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Conformational analysis of morpholine studied using Raman spectroscopy and density functional theoretical calculations

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ABSTRACT

Morpholine is a very interesting cyclic compound which is an ether as well as a secondary amine. The relative distribution of different conformations of morpholine depends on the medium. Using Raman spectroscopy and theoretical calculations, we found that, equatorial chair conformer is predominant in the pure liquid, but in aqueous solution, contribution from the axial conformer increases. The surface-enhanced Raman scattering (SERS) studies in presence of silver nanoparticles showed change in relative intensities of different vibrational modes of morpholine. It was found that the axial chair conformer is preferentially adsorbed vertically through the N—Ag bond on the nanoparticle surface.

1. Introduction

The study of adsorption of small, reactive organic compounds with noble metal nanoparticles is a very popular field. Most of these small heterocyclic compounds are part of active ingredients of different drugs and hence are very useful as models to understand how these drugs are supposed to bind with noble metal nanoparticles, which are being proposed as new age agents of targeted drug delivery to specified organs. We have earlier studied the interaction of a nitrogen containing six membered heterocyclic compound, piperizine, with silver (Ag) nanoparticles, and realized that an asymmetric conformer (equatorial–axial) of the same compound is preferably absorbed on the nanoparticle surface vertically through its axial H-atom [1]. Morpholine is very similar to piperazine, in the sense that, this is also a six-membered heterocyclic molecule with two heteroatoms in the ring. In piperazine, both the heteroatoms are N-atom (actually as a —N—H moiety), whereas in morpholine, one of the N-atoms is replaced by O-atom (as a —O— moiety). This makes morpholine a secondary amine as well as symmetric ether. Morpholine can have both chair and boat conformations in the ground state. Both these conformations again can have different conformers depending on whether the N—H bond is equatorial or axial with respect to the ring. The two chair forms, conventionally called equatorial and axial chair conformers are very close in energy, but their physical and chemical properties have interesting dissimilarities [2,3]. These peculiarities make the morpholine molecule, an attractive subject for many widely varying types of studies, from gas phase kinetics [4] to surface dynamics [5]. Xie et al. have studied the adsorption of morpholine on gold nanoparticles by using Raman and surface-enhanced Raman scattering (SERS) [5]. They have found that in higher concentration of morpholine, i.e., 10^{-1} M, axial conformer is preferentially adsorbed vertically on the nanoparticle surface whereas at lower concentrations, probably, the deprotonated morpholine molecule is adsorbed on the surface, that too in a flat orientation. Since many compounds show different adsorption behaviour in different noble metal nanoparticles, we studied the adsorption of morpholine on Ag nanoparticles by the SERS technique and these results were supported by theoretical calculations as required.

2. Experimental

Among the chemicals used in this letter, 99% pure solid morpholine, was procured from Sigma-Aldrich, and stored in a desiccator when not in use. $AgNO_3$, and $NaBH_4$ used for the preparation of Ag nanoparticles were procured from Fluka A G, and S. D. Fine Chemicals, India, respectively. These chemicals were used for the UV–vis, and Raman measurements without further purification. Ag nanoparticle was prepared by the chemical reduction of $AgNO_3$, with $NaBH_4$ using Creighton method [6]. In brief, 10 ml $AgNO_3$ (1×10^{-3} M) solution was added drop wise to 30 ml of 2×10^{-3} M ice-cold $NaBH_4$ solution with slow stirring. The Ag nanoparticle was yellow in colour and was stable at room temperature for several weeks. Morpholine (1 M) was added to the Ag nanoparticle and characterized using UV–vis absorption. The UV–vis absorption

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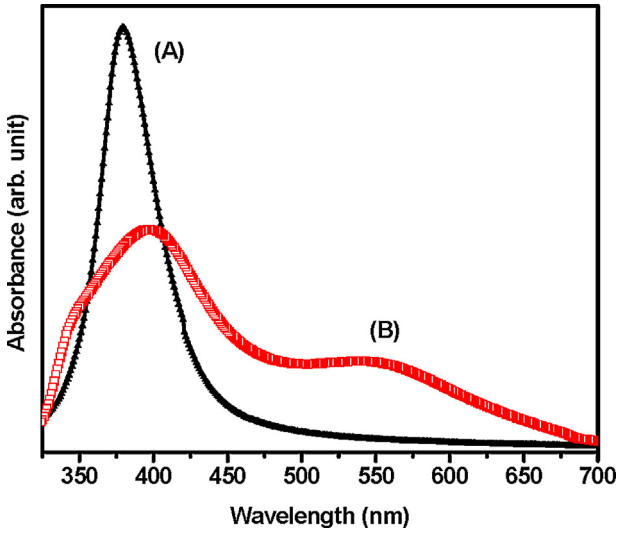

Figure 1. Surface plasmon absorption band of (A) Ag nanoparticle and (B) with 0.25 M morpholine solution added to it.

spectra were recorded using a Jasco V-650 spectrophotometer. Raman and SERS spectra of morpholine at different concentrations were recorded at room temperature using the 532 nm line, from a DPSS Nd^{3+}:YAG laser (Cobolt Samba 0532-01-0500 -500) M/s Cobolt AB, Sweden. The laser power used to record the Raman spectrum was 25 mW and the spot size on the sample was ~50 μm. For the Raman measurements, the sample solutions were taken in a standard 1 cm × 1 cm cuvette and the Raman scattered light was collected at 90° scattering geometry and detected using a CCD (Synapse, Horiba Jobin Yvon) based, monochromator (Triax550, Horiba Jobin Yvon, France) together with a notch filter, covering a spectral range of 200–1700 cm^{-1}.

3. Theoretical calculations

Density functional theoretical (DFT) calculations were done with GAUSSIAN 09 package [7] to support the experimental results. The ground state structures of the morpholine conformers were optimized at B3LYP/aug-cc-pvtz level of theory. The morpholine–Ag and morpholine–Ag_6 complex was optimized at B3LYP functional with aug-cc-pvtz (morpholine) and LANL2DZ (Ag) basis sets. In addition, in order to include dispersion interaction, the morpholine–Ag and morpholine–Ag_6 complex was optimized using the wb97xd functional. The Raman spectrum of different species was computed at the optimized geometry at the same level as the optimization.

4. Results and discussions

4.1. Absorption studies

As shown in Figure 1, the UV–vis absorption spectrum of Ag nanoparticle showed a single sharp peak appearing at 380 nm, due to the surface plasmon resonance band [8]. The position and shape of this peak depends strongly on the size and shape of the nanoparticle, their aggregation pattern, and dielectric constant of the medium. The nature of the spectrum changes considerably in the presence of surface active species and the change also depends on the nature of binding between the nanoparticle and the adsorbed species. As morpholine solution (0.25 M) was added to the Ag nanoparticle (yellow), its colour changes to pink, and a new broad peak appears around 510–570 nm. As morpholine molecules are adsorbed over the Ag nanoparticle surface, the nanoparticles aggregate and their absorption peak is red-shifted.

4.2. Transmission electron microscope studies

Transmission electron microscope (TEM) was used to characterize the Ag nanoparticle formed by $NaBH_4$ reduction and to study the effect of addition of morpholine on its size and shape. From the TEM image, freshly prepared Ag nanoparticle was found to consist of well-separated spherical particles of 10–15 nm, the average size being 12.5 nm (Figure 2(A)). Addition of morpholine (0.25 M) to the Ag nanoparticle facilitates the aggregation of the particles. The average size of the Ag nanoparticles upon aggregation was 18–25 nm, and the particles retained their spherical shape, as shown by their TEM image (Figure 2(B)).

4.3. Raman spectrum of pure liquid morpholine

The IR spectrum of pure liquid morpholine has been reported by Friedel et al. [9] and Vedal et al. [10]. The Raman spectrum of pure liquid morpholine has been recorded and all fundamental modes have been extensively assigned by both Vedal et al. [10] and Xie et al. [5]. Theoretical calculations (at MP2/aug-cc-pvtz level) have shown that the twist boat conformation is much higher in energy than both axial and equatorial chair conformers. The two chair conformers are close in energy, the equatorial one being slightly more stable in the gas phase. We optimized the structure of the two chair conformers, equatorial and axial of the isolated morpholine molecule in gas-phase, at B3LYP/aug-cc-pvtz level of theory, and the optimized structures are shown as Figure 3(A) and (B). We computed the theoretical Raman spectra of these two conformers at the same level, and they are shown in Figure 4(B) and (C). These two computed spectra were compared with the experimental Raman spectrum of pure morpholine (Figure 4(A)). From the figure, it is evident that there is marked similarity in the spectral

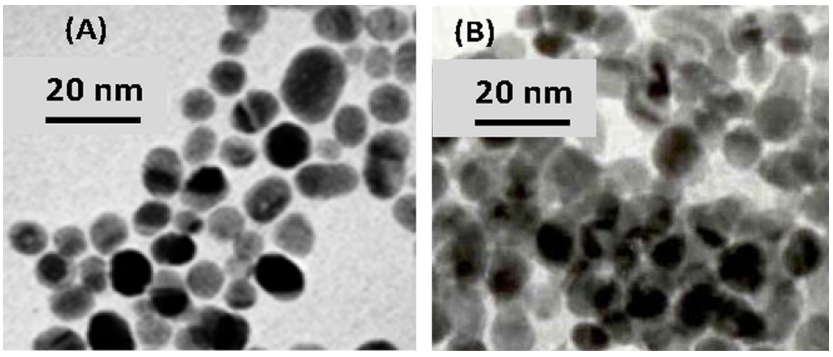

Figure 2. Transmission electron micrograph of (A) Ag nanoparticles and (B) aggregated Ag particles formed by addition of 0.25 M morpholine.