# Behaviour of the uranyl ($UO_2^{2+}$) ion in different strongly acidic media: characterisation of $UO_2^{2+}$ in common acids by electronic absorption spectroscopy

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The linear uranyl ($UO_2^{2+}$) ion has been characterised by electronic absorption spectroscopy in the media of four highly concentrated acids: sulfuric, nitric, acetic, and hydrochloric acids. In sulfuric acid, the magnitude of splitting ($cm^{-1}$) of the vibronic peaks in the $UO_2^{2+}$ spectra increased linearly as molar concentration of the acid increased from zero to 18 M. Such an unprecedented spectral progression has been attributed to the high concentrations of sulfuric acid reducing the extent of coordination of water molecules to the central uranium atom of $UO_2^{2+}$. This is believed to reduce the electron density in the uranium valence shell and decrease the electrostatic repulsion between the uranium and oxygen valence shells, making the U=O bonds stronger. It results in the observed increase in splitting of the vibronic peaks. In nitric acid, a completely different spectral feature of uranyl was observed. First, as molar concentration of nitric acid increased, the vibronic structure in the $UO_2^{2+}$ spectra disappeared gradually and the absorption band became continuous at 6 M. As the acid concentration further increased, vibronic lines were resolved in the lower-energy side of the spectra. The higher-energy side remained continuous with no vibronic structure observed. The convergence limit ($cm^{-1}$), the borderline between vibronic peaks in the lower-energy side and a continuous band in the higher-energy side, decreased linearly as the molarity of nitric acid increased from 8 M to 16 M. All this shows that nitric acid, with involvement of its conjugate nitrate anion, has made $UO_2^{2+}$ dissociative beyond the convergence limit of its excited state. In acetic acid, as the molar concentration of the acid increased from zero to 17.5 M, the $UO_2^{2+}$ spectra exhibited three-stages of progression due to a predominating coordination of a carboxyl group to $UO_2^{2+}$ ([HOAc] = 0–9 M), dissociation of $UO_2^{2+}$ at the convergence limit of its excited state ([HOAc] = 10–14 M), and formation of an undissociative excited state for $UO_2^{2+}$ ([HOAc] = 15–17.5 M). In hydrochloric acid, $UO_2^{2+}$ exhibited a comparable spectral feature to that observed in nitric and acetic acids due to a predominating coordination of the chloride anion to $UO_2^{2+}$.

**Keywords:** uranyl, vibronic structure, electronic spectra, dissociation limit

Investigation of the chemistry of the uranyl (VI) $UO_2^{2+}$ ion has received much attention, partially due to its importance in radioactive waste isolation and disposal.[1-3] On the other hand, this cation is highly oxidative in acidic solutions, exhibiting interesting and useful oxidation–reduction chemistry.[4] Since the uranium atom in $UO_2^{2+}$ is in the VI oxidation state and possesses a large size, many efforts have been made also in exploring its interesting coordination chemistry.[5-14] An effective method to study chemical speciation of the uranyl ion in aqueous solution is to apply molecular and electronic spectroscopies to it, and this has been carried out in establishing the coordination chemistry of $UO_2^{2+}$ under highly alkaline conditions.[1] Although the chemistry of $UO_2^{2+}$ has also been studied under acidic conditions,[4] the nature of interaction of the ion with an acid is not clear. Knowing this interaction would certainly help us understand and further explore the oxidation–reduction chemistry and spectroscopic properties of $UO_2^{2+}$.[15] We now report characterisation of the uranyl $UO_2^{2+}$ ion in various strongly acidic media by electronic absorption spectroscopy. Interesting, unprecedented spectral behaviour of $UO_2^{2+}$ has been found. This includes a quantitative linear relationship between the magnitude of splitting of vibronic energy levels in $UO_2^{2+}$ and acidity of the media, and distinctive progression of the $UO_2^{2+}$ spectra as a function of the acid concentration in the media of different acids. Our spectroscopic data have shown formation of a dissociative excited state of $UO_2^{2+}$ in the media of nitric and acetic acids.

## Experimental

The electronic absorption (UV-visible) spectra were recorded throughout this work using a UV-1601 Shimadzu spectrophotometer. The instrument consists of a light source, a sample chamber, a diode-array detector, and a data acquisition computer. The sample was placed between the light and the detector. The computer then measured the amount of UV or visible light that passed through the sample at varying wavelengths. It was then converted to absorbance.

Uranyl sulfate ($UO_2SO_4$) or uranyl nitrate hexahydrate ($[UO_2(NO_3)_2].6H_2O$), obtained from Sigma-Aldrich Chemical Company, were used as the source of uranyl (VI) ion ($UO_2^{2+}$). In the experiment conducted in the media of sulfuric acid, $UO_2SO_4$ was dissolved in distilled water and sulfuric acid at different concentrations (4.5 M, 9.0 M, 13.5 M, 15.8 M, and 18 M respectively), to make six $UO_2^{2+}$ aqueous solutions at various acidities. In each of the acidic solutions, the concentration of $UO_2^{2+}$ was maintained at 0.10 M. In the experiments which were conducted in the media of nitric acid, acetic acid, or hydrochloric acid, $[UO_2(NO_3)_2].6H_2O$ was dissolved in distilled water and each of the acids at different concentrations, respectively. Nine $UO_2^{2+}$ aqueous solutions were made in nitric acid with the acid molar concentrations being 0 M, 1.98 M, 3.95 M, 5.9 M, 7.9 M, 9.88 M, 11.9M, 13.8 M, and 15.8 M, respectively. In each of the solutions, the molar concentration of $UO_2^{2+}$ was maintained at 0.20 M. Twelve $UO_2^{2+}$ aqueous solutions were made in acetic acid with the acid molar concentrations being 0 M, 1.8 M, 3.5 M, 5.3 M, 7.0 M, 8.8 M, 10.5 M, 12.3 M, 14.0 M, 15.3 M, 16.6 M, and 17.5 M, respectively. In each of the solutions, the molar concentration of $UO_2^{2+}$ was maintained at 0.20 M. Nine $UO_2^{2+}$ solutions were made in hydrochloric acid with the acid molar concentrations being 0 M, 0.5 M, 1.0 M, 1.5 M, 4.0 M, 6.0 M, 8.0 M, 10.0 M, and 12.0 M, respectively. In each of the aqueous hydrochloric solutions, the molar concentration of $UO_2^{2+}$ was maintained at 0.10 M. A UV-visible cell (with thickness of 4 mm) was then filled with each of the $UO_2^{2+}$ solutions, and an electronic absorption (UV-visible) spectrum was recorded. Analysis of the spectrum was performed at the wavelength range of 300–600 nm (*e.g.* Fig. 1).

In all the spectra, the wavelengths of all the resolved absorption peaks were measured by the above-mentioned data acquisition computer which is integral to the spectrometer. For example, in the spectrum (Fig. 2) of $UO_2^{2+}$ in 18 M sulfuric acid (98%), the absorption peaks were measured as follows: peak 1 (453.5 nm, 22,050 $cm^{-1}$), peak 2 (437.5 nm, 22,860 $cm^{-1}$), peak 3 (423.5 nm, 23,610 $cm^{-1}$), peak 4 (411.5 nm, 24,300 $cm^{-1}$), and peak 5 (400.0 nm, 25,000 $cm^{-1}$). The splitting (spacing) in $cm^{-1}$ between two peaks,

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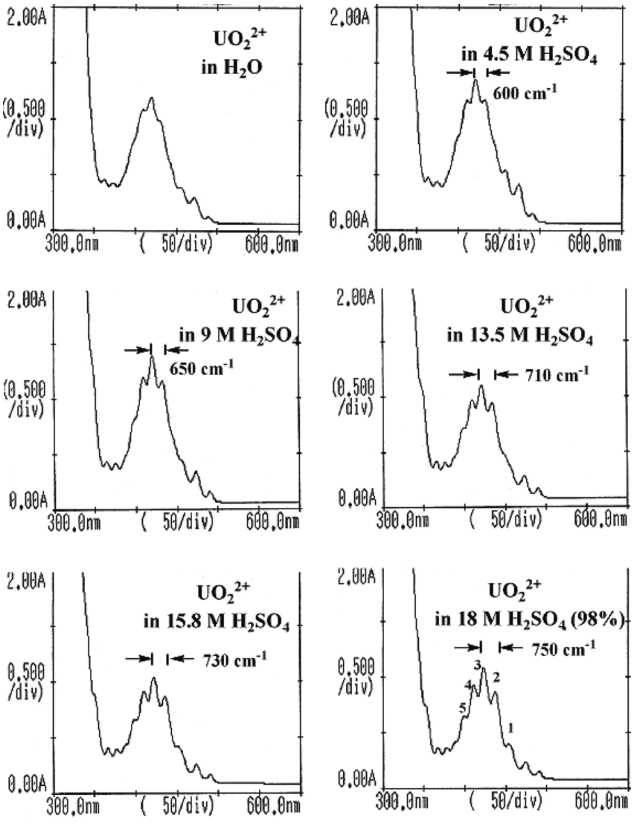

**Fig. 1** The UV-visible spectra of $UO_2^{2+}$ (0.10 M) in the media of sulfuric acid at different concentrations. Magnitude of splitting of vibronic peaks in each spectrum is indicated.

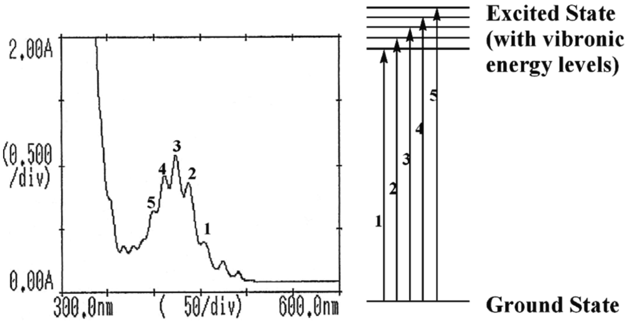

**Fig. 2** The vibronic structure of $UO_2^{2+}$ in sulfuric acid (18 M).

which corresponds to spacing ($\Delta$, cm$^{-1}$) between two vibronic energy levels of the cation in the excited state (see below), was calculated by difference (e.g. $\Delta_{2\text{-}3}$ = 23,610 – 22,860 = 750 cm$^{-1}$). Some data are included in Table 1.

## Results and discussion

*Electronic absorption spectra of $UO_2^{2+}$ in sulfuric acid*

The electronic absorption spectra of $UO_2^{2+}$ (0.10 M) in the media of different molar concentrations of sulfuric acid were recorded at 300–600 nm. (Fig. 1) All the spectra exhibited a broad absorption band centred in a narrow range of 420–423 nm, consistent with a bright yellow colour of all the samples due to $UO_2^{2+}$. Its maximum absorption peak had slight red shift within this narrow range as the concentration of sulfuric acid increased from 0 to 18 M. The strong absorption below 350 nm in each spectrum was due to water and sulfuric acid. The absorption band of $UO_2^{2+}$ centred at 420–423 nm can be reasonably assigned to the HOMO ($\pi$) – LUMO ($\pi^*$) transition in the linear $UO_2^{2+}$, *i.e.* $[O{=}U{=}O]^{2+}$, cation (see ref. 4 for its structure). The spectra in neutral and different acidic conditions showed poorly, fairly, or well resolved peaks depending on the acidity of the medium, attributable to the vibronic structure in the excited state of $[O{=}U{=}O]^{2+}$. (Fig. 2) Each peak originates from a transition from the ground state (HOMO) to a specific vibronic energy level in the excited state (LUMO) as illustrated in Fig. 2. The splitting (spacing) between two adjacent peaks in a spectrum corresponds to the difference in two adjacent vibronic energy levels. Sun and his former coworkers studied electronic absorption spectrum of an analogues triatomic linear dithiozolium $[S{=}N{=}S]^+$ ion.[16] The spectral feature of $[O{=}U{=}O]^{2+}$ coincides with that of the previously studied $[S{=}N{=}S]^+$ ion.

**Table 1** Splitting of vibronic energy levels ($\Delta$, cm$^{-1}$) of the uranyl $UO_2^{2+}$ ion in different molar concentrations of sulfuric acid

| Concentration of $H_2SO_4$ /M | $\Delta_{1\text{-}2}$ /cm$^{-1}$ | $\Delta_{2\text{-}3}$ /cm$^{-1}$ | $\Delta_{3\text{-}4}$ /cm$^{-1}$ | $\Delta_{4\text{-}5}$ /cm$^{-1}$ |
|---|---|---|---|---|
| 4.5 | N/A | 600 | 610 | N/A |
| 9 | N/A | 650 | 640 | N/A |
| 13.5 | 650 | 710 | 660 | 610 |
| 15.8 | 720 | 730 | 660 | 670 |
| 18 | 810 | 750 | 690 | 700 |

Comparison of all the $UO_2^{2+}$ spectra obtained in the media of different acidities (Fig. 1) revealed that as the concentration of sulfuric acid increased from 0 M to 18 M, the vibronic structure in the spectra were better resolved due to a gradual increase in splitting of the vibronic peaks. The magnitude of splitting (in cm$^{-1}$) between the highest central peak (peak 3) and its adjacent lower-energy peak (peak 2) in each of the spectra is indicated in Fig. 1 (see Fig. 2 for the peak numbering). We denote this splitting as $\Delta_{2\text{-}3}$ (in cm$^{-1}$), and the splittings of other adjacent vibronic peaks are denoted correspondingly as $\Delta_{1\text{-}2}$ (between peaks 1 and 2), $\Delta_{3\text{-}4}$ (between peaks 3 and 4), and $\Delta_{4\text{-}5}$ (between peaks 4 and 5). All these peak splitting data are included in Table 1. Since each absorption peak originates from a transition to a specific vibronic energy level, the peak splitting corresponds to the splitting ($\Delta$, difference) of two vibronic energy levels (in cm$^{-1}$) in the excited state. Quantitative examination of the data in Table 1 shows that the magnitude of splitting $\Delta$ (in cm$^{-1}$) in each pair of the adjacent vibronic energy levels in $UO_2^{2+}$ ($\Delta_{1\text{-}2}$, $\Delta_{2\text{-}3}$, $\Delta_{3\text{-}4}$, and $\Delta_{4\text{-}5}$) increased linearly (with a correlation coefficient being greater than 0.90) as a function of the molar concentration of sulfuric acid (Fig. 3). Especially good was the line of $\Delta_{2\text{-}3}$ versus $[H_2SO_4]$, which had a correlation coefficient of 0.998 and a slope of 11.4 cm$^{-1}$/M. This relationship, a representative of general good linear dependence of splitting of the vibronic energy levels in $UO_2^{2+}$ on the acid molar concentration, is formulated as follows

$$\Delta_{2\text{-}3}\ (\text{cm}^{-1}) = 11.4\ [H_2SO_4] + 550 \qquad (1)$$

Since spacing (difference) between vibronic energy levels is correlated directly to vibrational frequency in molecular spectroscopy (the higher the vibrational frequency, the stronger the U=O bond), the increasing splitting $\Delta$ of the vibronic energy levels in $UO_2^{2+}$ as a function of the $H_2SO_4$ molarity can be considered as a result of an increase in the U=O bond strength. All this shows that in the $UO_2^{2+}$ solutions the U=O bonds have been strengthened by sulfuric acid. The linear relationship [Eqn (1)] between the splitting of vibronic energy levels in $UO_2^{2+}$ and the concentration of $H_2SO_4$ implies a quantitative dependence of the U=O bond strength on the medium acidity.

Clark *et al.* reported spectroscopic characterisation of the uranyl ion under alkaline conditions and demonstrated that under these conditions the equatorial positions of the uranium atom in $UO_2^{2+}$ are coordinated by hydroxide $OH^-$ ions and/or water molecules, which increases electron density on the uranium metal centre and increases its electrostatic repulsion with the highly negative axial oxygen atoms to weaken the U=O bonds.[1] As a result, the splitting of vibronic peaks in the $UO_2^{2+}$ electronic absorption spectra recorded in alkaline conditions was found to decrease as increase in the hydroxide $OH^-$ concentration.[1] This strongly suggests that the U=O bond strength, which is believed to be directly proportional to the magnitude of splitting of vibronic peaks such as $\Delta_{2\text{-}3}$ (cm$^{-1}$),[17] is sensitive to the electrostatic repulsion between the uranium and oxygen valence electron shells, namely that the stronger (or weaker) the repulsion, the weaker (or stronger) the U=O bond. This can be readily studied by electronic absorption (UV-visible) spectroscopy. In our work, the $UO_2^{2+}$ ion was situated in the aqueous media with extremely high concentrations of sulfuric acid. This excludes the hydroxide $OH^-$ ion. $UO_2^{2+}$ was surrounded by $H_2SO_4$ molecules, the hydronium $H_3O^+$ ions, and/or water molecules, mainly depending on the concentration of the acid. As the concentration of $H_2SO_4$ increases, the water content

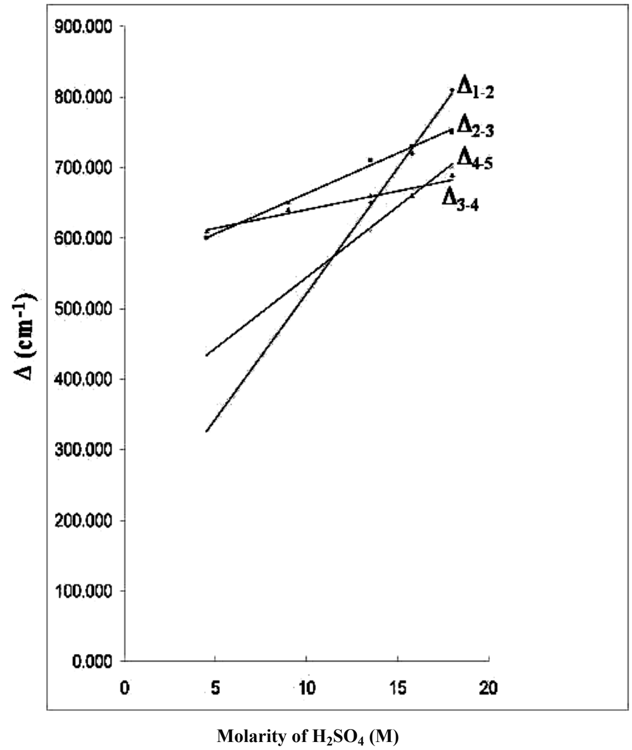

**Fig. 3** Splitting of vibronic energy levels in the uranyl $UO_2^{2+}$ ion ($\Delta$, cm$^{-1}$) as a function of molar concentration of sulfuric acid in the medium. The correlation coefficient and slope (cm$^{-1}$/M) of each $\Delta$ versus [$H_2SO_4$] line are determined as: $\Delta_{1-2}$ (0.996, 35.5), $\Delta_{2-3}$ (0.998, 11.4), $\Delta_{3-4}$ (0.901, 5.3), and $\Delta_{4-5}$ (0.998, 20.0).

in the media decreases. This reduces the extent of coordination of water molecules to the central uranium atom of $UO_2^{2+}$. As illustrated above, coordination of water molecules to the uranium atom of $UO_2^{2+}$ increases electron density in the uranium metal centre, weakening the U=O bonds due to an increase in electrostatic repulsion between the uranium and oxygen valence shells. Decrease in the extent of the coordination of water molecules to uranium in $UO_2^{2+}$ by increasing concentration of sulfuric acid in the media will have opposite result, that is to decrease electrostatic repulsion between the uranium and oxygen valence shells, strengthening the U=O bonds and increasing the splitting of vibronic peaks. All this explains the observed change in the $UO_2^{2+}$ spectral data as a function of the molar concentration of sulfuric acid in the aqueous media.

### *Electronic absorption spectra of $UO_2^{2+}$ in nitric acid: observation for dissociation of the uranyl ion in the excited state*

Figure 4 shows the electronic absorption spectra of the $UO_2^{2+}$ ion in the media of nitric acid at various concentrations. The progression of the $UO_2^{2+}$ spectra as a function of the molar concentration of nitric acid was substantially different than that observed in Fig. 1 in the sulfuric acid media. First, as the $HNO_3$ molarity increased from 0 M to 6 M, the splitting of vibronic peaks in the $UO_2^{2+}$ spectra decreased gradually. At [$HNO_3$] ~ 6 M, the absorption band of $UO_2^{2+}$ became essentially continuous. This change is attributable to increase in coordination of the nitrate $NO_3^-$ anion to the central uranium atom in $UO_2^{2+}$ as the molarity of nitric acid was enhanced. This type of coordination by $NO_3^-$ has been observed and structurally characterised recently in a ternary U–O–N compound $UO_2(NO_3)_2$-$N_2O_4$[9] and in some other systems containing $UO_2^{2+}$.[14] The coordination of $NO_3^-$ to uranium in $UO_2^{2+}$ increased the electron density in the uranium valence shell. As a result, the electrostatic repulsion between the valence electron shell in a terminal oxygen atom and that in uranium has increased. This weakens the U=O bonds, making the vibronic energy levels in the excited state continuous.

As the $HNO_3$ molarity further increased from 8 M to 16 M, the higher-energy side of the $UO_2^{2+}$ spectra remained essentially continuous. However, the lower-energy side of the spectra exhibited vibronic structure (Fig. 4). The vibronic peaks became better resolved as the molar concentration of $HNO_3$ increased. This pattern of the $UO_2^{2+}$ absorption spectra at [$HNO_3$] = 8 – 16 M is characteristic of a dissociative excited state (Fig. 5), indicated by the observed convergence (dissociation) limit, the borderline (peak 5) between the lower-energy vibronic peaks and the higher-energy continuous absorption band.[17] It shows that when $UO_2^{2+}$ is excited beyond the convergence limit, photodissociation would occur. Conceivably, formation of such a dissociative excited state beyond the convergence limit, which is indicated by a continuous absorption in the higher-energy side of the spectra as illustrated in Fig. 5, resulted from the strong coordination of $NO_3^-$ to uranium in $UO_2^{2+}$, weakening the U=O bonds. The data treatment for Table 2 shows that the convergence energy (dissociation limit, $\nu_5$) of $UO_2^{2+}$ decreased linearly as a function of the $HNO_3$ molarity [Eqn (2)]

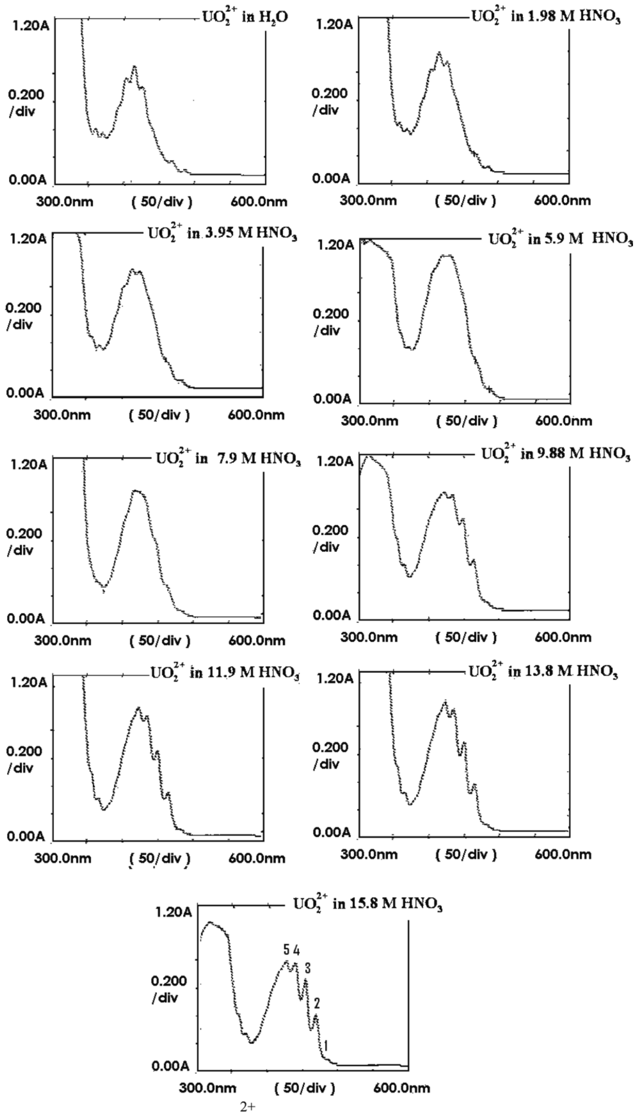

**Fig. 4** The UV-visible spectra of $UO_2^{2+}$ (0.20 M) in different concentrations of nitric acid.

$$\nu_5\ (\mathrm{cm}^{-1}) = -36.9\ [HNO_3] + 24{,}100\ (R^2 = 0.97) \qquad (2)$$

Clearly, this quantitative relationship is due to an increase in the extent of coordination by $NO_3^-$ to $UO_2^{2+}$ as [$HNO_3$] increases. It weakens the U=O bonds and makes the dissociation of $UO_2^{2+}$ take place more readily at lower energy.

### *Electronic absorption spectra of $UO_2^{2+}$ in acetic acid: the three-stages of spectral progression as a function of the HOAC molar concentration*

The electronic absorption spectra of $UO_2^{2+}$ in acetic acid (Fig. 6) exhibited three-stages of progression as the acid molar concentration increased from 0 to 17.5 M. First, as the HOAc molarity increased from 0 M to 9 M (the first stage), the splitting of vibronic peaks in

**Table 2** The wavenumbers of convergence (dissociation) limit peak 5 ($\nu_5$, cm$^{-1}$) in the $UO_2^{2+}$ spectra in different concentrations of nitric acid

| Concentration of $HNO_3$/M | Peak 5 wavenumber ($\nu_5$/cm$^{-1}$) |
|---|---|
| 7.9 | 23,830 |
| 9.8 | 23,700 |
| 11.9 | 23,640 |
| 13.8 | 23,590 |
| 15.8 | 23,560 |

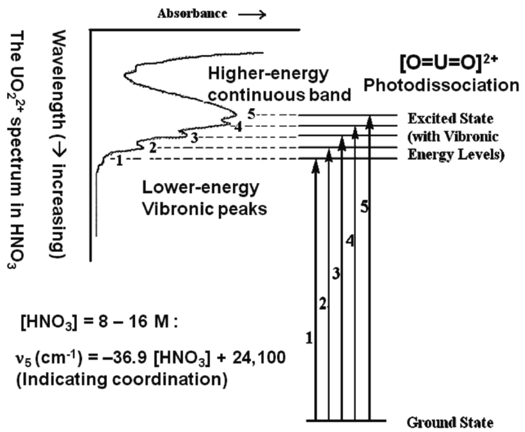

**Fig. 5** The UV-visible spectrum of $UO_2^{2+}$ (0.20 M) in 12 M $HNO_3$, showing a dissociative excited state due to coordination of nitrate to the $UO_2^{2+}$ ion.

the $UO_2^{2+}$ spectra decreased gradually, attributable to coordination of the acetic acid molecule (or the conjugated acetate anion) to the central uranium atom of $UO_2^{2+}$.[12] In this stage, the coordination of a carboxyl group/carboxylate to the central uranium atom of $UO_2^{2+}$ is the predominating interaction between the media and $UO_2^{2+}$. As the molarity of HOAc increased from 10 to 14 M (the second stage), a convergence (dissociation) limit in the excited state of $UO_2^{2+}$ was observed in the spectra, indicated by a borderline between lower-energy absorption peaks and a higher-energy continuous absorption band. This feature resembles the spectra of $UO_2^{2+}$ recorded in nitric acid at $[HNO_3]$ = 8–16 M (Fig. 4). In this stage, due to high concentrations of acetic acid in the media, the carboxyl group/carboxylate strongly coordinated to the central uranium further weakening the U=O bonds in $UO_2^{2+}$. This has led to formation of such a dissociative excited state that photodissociation of $UO_2^{2+}$ would occur beyond the dissociation limit.

Different from the spectra recorded in nitric acid, the spectra of $UO_2^{2+}$ in the media of acetic acid (Fig. 6) showed that after a dissociation limit in the excited state of $UO_2^{2+}$ was formed at [HOAc] = 10–14 M, as the molarity of HOAc further increased from 15 to 17.5 M (the third stage), vibronic peaks were observed (although only barely resolved) in the higher-energy side of the $UO_2^{2+}$ spectra in addition to those peaks in the lower-energy side. The convergence limit disappeared from the spectra. Particularly, this is true for the spectra recorded at [HAc] = 16.6 M and 17.5 M. It shows that the excited state of $UO_2^{2+}$ at [HOAc] = 15–17.5 M is no longer dissociative. In this third stage, as acetic acid became extremely concentrated with almost no water present, dimers of $(CH_3COOH)_2$ are formed via hydrogen bonds between the carboxyl groups. This resulted in a dramatic decrease in extent of coordination of the carboxyl groups to the uranium atom of $UO_2^{2+}$. As discussed above, decrease in coordination of a ligand to uranium would result in decrease in electronic repulsion between the uranium and oxygen valence shells, strengthening the U=O bonds and making it more difficult to dissociate. As a result, vibronic energy levels in the higher-energy region of the $UO_2^{2+}$ excited state became non-continuous, as shown by the barely resolved peaks in higher-energy side of the spectra. The ion became undissociative in its excited state.

### *Electronic absorption spectra of $UO_2^{2+}$ in hydrochloric acid*

The electronic absorption spectra of $UO_2^{2+}$ recorded in the hydrochloric acid media (Fig. 7) exhibited comparable progression to those recorded in nitric and acetic acids as a function of the acid molar concentration. As the molarity of HCl increased from 0 to 2.5 M, the central band of the $UO_2^{2+}$ spectra became continuous gradually. The splittings between the central vibronic peak and its higher-energy adjacent peak ($\Delta_{1\text{-}2}$, cm$^{-1}$) and between the central and its lower-energy adjacent peaks ($\Delta_{2\text{-}3}$, cm$^{-1}$) decreased linearly as a function of the HCl molar concentration (0–1.5 M) [(Eqns (3, 4)]

$$\Delta_{1\text{-}2}\ (\mathrm{cm^{-1}}) = -37\ [\mathrm{HCl}] + 635\ (R^2 = -0.99) \tag{3}$$

$$\Delta_{2\text{-}3}\ (\mathrm{cm^{-1}}) = -40\ [\mathrm{HCl}] + 705\ (R^2 = -0.97) \tag{4}$$

As discussed above, these quantitative relationships demonstrated that at this acid concentration range coordination of $Cl^-$ to the central uranium atom of $UO_2^{2+}$ in its equatorial positions is predominating. This type of coordination has been studied and structurally characterised previously.[5,7,8] It weakens the U=O bond and makes the vibronic levels of $UO_2^{2+}$ in the excited state gradually continuous.

As the molarity of HCl further increased from 4 to 12 M, vibronic peaks were clearly observed in the central band of the $UO_2^{2+}$ spectra.

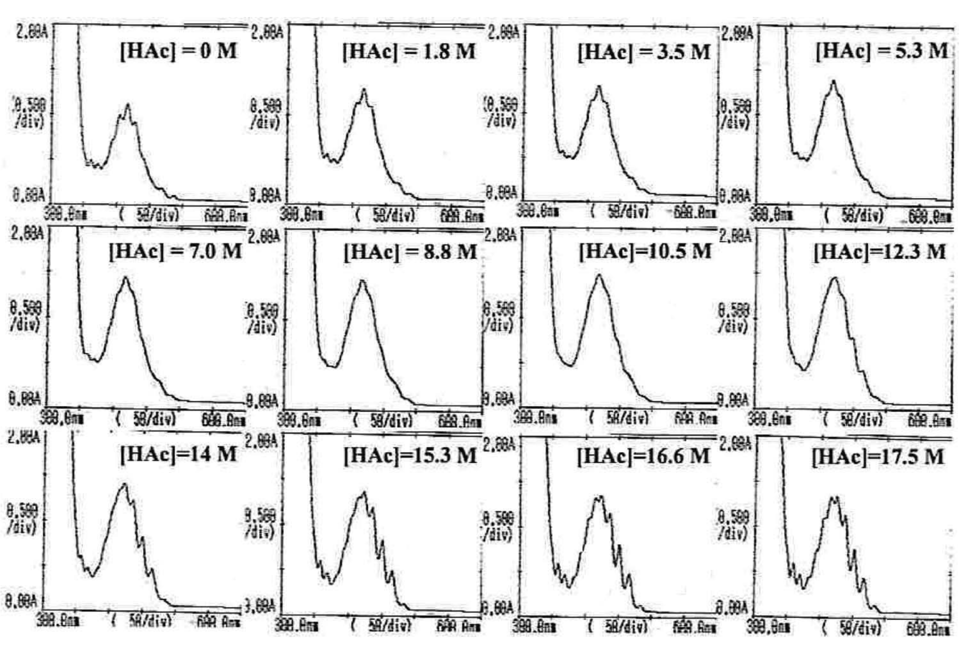

**Fig. 6** The UV-visible spectra of $UO_2^{2+}$ (0.2 M) in different concentrations of acetic acid.

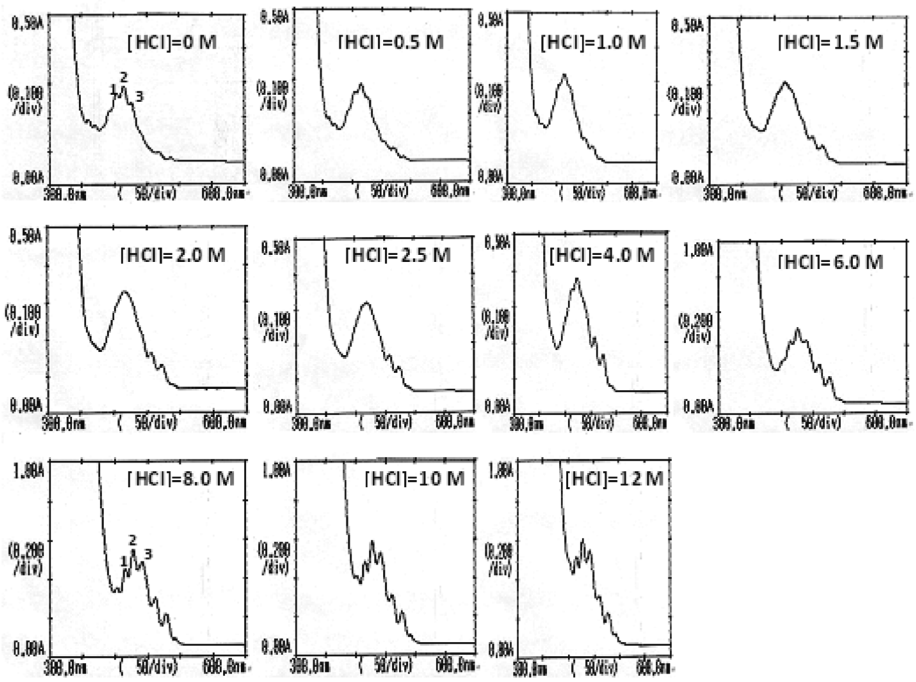

**Fig. 7** The UV-visible spectra of $UO_2^{2+}$ (0.1 M) in different concentrations of hydrochloric acid.

They became better resolved as the concentration of HCl increased. Quantitatively, the splittings between the central and adjacent higher-energy peaks ($\Delta_{1\text{-}2}$, $cm^{-1}$) and between the central and adjacent lower-energy peaks ($\Delta_{2\text{-}3}$, $cm^{-1}$) increased linearly as a function of the HCl molar concentration (6 – 12 M) [Eqns (5, 6)]

$$\Delta_{1\text{-}2}\ (\mathrm{cm}^{-1}) = 21\ [\mathrm{HCl}] + 610\ (R^2 = 0.97) \qquad (5)$$

$$\Delta_{2\text{-}3}\ (\mathrm{cm}^{-1}) = 29\ [\mathrm{HCl}] + 640\ (R^2 = 0.98) \qquad (6)$$

These relationships are in agreement with Eqn (1). Likely, at this acid concentration range (6–12 M), coordination of $Cl^-$ to the central uranium atom may have been saturated (completed). As the HCl molarity increased, the extent of coordination by chloride may not change any more. However, it may gradually prevent water molecules from coordinating to $UO_2^{2+}$. This could strengthen the U=O bonds increasing the splitting of vibronic peaks as observed.

## Conclusions

In this work, the uranyl $UO_2^{2+}$ ion has been characterised by electronic absorption spectroscopy in the media of several common acids (sulfuric, nitric, acetic, and hydrochloric acids). Quantitative linear relationship between the splitting of vibronic peaks ($\Delta$, $cm^{-1}$) and the acid molar concentration has been observed.

The conjugate anions of nitric acid (nitrate), acetic acid (acetate), and hydrochloric acid (chloride) strongly coordinate to the central uranium atom in $UO_2^{2+}$. The anionic coordination reduces the strength of the U=O bonds. As a result, a convergence limit in the $UO_2^{2+}$ spectra in nitric and acetic acids has been observed. This shows that in the media of nitric and acetic acids photodissociation of $UO_2^{2+}$ would take place in its excited state beyond the convergence limit, the borderline between the lower-energy non-continuous vibronic lines and the higher-energy continuous absorption band. A quantitative linear relationship between the convergence (dissociation) limit ($cm^{-1}$) and the concentration of nitric acid has been observed.

Our studies have demonstrated that the spectroscopic behaviour of the uranyl $UO_2^{2+}$ ion in the medium of a given acid, namely the progression of the $UO_2^{2+}$ spectra as a function of the molar concentration of the acid, is distinct. This has made it an interesting and informative area to extensively explore the electronic spectroscopic properties of $UO_2^{2+}$ in various acidic media.

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