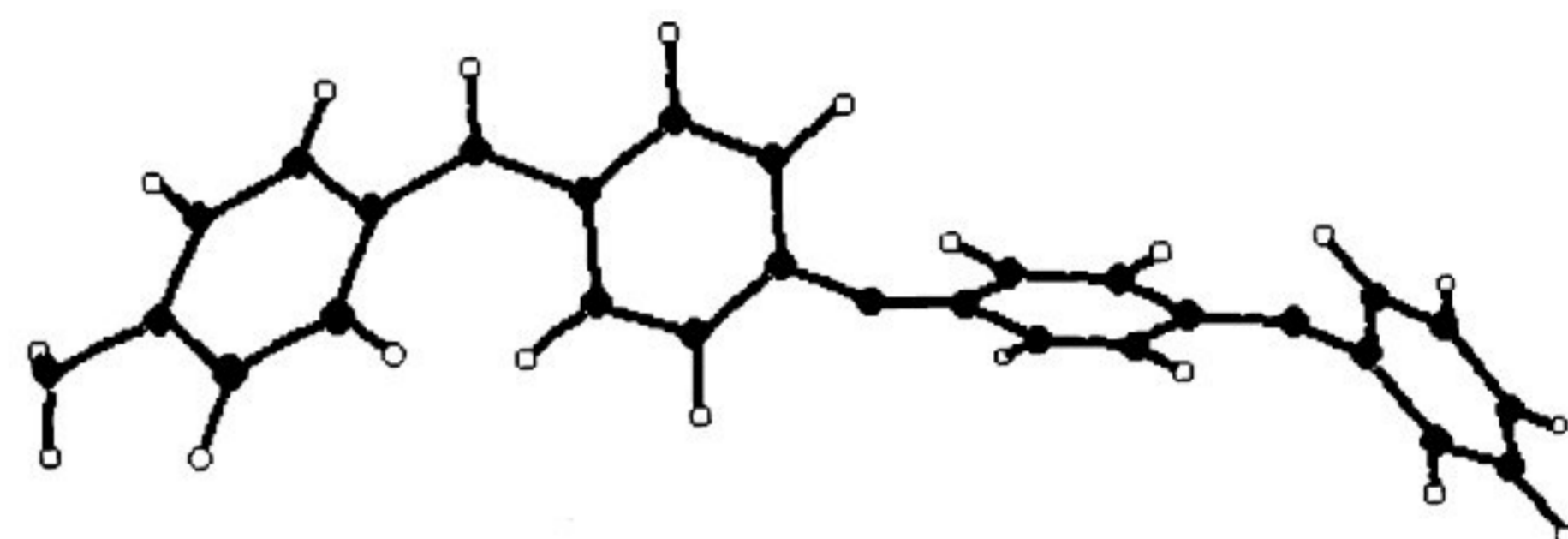

Figure 9. Schematic representation of a subunit for polyaniline (emeraldine base) as used in the calculation.

compound emeraldine was chosen, as shown in Figure 9. Comparing the IR bands of the adsorption product with those of pure aniline, it is obvious that the characteristic aniline bands at 1265 and 1604 cm^{-1} are shifted to 1285 and 1599 cm^{-1}, respectively (cf. Figures 6 and 8). The former shift indicates a shortening of the C–N bond,[19] whereas the latter effect indicates an elongation of the C=C bond. This is expected for the formation of polyaniline. Figure 10 shows the corresponding NIR-FT Raman spectrum; the frequencies obtained are included in Table 2. The characteristic bands of aniline are not present, but the measured bands agree with those of emeraldine. A further insight into the structure of the polymerization product is obtained by the ab initio calculations.

Ab Initio Calculations. A full use of experimental infrared and Raman spectroscopy for the purpose of structure determination requires the availability of a theoretical tool that can provide computed spectral data in a completely independent way and with an accuracy sufficient for a meaningful comparison with the experimental results. With current ab initio quantum-mechanical calculations, it has become possible to calculate
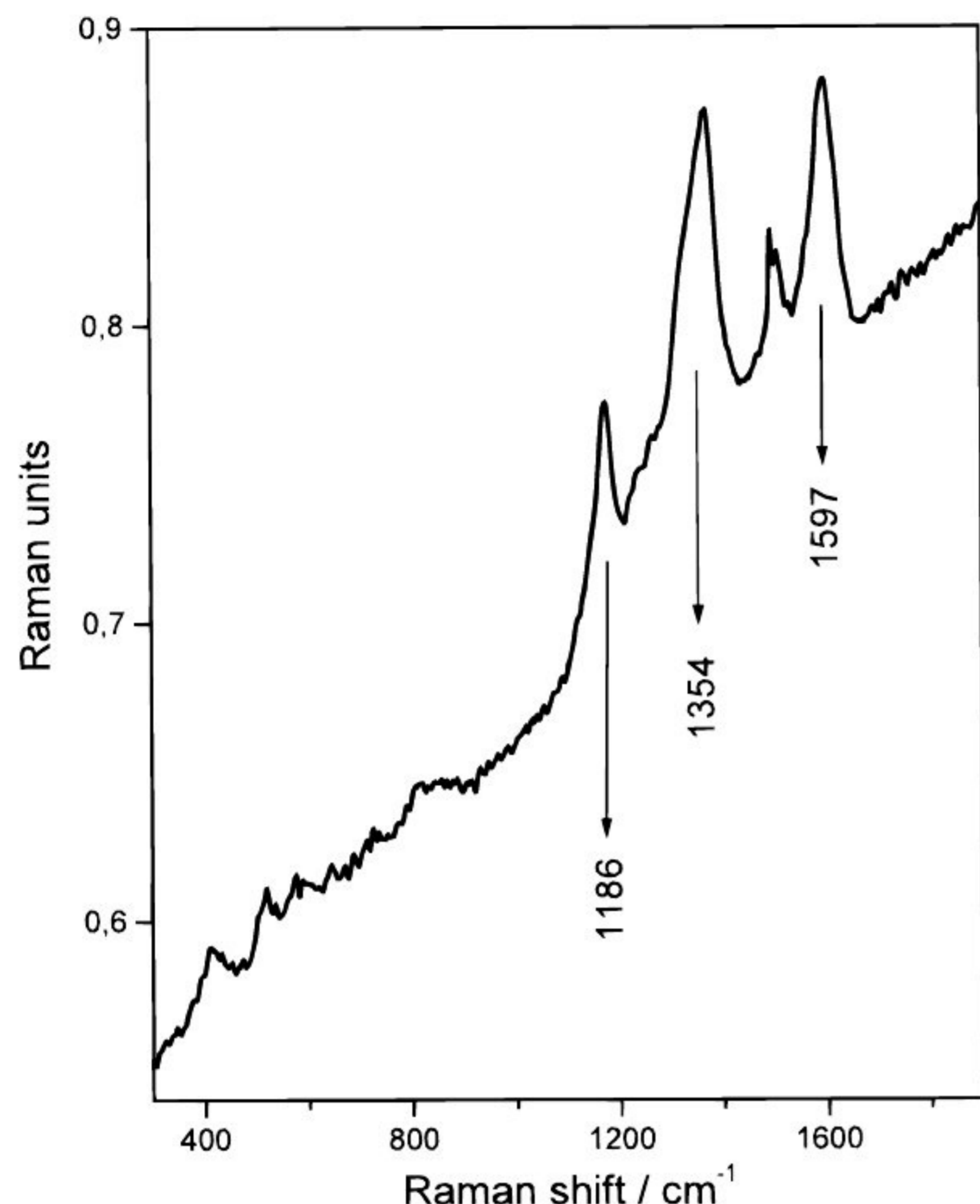
Figure 10. NIR-FT Raman spectrum of aniline (2.0 mmol g^{-1}) adsorbed on Cu(II) montmorillonite in the 400−1700 cm^{-1} region: laser power, 250 mW; number of scans, 100.

Table 2. Calculations (HF/6-31g*) of Characteristic Vibrational Frequencies (cm^{-1}) of the Emeraldine (EB) Repeat Unit of Polyaniline

scaled freqs	intensities		experiment		
	IR	Raman	Raman	IR	assignment
1667	85.8	15312.7			ring 2; C=N
1647	276.2	1260.3	1618	1659	ring 2; C=N
1624	131.2	16.2			NH$_2$
1602	6.1	125.6			ring 2; C=N
1599	**2.1**	**5346.5**	**1583**	**1599**	**ring 2; C=N**
1576	125.3	6268.1	1502	1573	ring 1, 3, 4
1500	274.2	104.2	1488	1531	ring 4; C−N
1490	**517.6**	**93.0**		**1493**	**ring 3; C−N**
1373	3.6	227	1349	1341	ring 4
1259	**155.5**	**50.4**	**1259**	**1285**	**ring 3, 4; C−N**
1186	154.0	731.3	1186	1166	ring 1, 2, 3, 4

vibrational frequencies and the corresponding intensities when the molecules are not too large. [21−23]

Aniline. The configuration of the amine group and its degree of tilting relative to the ring plane are still a matter of theoretical studies. Therefore, several theoretical ab initio calculations were carried out in the literature to determine the geometry of aniline.[24,25] The most important point for a vibrational analysis is a very good optimized geometry. Therefore, DFT using the 6-31g* basis and the three-parameter compound function of Becke (B3LYP) has been used for the calculation of the geometry, vibrational frequencies, and the IR and Raman intensities. The comparison of the scaled fundamental frequencies with ATR-FTIR and Raman experiments shows that the DFT theory is a very reliable tool for the
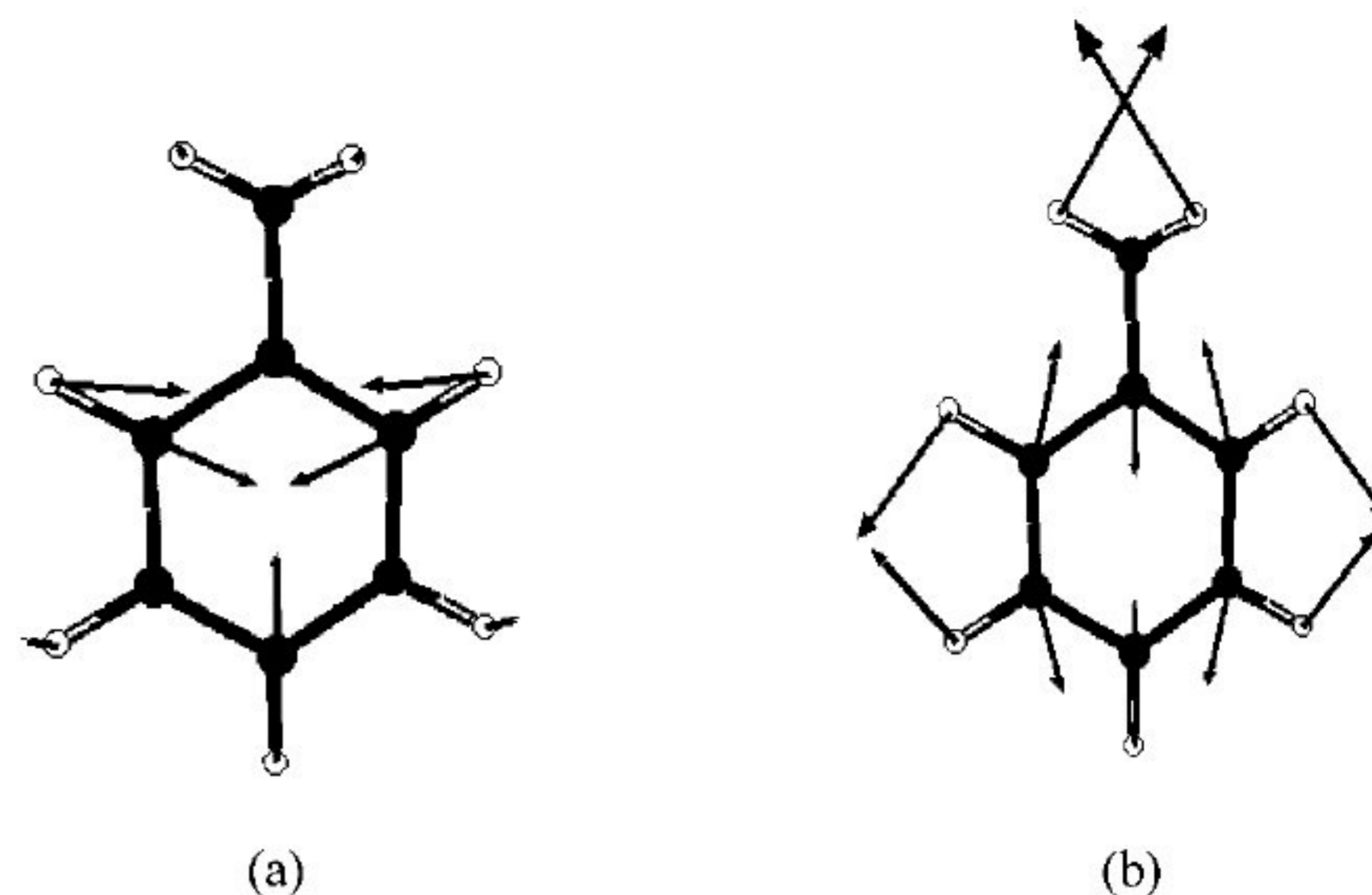
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(a)   (b)

Figure 11. Calculated eigenvectors of the ring-breathing mode (a) and a characteristic ring vibration at 1608 cm^{-1} (b) of aniline.

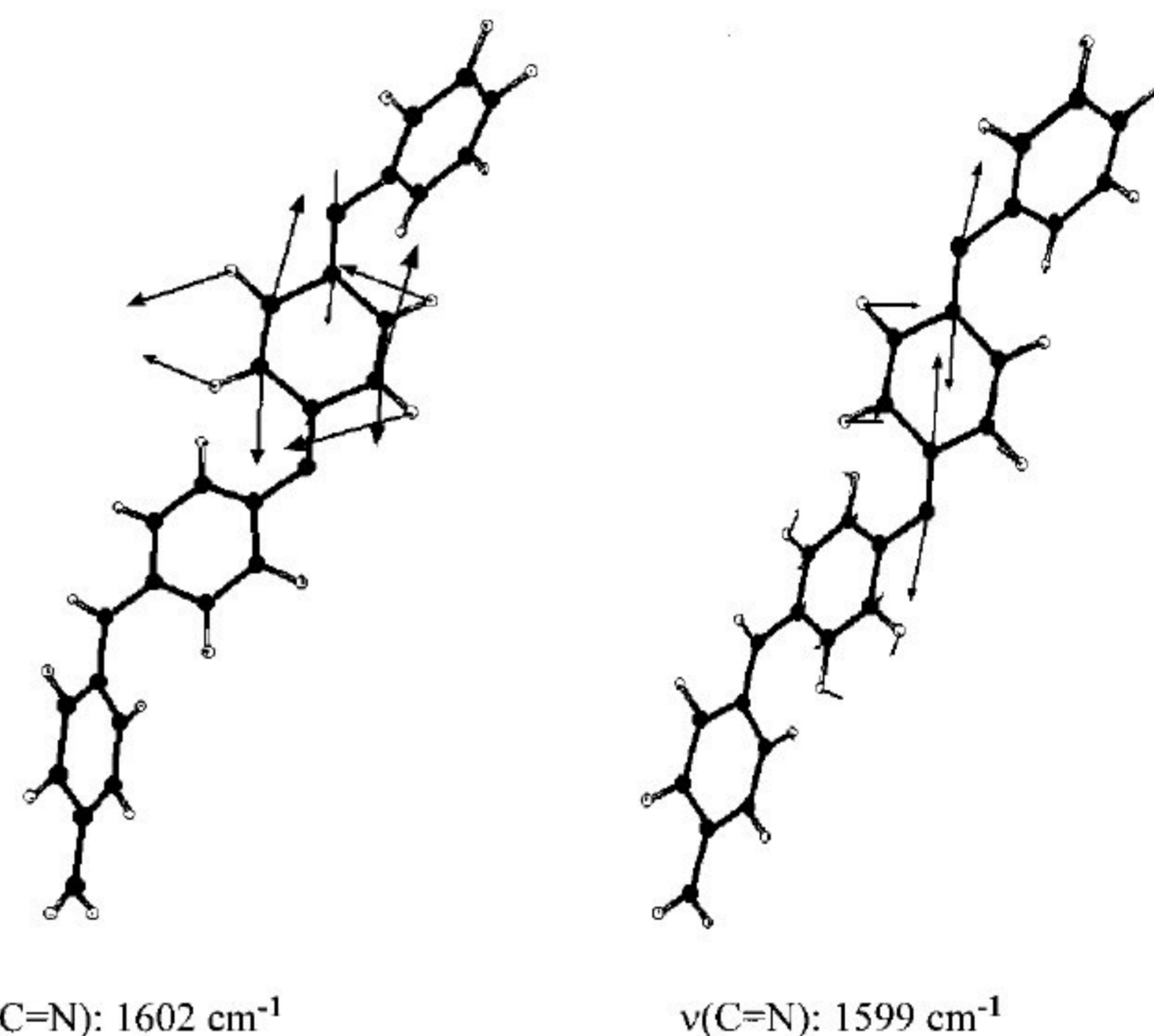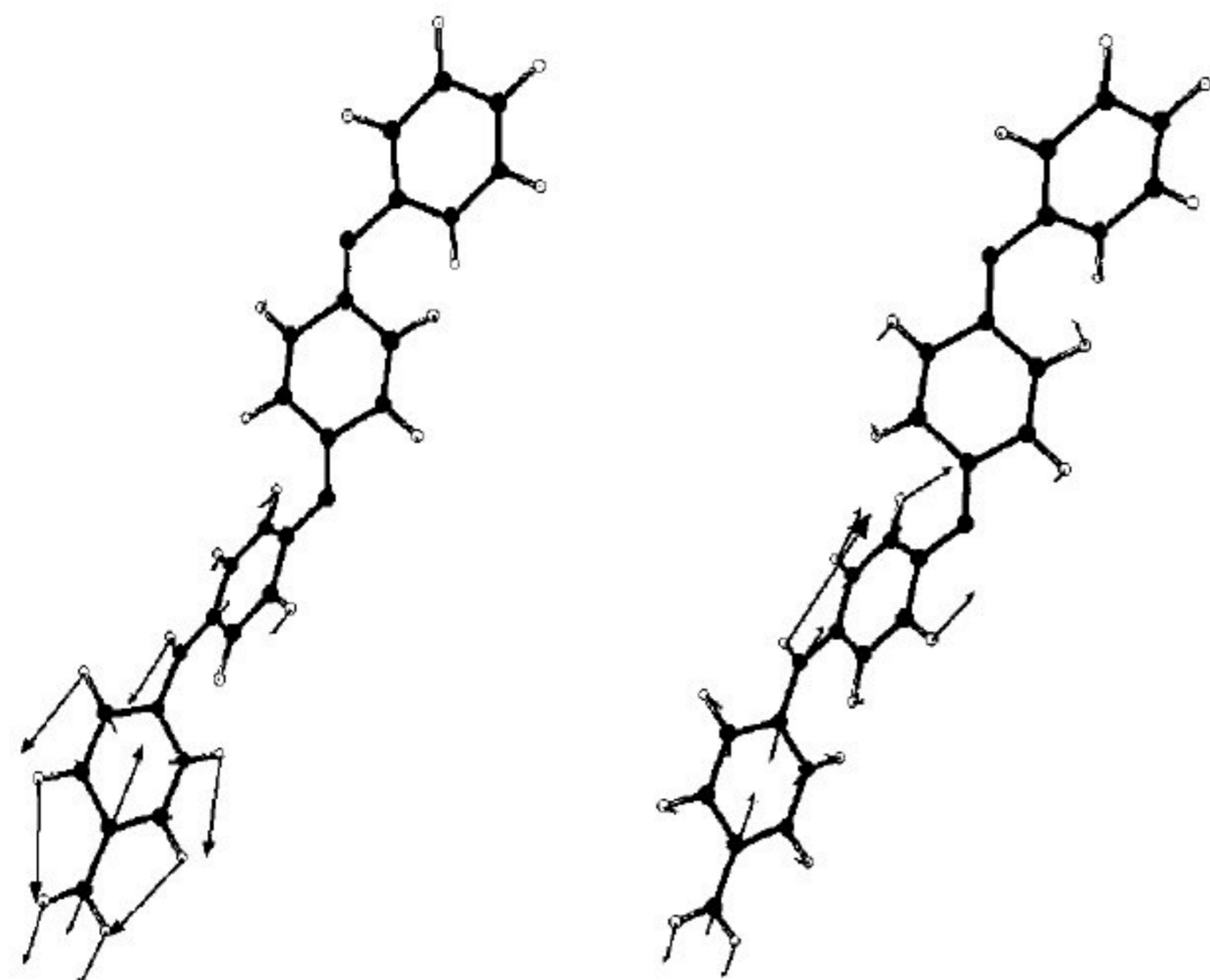ν(C=N): 1602 cm^{-1} ν(C=N): 1599 cm^{-1}

Figure 12. Calculated eigenvectors of the characteristic C=N vibrations of the double bond at 1602 and 1599 cm^{-1} in the −N=(C$_6$H$_4$)=N− unit of EB.

interpretation of IR and Raman spectra. Table 1 gives the assignment of the characteristic fundamentals based on the present calculation and on the experimental data. The eigenvectors of the ring-breathing mode at 994 cm^{-1} and the typical band at 1608 cm^{-1} (ring mode with a NH$_2$ contribution) are illustrated in Figure 11. As the geometry of the amino group (inversion and tilt angles ω and ϵ) is difficult to obtain experimentally, the very good agreement of the DFT calculated frequencies and the experimental data allows us to use the optimized geometry to determine ω and ϵ. The calculated values of the angles are $\omega = 43.6°$ and $\epsilon = 3.6°$ in the ortho position of the NH$_2$ group.

Emeraldine Base (EB). To assign the vibrational frequencies of the polyaniline molecule, we have considered an infinite, periodic, isolated, and helical chain with a straight helical axis model system. This emeraldine base (EB) consists of the quinone diimine −N=(C$_6$H$_4$)=N− unit (number 2 in Figure 5) and the amine NH−(C$_6$H$_4$)−NH unit (number 4 in Figure 5). Table 2 summarizes the measured and calculated frequencies and intensities for the schematic structure presented in Figure 9.

The calculated eigenvectors of the characteristic C=N vibrations of the double bond at 1602 and 1599 cm^{-1} in the −N=(C$_6$H$_4$)=N− unit are represented in Figure 12. The agreement between the vibration observed in the ATR spectrum at 1599 cm^{-1} and in the FT-Raman spectrum at 1597 cm^{-1} is very good. According to the

ν(C–N): 1246 cm^{-1} ν(C–N): 1259 cm^{-1}

Figure 13. Calculated eigenvectors of the characteristic C−N vibrations at 1246 cm^{-1} and 1259 cm^{-1} in the NH−(C$_6$H$_4$)−NH unit of EB.

broad experimental bands in this spectral range, the two calculated vibrations represented in Figure 8 and Figure 10 are not resolved.

The calculated eigenvectors of the characteristic C−N vibrations at 1246 and 1259 cm^{-1} in the NH−(C$_6$H$_4$)−NH unit are represented in Figure 13. The corresponding experimental frequencies are observed at 1285 cm^{-1} in the ATR spectrum and at 1261 cm^{-1} in the FT-Raman spectrum (not well resolved in the spectrum).

From the agreement between the experiments and the calculations of this characteristic C−N and C=N vibrations and the other assigned vibrational bands (cf. Table 2) of the emeraldine base unit, it can be concluded that aniline polymerizes on Cu(II)-montmorillonite by forming emeraldine.

It may be worth pointing out that the quantum-mechanical oligomer approach of polyaniline by EB is useful to simulate the polymer molecule by ab initio molecular orbital calculations.

Summary

The adsorption of aniline at Cu(II)-montmorillonite leads to polymerization beyond a critical concentration of 2.6 mmol dm^{-3}, and this process is catalyzed by Cu^{2+} ions in the interlayer space. Below that critical concentration the binding isotherm is linear, and the association constant for the 1:1 Cu−aniline complex is calculated as log(K_{assoc}/dm^3 mol^{-1}) = 1.5. The polymerization product can be well characterized in aqueous suspension by ATR-FTIR and NIR−FT Raman spectroscopy. By comparison with ab initio quantum-chemical calculations, it is possible to prove that the polymerization product is a copolymer of quinoidic and aromatic subunits.