Electronic absorption spectrum of titanium dioxide in neon matrices

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Anions of titanium dioxide produced by sputtering TiO$_2$/graphite composite rods were trapped in 6 K neon matrices following mass selection. The electronic absorption spectrum of titanium dioxide has been measured subsequently, after exposing the matrices to UV radiation, revealing absorptions in the visible and UV regions. Bent and linear forms of TiO$_2$ have been observed with absorptions in the visible range.

Two electronic systems of the bent isomer, $^1$B$_2$ $\rightarrow$ $^1$X$^1$A$_1$ and $^3$B$_1$ $\rightarrow$ $^1$X$^1$A$_1$, are observed with origins at 524 and 368 nm in agreement with theoretical calculations. The electronic transition lying at 524 nm shows a long vibronic progression due to excitations of the symmetric stretching and bending modes of TiO$_2$. The linear form shows a transition at 628 nm for which a progression involving the symmetric stretching mode of TiO$_2$ is apparent. The spectral assignments have been supported by analysis of the vibrational structure associated with each electronic transition.

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1. Introduction

Transition metals continue to be of special interest, partly due to the complexities associated with d shell electrons. The 3d-elements form a number of oxygen-containing clusters and compounds with variable oxidation states of the metal cation. Reactivity of these oxides is of interest to different chemistry areas: organometallic, surface science, catalysis, chemisorption processes, and interstellar matter. For these reasons, a large number of theoretical and experimental spectroscopic studies have been devoted to the monoxides and dioxides of the elements ranging from Sc to Zn, leading to reliable reference data about bond lengths, dissociation energies, dipole moments, and vibrational frequencies for both the ground and excited states of these oxides [1–4].

Titanium oxide (TiO), has been extensively studied spectroscopically due to its astrophysical interest [5–9]. Indeed, TiO is the main opacity source in the atmospheres of cool M-type stars in the visible and near infrared. In addition, owing to its importance in model atmosphere investigations and in quantum chemistry, a number of theoretical studies have been devoted to this species [10–13]. Its electronic structure is therefore well understood. In view of the high cosmic abundance of Ti and O [14], larger clusters of titanium oxides are believed to play an important role in dust formation processes from the gas-phase in circumstellar shells of oxygen-rich stars [15].

Titanium dioxide, is a technologically important material which has been widely studied as a prototypical transition metal oxide due to its rather simple electronic structure [16]. Compared to the TiO molecule, considerably less has been reported on TiO$_2$ [13,17–20]. The earliest work on TiO$_2$ was carried out in 1967 showing that this molecule has a dipole moment and therefore a bent structure [18]. Few years later, the emission spectrum of TiO$_2$ was measured for the first time reporting the origin emission band at 529 nm [19]. From these studies, the infrared spectrum of TiO$_2$ in neon matrices was also obtained. Two absorption bands were observed: a strong one at 934.8 cm$^{-1}$ and a weak one at 962.0 cm$^{-1}$, respectively assigned to the asymmetric stretch ($v_3$) and symmetric stretch ($v_1$). Similar works reported an infrared study on TiO$_2$ species produced by reactions of laser-ablated Ti and O$_2$ in argon matrix at 10 K, confirming the $C_2v$ symmetry of the $^1$A$_1$ ground state of this closed shell molecule [20].

TiO$_2$($n=1–3$) and TiO$_2(n)$ systems were also investigated by photoelectron spectroscopy (PES) to obtain vertical detachment energies [4]. For TiO$_2$, it was reported that both anion and neutral species have a bent structure. In addition, besides the vibrationally resolved ground state of TiO$_2$, two excited states were also observed at 1.96(10) and 2.4(2) eV, and assigned to the $A^3B_2$ and $a^1B_2$ excited states respectively [4]. Interestingly, they obtained for TiO$_2$ broad PES spectra indicating that large geometry changes occur between the anion and the two $B_2$ excited states of TiO$_2$. It was therefore suggested that these two states could be linear, which was found to be in agreement with SCF-CI calculations [17]. A large number of theoretical studies have been then devoted to titanium dioxide [21–26]. From these works, geometries, vibrational frequencies, electron affinities, and dissociation energies were obtained. In addition, different isomers of TiO$_2$, as the peroxo- and superoxo-ones, have also been considered and investigated. Recently, the electronic energy levels of TiO$_2$ have been calculated [27].
excitation energies were obtained for both the singlet and the triplet states. From these results, it is suggested that TiO₂ has a $C_{2v}$ structure in the $A_1, B_2, B_1$, and $A_2$ excited states which have similar geometries and excitation energies for both the singlet and the triplet multiplicities, with the latter lying 0.03 to 0.05 eV below the singlet ones. Similar results were obtained for the linear excited states which are predicted to be only 0.3 to 0.4 eV less stable than their bent counterparts.

All the results cited above make it a challenge to understand the electronic spectrum of titanium dioxide. The present article is a contribution to this understanding. The electronic absorption spectrum of TiO₂, using mass-selective neon matrix isolation spectroscopy, is presented for the first time. The spectral assignments will be discussed by comparison with experimental and calculated data previously reported.

2. Experimental

The electronic absorption spectra of titanium dioxide were recorded following mass-selective deposition in neon matrices using the described experimental set-up [28]. The anions were produced in a negative cesium ion sputter source from TiO₂/graphite composite rods in a ratio 2:1. The beam is then focused and directed into a quadrupole mass filter using a series of electrostatic optics. The TiO₂ anions were selected (m/e = 80) with a mass resolution of ±1 amu and the typical ion currents achieved were about 2–3 nA. The mass-selected anions, with a kinetic energy of ~50 eV, were co-deposited over a period of 4 h with an excess of neon onto a rhodium coated sapphire substrate held at 6 K.

After deposition, the electronic absorption spectra of the species embedded in neon were recorded with monochromatic light from halogen and xenon arc lamps with beams running parallel to the substrate surface. Absorption spectra were recorded between 220 and 1100 nm using photomultiplier and silicon diode detectors. The effective optical path of the light through the matrix using a waveguide technique is about 2 cm. Infrared spectra in the 4000–6000 cm⁻¹ range were recorded by doubly reflecting light at an acute angle from a Fourier-transform infrared spectrometer through the matrix, of about 150 μm thickness, achieving a path length of about 1 mm. This method used to measure infrared spectra is an order of magnitude less sensitive than the waveguide approach.

The matrix samples were then exposed to a medium-pressure mercury lamp (λ > 305 nm) resulting in electron detachment. After each irradiation, a spectrum was recorded to distinguish the electronic transitions of neutral species from those of the ions.

3. Results

The trapping of the mass-selected TiO₂ anions in a neon matrix gave rise to a number of absorptions in the 220–1100 nm region. Fig. 1 shows the electronic absorption spectra measured in the visible range (400–650 nm). The lower trace corresponds to the deposition spectrum and the upper to the one recorded after irradiation and annealing of the matrix. According to the data in the literature, some of the absorption bands are easily assigned to titanium [29,30], titanium monoxide and its anion [19,31], as indicated in Fig. 1. TiO₂ is due to fragmentation of the mass-selected TiO₂ species hitting the matrix with a ~50 eV kinetic energy. Besides these bands, several broad weak absorption bands, close to those of TiO, are observed in the visible range (Fig. 1). The vicinity of these bands to those of TiO complicates the identification. Nevertheless, the results of the photobleaching and annealing point out to neutral TiO₂ being responsible for these new electronic absorption bands. Warming the matrix sharpens the absorption bands of TiO and enhances the electronic and infrared absorption bands assigned to the TiO₂ neutral species. The presence of an absorption band at 935.6 cm⁻¹ in the infrared spectrum is due to the asymmetric stretching mode ($v_3$) of TiO₂ [19,20]. This is present after deposition and grows in intensity upon irradiation and annealing, as seen in Fig. 2, confirming the assignment. The fringe patterns in the infrared spectrum are due to interference of the light.

In order to avoid misassignment of the absorption bands, which could be due to the species $C_{2v}$ of TiO₂ with the same mass as TiO₂ (m/e = 80), experiments were also performed using TiO₂/graphite composite rods which led to the same results.

Irradiation and annealing of the neon matrix reveal two band systems in the visible range. The first one shows a progression commencing at 628 nm with a maximum near 540 nm and a vibrational spacing of about 840 cm⁻¹ (Fig. 1). No absorption band was observed at higher wavelengths suggesting that the origin band of this system is at 628 nm. The overlap and the presence of absorptions of titanium (at 530 nm) and titanium oxide in the range 520–550 nm, as observed in Fig. 1, make it difficult to locate the origin

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**Fig. 1.** Electronic absorption spectra recorded in a 6 K neon matrix: (a) after mass-selected deposition of TiO₂ produced from TiO₂/graphite composite rods in a cesium sputter ion source and (b) after subsequent UV irradiation and annealing of the matrix. Asterisks indicate the vibronic bands of the bent to bent electronic transition $B_2^0 → X' A_1$ of TiO₂. Squares are for the vibronic bands of TiO₂ linear, and circles for the absorption bands of TiO.

**Fig. 2.** Infrared spectrum recorded in a 6 K neon matrix: (a) after mass-selected deposition of TiO₂ produced from TiO₂/graphite composite rods in a cesium sputter ion source, (b) after UV irradiation ($λ > 305$ nm), and (c) after annealing of the matrix. The periodic structure in the baseline is an artefact (interference).
and vibrational members of the second band system. However, based on the intensity distribution, the onset of this absorption might be at 524 nm. This system is characterized by a long vibronic progression showing an irregular pattern between 460 and 520 nm indicating that two fundamental modes are active in the excited state leading to overtones and combination bands. Vibrational spacings of about 850 cm\(^{-1}\) and 180 cm\(^{-1}\) are inferred. The assignment was complicated owing to the broadness and the vicinity of the absorptions of TiO\(_2\) to those of TiO. As reported in Table 1, vibrational spacings on the linear form of TiO\(_2\) and TiO makes it also difficult to assign the TiO\(_2\) bands. Nevertheless, by looking at the spectra in detail, an absorption band of the anion was found around 540 nm (Fig. 1).

### 4. Assignment and discussion

The electronic system at shorter wavelengths has an origin band at 524 nm (2.37 eV) as seen in Fig. 1. This system corresponds to that one observed by emission at 529 nm (2.34 eV) [19] and photoelectron spectroscopy at 516 nm (2.40 eV) [4]. The long progression observed for this system indicates that the equilibrium Ti–O bond length and/or OTiO angle in the excited state differ from those in the ground state. As reported in Table 1, vibrational spacings of about 180 cm\(^{-1}\) are observed in this progression. These intervals are too small for any of the stretching modes of TiO\(_2\) and could only be assigned to excitations of its bending mode \(v_2\). The decrease of the bending frequency shows that the OTiO angle is smaller in the excited state. The larger vibronic spacings of about 850 cm\(^{-1}\) observed for this electronic system are assigned to excitations of the symmetrical stretching mode \(v_1\). The vibrational frequency being lower in the excited state than in the ground state is indicative that the bond length has increased.

Theoretical calculations carried out show that two of the bent excited states, \(^1B_2\) and \(^1B_2\), have a vertical excitation energy of 2.43 and 2.40 eV respectively at the MRCI level of theory, and 2.33 and 2.35 eV with DFT [27]. These values are close to our experimental result (2.37 eV). The transition to \(^1B_2\) is in addition predicted to have a quite high oscillator strength. Furthermore, the reported DFT calculations provide information on the structures of the excited states and indicate an elongation of the bond length as well as a decrease of the angle for the \(B_2\) excited states [27], in agreement with the observations. In addition, the \(v_1\) and \(v_2\) excitations observed in neon matrix (about 825 and 194 cm\(^{-1}\), Table 1) are in good agreement with the harmonic vibrational frequencies calculated for the optimized \(B_2\) states (about 880 and 195 cm\(^{-1}\)). In view of these comparisons, the electronic system is assigned to the dipole-allowed bent to bent electronic transition \(^1B_2\) \(\rightarrow \ X^1A_1\).

Consequently, the weak absorption band observed in the UV range at 368 nm (27.174 cm\(^{-1}\), 3.37 eV) is assigned to the \(^1B_1\) \(\rightarrow \ X^1A_1\) electronic transition in agreement with the vertical excitation energies of 3.57 and 3.66 eV calculated at the MRCl and DFT level of theory [27].

The electronic band system seen at longer wavelengths shows a vibronic progression with spacings of about 840 cm\(^{-1}\). The origin band observed at 628 nm (1.97 eV) is consistent with the system at 632 nm (1.96 eV) observed by photoelectron spectroscopy [4]. However, none of the bent excited states of TiO\(_2\) given in [27] have a vertical excitation energy lower than 2.40 eV. It is thus suggested that this electronic system is due to an other isomer of titanium dioxide.

Different isomers of titanium dioxide, as the linear OTiO, the peroxy (cyclic structure), and the superoxy (TiOO) ones, were investigated theoretically [21,23–27]. From these studies, the energetic ordering of these isomers is as follows: linear < peroxy < superoxy, with the bent one being the most stable. The linear isomer is found to lie 2 eV above the ground state of the bent one while the other two are much higher in energy at about 4.46 and 5.5 eV, respectively. The possibility to form the peroxy and superoxy isomers, being very high in energy, can be ruled out. Therefore, the only plausible isomer which could lead to the results obtained in neon matrix is the linear OTiO species. Photoelectron and solid matrices infrared studies of metal dioxides have shown that these species tend to have different structures [32–34] as the FeO\(_2\) species which has been trapped in a low temperature argon matrix in three different structures, with two of the isomers being 2.12 and 2.55 eV higher in energy than the most stable one [34]. Consequently, we suggest that the electronic band system with an origin at 628 nm is due to the linear isomer of titanium dioxide, with a \(^1\Sigma^+\) ground state. In addition, the vibrational interval observed in neon matrix for this electronic system (about 835 cm\(^{-1}\)) is consistent with the harmonic frequencies calculated for the \(v_1\) and \(v_2\) modes of the linear form (884 cm\(^{-1}\) and 854 cm\(^{-1}\) respectively) [27]. Because it is predicted that the \(v_2\) mode has no oscillator strength, the observed vibronic progression is due to excitations in the symmetric stretching \(v_1\) mode. No infrared absorption band of the linear isomer could be observed. Finally, it is worthwhile to note the persistence of the linear isomer after annealing of the matrix up to 8.5 K due to stabilization effects of the solid environment. Analogous observations were made for the high energy isomers of iron dioxide [34].

### 5. Conclusion

The electronic absorption spectrum of TiO\(_2\) in 6 K neon matrices is reported for the first time. The transitions observed reveal that titanium dioxide exists in both bent and linear forms in the matrix environment with absorptions in the visible and UV regions. Two electronic band systems with origins at 524 and 368 nm were observed and assigned to the bent \(^1B_2\) and \(^1B_1\) excited states of TiO\(_2\) whereas a transition with origin at 628 nm was found to be due to a linear isomer. As no higher excited states of the linear form have been calculated, assignment of the electronic transition has not been made. This opens the way for future theoretical calculations on the linear form of TiO\(_2\).

### Table 1

<table>
<thead>
<tr>
<th>Species</th>
<th>(\lambda) (nm)</th>
<th>(\nu) (cm(^{-1}))</th>
<th>(\delta) (cm(^{-1}))</th>
<th>Assignment</th>
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<tr>
<td>TiO(_2)</td>
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<td>15,924</td>
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<td>(^1B_2) (\rightarrow) (^1X^1A_1)</td>
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<td>568</td>
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<td></td>
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<td>(3v_1)</td>
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<td>(^1B_1) (\rightarrow) (^1X^1A_1)</td>
</tr>
<tr>
<td>TiO(_2)</td>
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<td>19,920</td>
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<td>497</td>
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<tr>
<td></td>
<td>485</td>
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<td>1535</td>
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<td>(^1B_1) (\rightarrow) (^1X^1A_1)</td>
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The results presented here provide data to complement existing spectroscopic and theoretical studies on titanium dioxide and will serve as a basis for gas-phase spectroscopic measurements which would be useful in the detection of this astrophysically important species. As titanium is one of the most abundant transition metals in space, its dioxide is thought to be the most promising candidate for the primary condensate in oxygen-rich circumstellar shells [35].

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References