Visible spectrum of titanium dioxide†

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The electronic spectrum in the region 17 500 cm−1 to 18 850 cm−1 of a cold molecular beam of TiO2 has been investigated using laser induced fluorescence (LIF) and mass-resolved resonance enhanced multi-photoionization (REMPI) spectroscopy. Bands at 18 412 cm−1, 18 470 cm−1 and 18 655 cm−1 were recorded at a resolution of 35 MHz, rotationally analyzed, and assigned as the A1′B2(0,1,2) ← X1′A1(0,0,0), A1′B2(1,0,0) ← X1′A1(0,0,0) and A2′B2(1,1,0) ← X1′A1(0,0,0) transitions. The dispersed fluorescence from the A1′B2(0,1,2) and A2′B2(1,0,0) levels were combined with previous results to produce an improved set of vibrational parameters for the X1′A1 state. The optical Stark effect in the A1′B2(0,1,2) ← X1′A1(0,0,0) and A1′B2(1,0,0) ← X1′A1(0,0,0) bands were recorded and combined with earlier results for A2′B2(1,1,0) ← X1′A1(0,0,0) to determine the permanent electric dipole moment for these states. The origin and harmonic and anharmonic vibrational constants for the A1′B2 states were determined to be: $\omega_{000} = 17 593(5)\text{ cm}^{-1}$, $\omega_1 = 876(3)\text{ cm}^{-1}$, $\omega_2 = 184(1)\text{ cm}^{-1}$, and $\omega_3 = 316(2)\text{ cm}^{-1}$. A normal coordinate analysis was performed and Franck–Condon factors calculated.

1. Introduction

There has been an intense effort to measure and predict the properties of the monomer and small clusters of TiO2 and to correlate the determined properties with those of the bulk material. Recently, we reported on the mass selected resonant enhanced multi-photon ionization (REMPI) and laser induced fluorescence (LIF) spectra of a supersonic molecular beam sample of TiO2. A strong band system at 18 655 cm−1 observed in the REMPI spectrum was recorded at high-resolution using LIF detection and the rotational structure analyzed. In addition, the optical Stark and dispersed LIF spectra of this band were measured and interpreted. Previously, this band was tentatively assigned as the A1′B2(0,0,0) ← X1′A1(0,0,0) transition. The assignment of the lower energy terminus as the X1′A1(0,0,0) state is indisputable because of the cold sample conditions, the agreement of the determined spectroscopic parameters with those derived from the analysis of the pure-rotational spectrum, and the observation of no features to the blue of the excitation wavelength in the dispersed LIF spectrum. The assignment of A1′B2 as the excited state is consistent with the most recent wavefunction based predictions and time dependent density functional theory (TDDFT) based predictions for the excitation energy of 2.33 eV and 2.22 eV, respectively. The assignment was also consistent with the photoelectron spectrum (PES). The PES recorded some time ago was interpreted to give term values for the A1′B2 and A2′B2 states of $15 800 \pm 800 \text{ cm}^{-1}$ and $19 350 \pm 1600 \text{ cm}^{-1}$, respectively.

The same group re-recorded the PES spectrum more recently at higher resolution. The measured $17 740 \pm 800 \text{ cm}^{-1}$ difference between the adiabatic detachment energies was interpreted as the splitting between the X1′A1 and A2′B2 states. The PES spectrum was assigned assuming that the A2′B2 state is lower in energy than the isoconfigurational A1′B2 state. The recent wavefunction based predictions and TDDFT predictions demonstrate that the A2′B2 and A1′B2 states are nearly degenerate and that peak in the higher resolution PES spectrum is due to both the A2′B2 and A1′B2 states.

It is difficult to explain the observed presence of bands to the red of 18 655 cm−1 in both the REMPI and low-resolution LIF (vide infra) with its assignment as the A1′B2(0,0,0) ← X1′A1(0,0,0) transition. Furthermore, it is expected (vide infra) that the A1′B2(0,0,0) ← X1′A1(0,0,0) vibronic transition would be a relatively weak spectral feature in both the REMPI and LIF spectra due to the observed change in structure. Specifically, the bond angle, $\theta$, and length, $R_{\text{Ti-O}}$, for the excited state of the 18 655 cm−1 band were determined to be 100.1° and 1.704 Å, respectively, from the rotational analysis whereas the corresponding values for the X1′A1(0,0,0) state, as derived from the microwave spectrum are 1.651 Å and 111.6°. Here we report on a thorough investigation of the optical spectrum of TiO2 to derive a global understanding of the complex excited vibronic state distribution. REMPI spectra with improved sensitivity for both the 48Ti18O2 and 48Ti16O2 isotopologues have been recorded and compared with the low-resolution LIF spectrum. Three bands to the red of the 18 655 cm−1 band, at 18 240 cm−1, 18 412 cm−1 and 18 470 cm−1, have been recorded at high resolution with LIF detection. The bands at 18 412 cm−1 and 18 470 cm−1 were analyzed to determine the excited state rotational parameters from which structures have been determined. Additional features in the 18 655 cm−1 band have also been measured and added to the previous data to produce an improved set of excited state parameters and structures. The determined inertial defects for
the three excited states are used to assign the 18 412 cm\(^{-1}\), 18 470 cm\(^{-1}\) and 18 655 cm\(^{-1}\) bands. The optical Stark spectrum of numerous branch features in the \(\tilde{A}^1 B_j (0,1,2) \leftrightarrow \tilde{X}^1 A_j (0,0,0)\) and \(\tilde{A}^1 B_2 (1,0,0) \leftrightarrow \tilde{X}^1 A_1 (0,0,0)\) bands have been recorded and combined with the previous and new measurements for the \(\tilde{A}^1 B_2 (1,1,0) \leftrightarrow \tilde{X}^1 A_1 (0,0,0)\) band\(^4\) to determine the permanent electric dipole moments, \(\mu\), for these states. The dispersed fluorescence spectra were recorded and combined with previous results to produce an improved set of vibrational parameters for the \(\tilde{X}^1 A_j\) state. Time-dependent fluorescence decay data for numerous bands in the 17 500 cm\(^{-1}\) to 18 850 cm\(^{-1}\) spectral range have been collected. The vibrational dependence of \(\mu\) and the lifetimes are discussed.

A relatively complete account of the experimental and theoretical studies of TiO\(_2\) can be found in ref. 1. In addition to the PES studies mentioned above, the electronic absorption spectroscopic studies of a neon matrix isolated TiO\(_2\) sample performed by the Basels\(^7\) group are of particular relevance. In those studies a mass selected deposition technique using TiO\(_2\) anions was employed and neutral TiO\(_2\) was generated by photo-detachment. Progressions in two band systems in the visible range were assigned. The origin of one band, having a vibrational progression with spacing of 840 cm\(^{-1}\), was at 628 nm. It was suggested that this band was due to an electronic transition for the linear isomer. The second band system exhibited two vibrational progressions, one with a spacing of 850 cm\(^{-1}\), and another of 180 cm\(^{-1}\). The origin of this band was difficult to assign because of overlapping TiO features, but was estimated to be 524 nm and assigned as the \(\tilde{A}^1 B_2 \leftrightarrow \tilde{X}^1 A_1\) transition of the bent oxo (O=Ti=O) form. A third, weak, band system with an origin at 368 nm was assigned as the \(\tilde{C}^1 B_1 \leftrightarrow \tilde{X}^1 A_1\) transition of the same isomer.

2. Experimental

The experimental set-up for the REMPI, LIF, dispersed LIF and optical Stark measurements are nearly identical to that of the previous study.\(^1\) A cold molecular beam sample of TiO\(_2\) was generated by laser ablation of a solid titanium rod in the presence of a supersonic expansion of a 95% Ar or He/5% O\(_2\) mixture. The mass selected REMPI spectra of Ti\(^{16}\)O\(_2\) were obtained using \(^{16}\)O\(_2\). REMPI spectra were recorded at the University of Basel (UB) and a description of the spectrometer can be found in ref. 8 and references therein. Low-resolution (\(\Delta \nu = \pm 90\) GHz) REMPI spectra were recorded using an OPO system (excitation laser) and an F\(_2\) excimer laser (\(\lambda = 157\) nm) as the ionization source. The high and low resolution LIF, dispersed fluorescence, optical Stark and radiative lifetime measurements were performed at Arizona State University. The expansion was skimmed to produce a well collimated molecular beam which was probed 0.5 metre from the source with a cw- or pulsed dye laser. The fluorescence was viewed either through a 650 nm long-pass filter or a 2/3 metre monochromator and detected with a cooled photon-multiplier. The dispersed fluorescence spectra were recorded by scanning the monochromator. The low-resolution LIF spectra were recorded by replacing the single longitudinal mode cw-dye laser with a pulsed dye laser that had a spectral resolution of 0.05 cm\(^{-1}\). The lifetimes were measured using this pulsed laser system. The fluorescence decay was viewed through a 650 ± 70 nm band-pass filter, detected with a cooled PMT and recorded directly on a digital storage oscilloscope.

The Stark plate assembly and calibration procedure was modified from that of the previous study in an effort to reduce systematic errors. The Stark plates consisted of one solid polished stainless steel disc 10 cm in diameter and 0.5 cm thick and a 5 x 5 cm square neutral density filter that transmitted approximately 90% of the light for the second plate. The field strength was determined by analysis of the optical Stark spectra of a secondary standard.\(^9\) The calibration procedure demonstrated that the systematic errors of the determined \(\mu\) values are less than 1%.

3. Observation

The \(^{48}\)Ti\(^{16}\)O\(_2\) and \(^{48}\)Ti\(^{18}\)O\(_2\) mass-selected REMPI spectra in the 17 500 cm\(^{-1}\) to 23 000 cm\(^{-1}\) region are presented in Fig. 1 and the transition wavenumbers and assignment (vide infra) are given in Table 1. There are no features to the red of 17 500 cm\(^{-1}\). The \(^{48}\)Ti\(^{16}\)O\(_2\) and \(^{48}\)Ti\(^{18}\)O\(_2\) REMPI and the low-resolution LIF spectra in the 17 500 cm\(^{-1}\) to 18 900 cm\(^{-1}\) region are presented in Fig. 2. The relative intensities and shape of the bands of the REMPI spectrum are generally in excellent agreement with those of the LIF spectrum. The \(\tilde{A}^1 B_2 (0,2,0) \leftrightarrow \tilde{X}^1 A_1 (0,0,0) (\nu = 17 960\) cm\(^{-1}\)) band appears slightly more intense in the LIF than in the REMPI spectrum because of spectral overlap with the \(B^2 \Pi (\nu = 3) \leftrightarrow X^2 \Delta (\nu = 0)\) transition of TiO.\(^10\) The \(\tilde{A}^1 B_2 (1,1,0) \leftrightarrow \tilde{X}^1 A_1 (0,0,0) (\nu = 18 655\) cm\(^{-1}\)) band is also overlapped, but to a much lesser extent, with the \(B^2 \Pi (\nu = 3) \leftrightarrow X^2 \Delta (\nu = 0)\) transition of TiO. The \(\tilde{A}^1 B_2 (1,1,0) \leftrightarrow \tilde{X}^1 A_1 (0,0,0) (\nu = 18 655\) cm\(^{-1}\)) band was the subject of the previous high-resolution study\(^1\) and the \(\tilde{A}^1 B_2 (0,0,2) \leftrightarrow \tilde{X}^1 A_1 (0,0,0) (\nu = 18 240\) cm\(^{-1}\)), \(\tilde{A}^1 B_2 (0,1,2) \leftrightarrow \tilde{X}^1 A_1 (0,0,0) (\nu = 18 412\) cm\(^{-1}\)), \(\tilde{A}^1 B_2 (1,0,0) \leftrightarrow \tilde{X}^1 A_1 (0,0,0) (\nu = 18 470\) cm\(^{-1}\)) transitions were recorded at high resolution presently. These bands were selected because they are the most intense features in the operating range (\(\lambda = 850\) nm to 525 nm) of the high-resolution spectrometer. The \(\tilde{A}^1 B_2 (0,0,0) \leftrightarrow \tilde{X}^1 A_1 (0,0,0) (\nu = 17 591\) cm\(^{-1}\)) band is too weak for high-resolution

![Fig. 1](image-url) The \(^{48}\)Ti\(^{16}\)O\(_2\) and \(^{48}\)Ti\(^{18}\)O\(_2\) mass-selected REMPI in the 17 500 cm\(^{-1}\) to 23 000 cm\(^{-1}\) region.
The observed and predicted high resolution LIF spectrum of the $\tilde{A}^1B_2(0,1,2) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18412 \text{ cm}^{-1}$) and $\tilde{A}^1B_2(1,0,0) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18470 \text{ cm}^{-1}$) bands are presented in Fig. 3 and 4. The “stick spectra” were obtained using the final optimized set of spectroscopic parameters (see below). The $\tilde{A}^1B_2(0,1,2) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18412 \text{ cm}^{-1}$) band is less complicated because the source conditions were optimized to produce a lower rotational temperature (approx. 8 K vs. 20 K). TiO$_2$ is experimentally determined to be a near prolate asymmetric top in the $\tilde{X}^1A_1$ state with the $b$-inertia axis coinciding with the $C_2$ symmetry axis. The observed fine level structure of the $\tilde{A}^1B_2(1,0,0) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18655 \text{ cm}^{-1}$) band demonstrated that the excited state is also a near prolate asymmetric top with the $b$-inertia axis coinciding with the $C_2$ symmetry axis, consistent with $B_2$ vibronic symmetry. It is expected that all of the intense visible LIF and REMPI spectral features involve transitions to vibrational levels of the $\tilde{A}^1B_2$ state that have a combined $a_1$ symmetry (i.e. $\tilde{A}^1B_2(\nu,\nu_2,2 \times \nu_3)$ vibronic levels). The allowed rotational levels of the $\tilde{X}^1A_1(0,0,0)$ vibronic state have ($K_a, K_c$) $e$ ($A_1$) and $0$ ($A_2$). The allowed levels for the $\tilde{A}^1B_2(\nu,\nu_2,2 \times \nu_3)$ bands are $e$ ($B_1$) and $o$ ($B_2$) rotational levels. The analysis of the $\tilde{A}^1B_2(1,0,0) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18412 \text{ cm}^{-1}$) band, as well as the $\tilde{A}^1B_2(0,1,2) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18655 \text{ cm}^{-1}$) and $\tilde{A}^1B_2(1,0,0) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18470 \text{ cm}^{-1}$) bands (vide infra), reveals that only the $e$ and $o$ excited state levels exist, as expected for the $\tilde{A}^1B_2(\nu,\nu_2,2 \times \nu_3)$ vibronic states.

As was the case for the $\tilde{A}^1B_2(1,1,0) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18655 \text{ cm}^{-1}$) band, the $\tilde{A}^1B_2(0,1,2) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18412 \text{ cm}^{-1}$) and $\tilde{A}^1B_2(1,0,0) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18470 \text{ cm}^{-1}$) bands have been assigned as parallel ($\Delta K_a = 0$), $a$-type transitions. The $\Delta K_a = 0$, $K_c = 0$, 1, 2, . . . bands are all present and overlap resulting in complex spectra. A total of 135 and 64 lines for $\tilde{A}^1B_2(0,0,0) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18470 \text{ cm}^{-1}$) and $\tilde{A}^1B_2(0,1,2) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18614 \text{ cm}^{-1}$) bands, respectively, were precisely measured and assigned and used as the input to a least square fitting procedure. The data set for the 18470 cm$^{-1}$ band includes principle rotational quantum number, $N$, values up to 17 and $K_a$ values from 0 to 6. The 18412 cm$^{-1}$ band, which was recorded under colder conditions, includes transitions involving $N$ quantum numbers to only 11 and $K_a$ values from 0 to 4. Portions of the $\tilde{A}^1B_2(1,1,0) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18655 \text{ cm}^{-1}$) band were re-recorded under improved conditions and the previous data set was expanded from 87 lines to 116. The measured transition wavenumbers, branch assignment and the difference between the measured and observed values for the $\tilde{A}^1B_2(0,1,2) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18412 \text{ cm}^{-1}$), $\tilde{A}^1B_2(1,0,0) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18470 \text{ cm}^{-1}$), and $\tilde{A}^1B_2(1,0,0) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18655 \text{ cm}^{-1}$) bands are presented in Tables S1-S3 (ESI).

A portion of the dispersed LIF spectrum resulting from the excitation of the P717 ($\nu = 18468.0024 \text{ cm}^{-1}$) line of the $\tilde{A}^1B_2(1,0,0) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18470 \text{ cm}^{-1}$) band and excitation of the R262 ($\nu = 18413.6653 \text{ cm}^{-1}$) of $\tilde{A}^1B_2(0,1,2) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18412 \text{ cm}^{-1}$) is presented in Fig. 5. No features to the blue of the excitation wavelength were observed, which confirms that the lower state associated with these two transitions is the $\tilde{X}^1A_1(000)$ ground state. The dispersed LIF spectrum of the $\tilde{A}^1B_2(1,0,0) \leftrightarrow \tilde{X}^1A_1(0,0,0)$ ($\nu = 18470 \text{ cm}^{-1}$)
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band is similar to that previously observed for $\tilde{A}^1B_2$ (1,1,0) $\leftrightarrow \tilde{X}^1A_1$ (0,0,0) ($v = 18 655 \text{ cm}^{-1}$) and exhibits a long progression in the bending mode $\nu_2(a_1)$. The dispersed LIF spectrum of the $\tilde{A}^1B_2$ (0,1,2) $\leftrightarrow \tilde{X}^1A_1$ (0,0,0) ($v = 18 412 \text{ cm}^{-1}$) band is very different. The first prominent feature is shifted to the red by about 950 cm$^{-1}$ relative to the laser and is assigned as emission to the symmetric stretching mode, $\tilde{X}^1A_1$ (1,0,0). The symmetric stretching frequency $\omega_1$ for the $\tilde{X}^1A_1$ state is nearly equal to $3 \times \omega_2$ and the two dispersed LIF features cannot be resolved in our experiment. The observed features to longer wavelength in the dispersed fluorescence spectrum of the $\tilde{A}^1B_2$ (0,1,2) $\leftrightarrow \tilde{X}^1A_1$ (0,0,0) ($v = 18 412 \text{ cm}^{-1}$) transition are assigned to a progression in the combination bands (i.e. $\tilde{A}^1B_2$ (0,1,2) $\rightarrow \tilde{X}^1A_1$ (1,$\nu_2$,0)). The measured wavelength shifts of the dispersed LIF spectra for the 18 470 cm$^{-1}$ and 18 412 cm$^{-1}$ bands, along with the previous measurements for the 18 655 cm$^{-1}$ band, are given in Table 2.

The LIF decay curves for all the intense bands in the 17 590 cm$^{-1}$ to 18 840 cm$^{-1}$ region were recorded. The curves exhibit a nearly pure single exponential dependence for times less than 3 $\mu$s. The resulting fitted lifetimes, $\tau$, and assignments are collected in Table 3. The data for times greater than 3 $\mu$s were excluded from the fit because the molecules drift out of the 1 mm LIF collection distance.

The $R_{111}(\nu = 18 412.8197 \text{ cm}^{-1})$, $R_{202}(\nu = 18 413.6653 \text{ cm}^{-1})$ and $Q_{111}(\nu = 18 411.9723 \text{ cm}^{-1})$ lines of the $\tilde{A}^1B_2$ (0,1,2) $\leftrightarrow \tilde{X}^1A_1$ (0,0,0) ($v = 18 412 \text{ cm}^{-1}$) band and the $P_{202}(\nu = 18 470.6002 \text{ cm}^{-1})$ and $P_{313}(\nu = 18 469.8661 \text{ cm}^{-1})$ of $\tilde{A}^1B_2$ (1,0,0) $\leftrightarrow \tilde{X}^1A_1$ (0,0,0) ($v = 18 470 \text{ cm}^{-1}$) were selected for optical Stark
measurements because they are intense, unblended, and exhibit rapid tuning. Additional Stark measurements for the R202 (ν = 18657.9870 cm$^{-1}$) line and new measurements for the P202 (ν = 18655.1047 cm$^{-1}$) of the $\tilde{A}^1B_2 (1,0,0)$ ← $\tilde{X}^3\tilde{A}_1 (0,0,0)$ band were also performed due to the improved field calibration and enhanced signal-to-noise ratio. The observed Stark spectra for the R202 line of the 18 412 cm$^{-1}$ band recorded field-free and in the presence of an electric field of 2507 V cm$^{-1}$, with parallel and perpendicular orientation are presented in Fig. 7. The associated energy levels as a function of applied electric field and spectral assignments are also shown in Fig. 6 and 7. The observed Stark shifts, quantum number assignments and difference between the observed and calculated shifts obtained by using the optimized dipole moments (vide infra) for the three bands are given in Table 4.

4. Analysis
The vibrational frequencies, $\omega_1$ and $\omega_2$, for the symmetric stretching, $\nu_1(a_1)$, and bending, $\nu_2(a_1)$, modes for the $\tilde{X}^3\tilde{A}_1$ state were obtained by fitting the dispersed fluorescence data given in Table 2 to a simple harmonic oscillator model. The determined $\omega_1$ and $\omega_2$ values and associated errors for fits to the individual bands and a fit to the combined data are presented in Table 2. The analysis of the high resolution LIF spectrum was identical to the previous work. The field free energy levels of the $\tilde{X}^3\tilde{A}_1 (0,0,0)$, $\tilde{A}^1B_1 (0,1,2)$, $\tilde{A}^1B_2 (1,0,0)$ and $\tilde{A}^1B_2 (1,0,0)$ states were analyzed by using the optimized dipole moments (vide infra) for the three bands are given in Table 4.
A\tilde{1}B_2 (1,1,0) vibronic states were modeled using a Watson A-reduced Hamiltonian operator.\textsuperscript{11} The matrix representation was constructed using a Wang transformed linear combination of prolate symmetric top basis functions. The ground state parameters were held fixed to the values determined from the pure rotational spectrum,\textsuperscript{2} which used the same model Hamiltonian. Only the $D_K$ quartic centrifugal distortion parameter for the $A\tilde{1}B_2$ state was required. The standard deviation of the fits were 27 MHz, 38 MHz and 36 MHz, for the $A\tilde{1}B_2$ (0,1,2) $\leftrightarrow \tilde{X} \tilde{A}_1 (0,0,0)$ ($\nu = 18413.6653$ cm$^{-1}$), $A\tilde{1}B_2$ (1,0,0) $\leftrightarrow \tilde{X} \tilde{A}_1 (0,0,0)$ ($\nu = 18470$ cm$^{-1}$), and $A\tilde{1}B_2$ (1,1,0) $\leftrightarrow \tilde{X} \tilde{A}_1 (0,0,0)$ ($\nu = 18655$ cm$^{-1}$) bands which are commensurate with the estimated measurement uncertainty. The optimized parameters ($A$, $B$, $C$, $D_K$ and origin) along with the error estimates for the $A\tilde{1}B_2$ (0,1,2), $A\tilde{1}B_2$ (1,0,0) and $A\tilde{1}B_2$ (1,1,0) vibronic states are given in Table 5. The bond angle, $\theta$, bond distance, $R_{Ti-O}$, and inertial defect, $\delta$, derived from the rotational parameters are also presented.

The behavior of the energy levels in the presence of the applied electric field was modeled by:

$$\hat{H}_{\text{Stark}} = -\mu \vec{E} \quad (1)$$

Fig. 6 The optical Stark spectrum of the $R_{2\alpha}(\nu = 18413.6653$ cm$^{-1}$) line of the $A\tilde{1}B_2 (0,1,2) \leftrightarrow \tilde{X} \tilde{A}_1 (0,0,0)$ transition of TiO$_2$ and associated energy levels recorded field-free and at 1833 V cm$^{-1}$ with parallel (I) and perpendicular ($\perp$) orientation. The spectral features marked the ‘*' are Stark shifted components of the $R_{3\alpha}(\nu = 18413.7091$ cm$^{-1}$) line. The energy level pattern was predicted using the parameters in Table 5.

Fig. 7 The optical Stark spectrum of the $P_{2\alpha}(\nu = 18470.6002$ cm$^{-1}$) line of the $A\tilde{1}B_2 (1,0,0) \leftrightarrow \tilde{X} \tilde{A}_1 (0,0,0)$ transition of TiO$_2$ and associated energy levels recorded field-free and at 2507 V cm$^{-1}$ with parallel (I) and perpendicular ($\perp$) orientation. The energy level pattern was predicted using the parameters in Table 5.
Table 4 The observed and calculated shifts of TiO₂

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<td>±1</td>
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<td>±1</td>
<td>614</td>
<td>−20</td>
<td>±1</td>
<td>±1</td>
</tr>
</tbody>
</table>

Table 5 The spectroscopic parameters for \( \tilde{X}^1A_1 \) (0,0) and \( \tilde{A}^1B_2 \) (ν₁,ν₂,2 × ν₃) states of TiO₂

<table>
<thead>
<tr>
<th>Parameters</th>
<th>( \tilde{A}^1B_2 ) (0,1,2)</th>
<th>( \tilde{A}^1B_2 ) (1,0,0)</th>
<th>( \tilde{A}^1B_2 ) (1,1,0)</th>
<th>( \tilde{X}^1A_1 ) (0,0,0)</th>
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</thead>
<tbody>
<tr>
<td>A/cm⁻¹</td>
<td>0.755732(65)²</td>
<td>0.711659(65)²</td>
<td>0.734474(89)²</td>
<td>1.018056⁶</td>
</tr>
<tr>
<td>B/cm⁻¹</td>
<td>0.300502(16)</td>
<td>0.310784(10)</td>
<td>0.308565(10)</td>
<td>0.282586⁶</td>
</tr>
<tr>
<td>C/cm⁻¹</td>
<td>0.211883(10)</td>
<td>0.215151(46)</td>
<td>0.213527(4)</td>
<td>0.220606⁶</td>
</tr>
<tr>
<td>Dₙ/cm⁻¹</td>
<td>0</td>
<td>0.00014(2)</td>
<td>0.000304(4)</td>
<td>0.0000244⁶</td>
</tr>
<tr>
<td>Origin/cm⁻¹</td>
<td>18412.1538(35)</td>
<td>18471.5815(38)</td>
<td>18656.4313(38)</td>
<td>0</td>
</tr>
<tr>
<td>Standard dev.</td>
<td>0.0009</td>
<td>0.0013</td>
<td>0.0012</td>
<td>—</td>
</tr>
<tr>
<td>A/amu Å⁻¹</td>
<td>1.156</td>
<td>1.156</td>
<td>1.156</td>
<td>1.156</td>
</tr>
<tr>
<td>θ/⁰</td>
<td>1.0167</td>
<td>1.0167</td>
<td>1.0167</td>
<td>1.0167</td>
</tr>
<tr>
<td>R₁₁,₀/Å</td>
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<td>1.708</td>
<td>1.708</td>
<td>1.708</td>
</tr>
<tr>
<td>μ/Debye</td>
<td>4.80(11)</td>
<td>4.98(7)</td>
<td>6.79(4)</td>
<td>6.11(10)</td>
</tr>
<tr>
<td>θ/⁰—theory</td>
<td>96.3²</td>
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<td>108.2°</td>
<td>108.2°</td>
</tr>
<tr>
<td>R₁₁,₀/Å—they</td>
<td>1.703²</td>
<td>1.651°</td>
<td>1.651°</td>
<td>1.651°</td>
</tr>
</tbody>
</table>

* Difference between the observed and calculated shifts obtained using the optimized dipole moments.

where \( \tilde{E} \) is the applied static electric field vector. The matrix representation of \( \tilde{H}^\text{Stark} \) is block diagonal in \( M_N \), the projection of the total angular momentum along the electric field axis, and of infinite dimension. The representation was truncated to include the nuclear spin statistic allowed levels for \( N = 0-4 \) resulting in the 13 × 13 and 12 × 12 representation for \( \tilde{X}^1A_1 \) (0,0,0) and \( \tilde{A}^1B_2 \) (ν₁,ν₂,2 × ν₃) vibronic states, respectively. The Stark shifts of Table 4 were input to a non-linear least-squares fitting program to obtain optimized \( \mu \) values and associated errors. A simultaneous fit for all three bands was performed as means of reducing the statistical error for \( \mu \) of the \( \tilde{X}^1A_1 \) (0,0,0) state. The results are presented in Table 5. The correlation coefficients were all less than 0.5. The errors represent a statistical 90% confidence limit. Due to the improved calibration scheme, the systematic errors are estimated to be <1%. The
standard deviation of the fit was 20 MHz, which is commensurate with the estimated measurement uncertainty.

Modeling the spectra was essential for the field free and Stark analysis. The intensities were calculated by generating the electric dipole transition moment when this is then squared, and multiplied by a Boltzmann factor. The transition moment for each spectral feature was obtained by cross multiplication of the prolate symmetric top electric-dipole transition moment matrix with the eigenvectors for the $\tilde{X}^1 A_1$ and $\tilde{A}^1 B_2$ states.

5. Discussion

The inertial defects, $\Delta$, for the excited states associated with the transitions at 18 412 cm$^{-1}$, 18 470 cm$^{-1}$ and 18 655 cm$^{-1}$ vary significantly with that for the 18 470 cm$^{-1}$ transition (0.422 amu Å$^2$) being considerably less than that for the 18 655 cm$^{-1}$ (1.364 amu Å$^2$) and 18 412 cm$^{-1}$ (1.165 amu Å$^2$) transitions. It has been shown that the inertial defect has contributions from vibrational and electronic motion and centrifugal distortions.$^{12,13}$

$$\Delta = \Delta^{\text{vib}} + \Delta^{\text{dec}} + \Delta^{\text{cent}}.$$  \hspace{1cm} (2)

The centrifugal distortion contribution is normally very small and will be ignored. The electronic part results from off-diagonal matrix elements of the orbital angular momentum operator and should be nearly independent of vibrational excitation. The observed large variation in $\Delta$ for the three vibronic states indicates that the dominant contribution to $\Delta$ is due to $\Delta^{\text{vib}}$. Therefore, the observed inertial defects can be used to assign the vibrational quantum numbers of the excited states. A similar procedure was used for assigning the electronic spectrum of SO$_2$.$^{14}$

For an XY$_2$ molecule of C$_{2v}$ symmetry, $\Delta^{\text{vib}}$ is related to the Coriolis coupling constants, $\zeta_{ik}$, by$^{12,13}$

$$\Delta^{\text{vib}} = \frac{\hbar}{4\pi^2 \varepsilon_{\text{L}}^2} \left[ (v_1 + \frac{1}{2}) \left( \frac{-\omega_1^2 - \omega_2^2}{\omega_1 \omega_3} \right) r_{23}^2 + (v_2 + \frac{1}{2}) \left( \frac{-\omega_2^2 - \omega_3^2}{\omega_2 \omega_3} \right) r_{23}^2 + (v_3 + \frac{1}{2}) \left( \frac{-\omega_3^2 - \omega_1^2}{\omega_3 \omega_1} \right) r_{23}^2 \right],$$  \hspace{1cm} (3)

where $\omega_i$’s are the harmonic vibrational frequencies. Assuming that the excited vibronic states of the bands at 17 591 cm$^{-1}$, 17 776 cm$^{-1}$, 18 234 cm$^{-1}$ and 18 470 cm$^{-1}$ are the (0,0,0), (0,1,0), (0,0,2) and (1,0,0) vibrational levels of the $\tilde{A}^1 B_2$ state, then initial estimates for $\omega_1$, $\omega_2$ and $\omega_3$ are 879 cm$^{-1}$, 185 cm$^{-1}$ and 321 cm$^{-1}$, respectively. The ab initio predicted values$^3$ are 874 cm$^{-1}$, 185 cm$^{-1}$ and 480 cm$^{-1}$. The required Coriolis coupling constants, $\zeta_{ik}$, needed for the prediction of $\Delta^{\text{vib}}$ can be obtained using the results of a Wilson GF matrix method$^{15}$ normal mode analysis. Specifically,$^{13}$

$$\zeta_{13} = \frac{\zeta_{13}^{\text{calc}}}{\omega_1 \omega_3},$$  \hspace{1cm} (4)

and

$$\zeta_{23} = \frac{\zeta_{23}^{\text{calc}}}{\omega_2 \omega_3},$$  \hspace{1cm} (5)

where $F_{11}$ is the element of the force matrix and $(G^{-1})_{11}$ is an element of the inverse of the geometry matrix constructed in the internal symmetry coordinates $S_1 = \frac{1}{\Delta}(\Delta_1 + \Delta_2)$ and $S_2 = \tau \Delta$. Normal mode analyses for the $\tilde{A}^1 B_2$ and $\tilde{X}^1 A_1$ states using experimental vibrational frequencies and structure are given in Appendix A. The determined values of $F_{11}$, $(G^{-1})_{11}$, $\lambda_1$ and $\lambda_2$ for the $\tilde{A}^1 B_2$ state are 5.692 mdyn Å$^{-1}$, 13.355 amu, 0.4552 mdyn Å$^{-1}$ amu$^{-1}$ and 0.02015 mdyn Å$^{-1}$ amu$^{-1}$, which upon substitution into eqn (4) and (5) give 0.0665 and 0.9335 for $\zeta_{13}$ and $\zeta_{23}$, respectively. $\bar{A}^{\text{vib}} (0.1,2)$, $\bar{A}^{\text{vib}} (1,0,0)$ and $\bar{A}^{\text{vib}} (1,1,0)$ are then calculated using eqn (3) to be 1.124 amu Å$^2$, 0.424 amu Å$^2$ and 1.435 amu Å$^2$, respectively, which are in excellent agreement with observed values of 1.156 amu Å$^2$, 0.422 amu Å$^2$ and 1.364 amu Å$^2$ for the vibronic states at 18 412 cm$^{-1}$, 18 470 cm$^{-1}$ and 18 655 cm$^{-1}$. The 18 412 cm$^{-1}$, 18 470 cm$^{-1}$ and 18 655 cm$^{-1}$ bands can unambiguously be assigned as the $\tilde{A}^1 B_2$ (0,1,2) $\leftrightarrow \tilde{X}^1 A_1$ (0,0,0), $\tilde{A}^1 B_2$ (1,0,0) $\leftrightarrow \tilde{X}^1 A_1$ (0,0,0) and $\tilde{A}^1 B_2$ (1,1,0) $\leftrightarrow \tilde{X}^1 A_1$ (0,0,0) transitions, respectively. Assignment of the remaining bands follows from the initial estimates of $\omega_1$, $\omega_2$ and $\omega_3$ values.

The observed transition wavenumbers of the low-resolution LIF spectrum were fit to the phenomenological expression:$^{16}$

$$G(v_1, v_2, v_3) = T_\infty + \sum_{i=1,3} \omega_i (v_i + \frac{1}{2})$$
$$+ \sum_{i=1,3} \sum_{k=-1,1} x_{ik} (v_i + \frac{1}{2})(v_k + \frac{1}{2}),$$  \hspace{1cm} (6)

using the assigned vibrational quantum numbers. Only the bands measured with LIF (Fig. 2) were used because of the lower measurement error ($\pm 0.5$ cm$^{-1}$) compared to the REMPI ($\pm 3$ cm$^{-1}$). In the end the coupling terms, $x_{ik}$, were not required. The resulting optimized $T_\infty$ and $\omega_i$ values for the $\tilde{A}^1 B_2$ state are presented in Table 6. The energy of the $\tilde{A}^1 B_2$ state is determined to be 18 020 cm$^{-1}$ by combining the zero point energies for the $\tilde{A}^1 B_2$ state ($\sim 691.5$ cm$^{-1}$) and $\tilde{X}^1 A_1$ ($\sim 1118.5$ cm$^{-1}$) with $T_\infty$. The predicted $T_\infty$ values for the $\tilde{A}^1 B_2$ state from the recent MRCl$^2$ and DFT$^4$ calculations are 19 400 cm$^{-1}$ and 16 800 cm$^{-1}$, respectively. Note that the experimentally determined $\omega_i$($\tilde{A}^1 B_2$) (316(2) cm$^{-1}$) is significantly less than the MRCl predicted$^3$ value (480 cm$^{-1}$).

A comparison with the previous PES$^{5,6}$ and the matrix isolation measurement$^7$ is warranted. The band system with an origin at 628 nm observed in the absorption spectrum of a neon matrix isolated sample$^7$ was not detected in the gas phase sample studied here. This is consistent with the assignment of ref. 7 that the carrier of that band is the higher energy linear isomer which is expected to not be present in the laser ablation products. The observed $\tilde{A}^1 B_2$ (0,0,0) $\leftrightarrow \tilde{X}^1 A_1$ (0,0,0) ($\nu = 17 591$ cm$^{-1}$) band is shifted to the red by nearly 1500 cm$^{-1}$ compared to the 524 nm ($\sim 19 080$ cm$^{-1}$) origin assigned in the neon matrix isolation study.$^7$ This unrealistically large matrix shift suggests that the first features of the progression observed in the neon matrix spectrum were too weak to be observed. The separation of the first two peaks in the PES spectrum$^5$ is 17 740 ± 800 cm$^{-1}$ consistent with the
Table 6: Measured and predicted LIF transition wavenumbers and Franck-Condon factors for TiO²⁻

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Transition wavenumber/cm⁻¹</th>
<th>Predicted</th>
<th>FCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,0,0 → 0,1,2,3</td>
<td>17593.0</td>
<td>17594.4</td>
<td>-1.4</td>
</tr>
<tr>
<td>0,1,0</td>
<td>17776.1</td>
<td>17779.0</td>
<td>-2.9</td>
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<td>0,2,0</td>
<td>17563.0</td>
<td>17563.7</td>
<td>-0.7</td>
</tr>
<tr>
<td>0,3,0</td>
<td>18152.7</td>
<td>18148.3</td>
<td>4.4</td>
</tr>
<tr>
<td>0,0,2</td>
<td>18231.0</td>
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<td>2.6</td>
</tr>
<tr>
<td>0,4,0</td>
<td>18333.6</td>
<td>18332.9</td>
<td>0.7</td>
</tr>
<tr>
<td>0,1,2</td>
<td>18413.5</td>
<td>18413.0</td>
<td>0.5</td>
</tr>
<tr>
<td>1,0,0</td>
<td>18472.9</td>
<td>18470.4</td>
<td>2.4</td>
</tr>
<tr>
<td>0,2,2</td>
<td>18594.4</td>
<td>18597.6</td>
<td>-3.8</td>
</tr>
<tr>
<td>1,1,0</td>
<td>18655.9</td>
<td>18655.1</td>
<td>0.8</td>
</tr>
<tr>
<td>1,2,0</td>
<td>18856.4</td>
<td>18859.7</td>
<td>-3.3</td>
</tr>
</tbody>
</table>

a Measured maximum intensity peak in the low-resolution LIF spectrum (Fig. 2). Predicted using optimized parameters (in cm⁻¹) \( T_{\text{m00}} = 17.593(5), \omega_0 = 876(3), \omega_2 = 184(1), \omega_3 = 316(2) \). Predicted Franck-Condon factors.

The \( \tilde{A}^2 B_2 (0,0,0) \) ← \( \tilde{X}^2 A_1 (0,0,0) \) transition is described in Appendix B. The one-dimensional integral associated with the two \( a_1 \)-modes and FC factors are relatively narrow (FWHM ≈ 0.4 eV).

The low resolution LIF and REMPI spectra were predicted using the determined \( T_i \) and \( \omega_i \) values for the \( \tilde{A}^2 B_2 \) state and predicted Franck-Condon factors (FCF). The FCF for the \( \tilde{A}^2 B_2 (ν_1, ν_2, ν_3) \) ← \( \tilde{X}^2 A_1 (0,0,0) \) transitions can be calculated using simple analytical expressions, if it is assumed that the \( \tilde{A}^2 B_2 \) and \( \tilde{X}^2 A_1 \) potentials can be modeled as displaced and distorted harmonic oscillators. Under these assumptions the FCF is given as the product of the square of two-dimensional integral associated with the two \( a_1 \)-modes and the square of the one-dimensional integral associated with the \( b_2 \) mode:

\[
\text{FCF} = |\langle 0,0 | ν_1 ν_2 \rangle|^2 |\langle 0 | ν_3 \rangle|^2.
\] (7)

The evaluation of the two dimensional integral, \( \langle 0,0 | ν_1 ν_2 \rangle \), which was evaluated using the analytical expression from ref. 19, is described in Appendix B. The one-dimensional integral, \( \langle 0 | ν_3 \rangle \), was evaluated using the analytical expression of ref. 20. With the exception of \( \omega_i (\tilde{X}^2 A_1) \), which was taken from ref. 3, only experimental data (bond lengths, bond angles, and harmonic frequencies) were used in the FCF calculation. The calculated \( \omega_i (\tilde{X}^2 A_1) \) value of 946 cm⁻¹ is close to the value determined from the infrared absorption spectroscopic study of a matrix isolated sample of 917.1 cm⁻¹.

Under the customary assumption that the geometric displacement of the asymmetric stretch normal coordinate, \( ΔQ_3 \), is zero, the values for \( |\langle 0 | 0 \rangle|^2 \) and \( |\langle 0 | 2 \rangle|^2 \) are calculated to be 0.866 and 0.107. Consequently the transitions to vibronic levels involving excitation of \( ν_3 \) in the \( \tilde{A}^2 B_2 \) state (e.g. \( \tilde{A}^2 B_2 (002) \) ← \( \tilde{X}^2 A_1 (000) \)) are predicted to be significantly less intense than the transitions for which \( ν_3 = 0 \) (e.g. the \( \tilde{A}^2 B_2 (000) \) ← \( \tilde{X}^2 A_1 (000) \)). As is evident from Fig. 1 and 2 the \( \tilde{A}^2 B_2 (002) \) ← \( \tilde{X}^2 A_1 (000) \) band is actually observed to be more intense than the \( \tilde{A}^2 B_2 (000) \) ← \( \tilde{X}^2 A_1 (000) \) band.
6. Conclusion

The inertial defect has been used to assign the visible spectrum of TiO$_2$ in the region from 17 500 cm$^{-1}$ to 19 000 cm$^{-1}$. The geometric structure and permanent electric dipole moments for the $\tilde{A}$B$_2$ (0,1,2), $\tilde{A}$B$_2$ (1,0,0) and $\tilde{A}$B$_2$ (1,1,0) vibronic states have been accurately determined. Normal mode analyses for the $\tilde{A}$B$_2$ and $\tilde{X}$A$_1$ states have been performed from which force constants and FCF were predicted. The trend in excited state dipole moments, FCF and radiative lifetimes indicates strong vibronic coupling, particularly for the $\nu_3$ mode. The precisely determined permanent electric dipole moments, structure and term energies for the $\tilde{X}$A$_1$ and $\tilde{A}$B$_2$ states will serve as benchmark data for assessing of future electronic structure predictions.

Appendix A: normal mode analysis of the $\tilde{X}$A$_1$ and $\tilde{A}$B$_2$ states

The GF matrix was constructed in a symmetric internal coordinate system $S_1 = \frac{1}{\sqrt{2}} (\Delta r_1 + \Delta r_2)$ and $S_2 = r \Delta \theta$. The elements of $G_{\text{sym}}$ are readily calculated using the expressions from ref. 22 and the experimental bond lengths and angles given in Table 5 to be:

$$G_{\text{sym}}(\tilde{X}A_1) = \begin{pmatrix} 0.0757 & -0.0274 \\ 0 & 0.18212 \end{pmatrix}$$ (A1)

and

$$G_{\text{sym}}(\tilde{A}B_2) = \begin{pmatrix} 0.0797 & -0.0290 \\ 0 & 0.1741 \end{pmatrix}.$$ (A2)

The units for $G_{\text{sym}}$ are amu$^{-1}$. Spectroscopic information is insufficient to determine all three elements in the force matrices, $F_{\text{sym}}(\tilde{X}A_1)$ and $F_{\text{sym}}(\tilde{A}B_2)$. Making the realistic assumption that the bend–stretch interaction force constant is zero, then the observed harmonic frequencies for $\nu_1$ and $\nu_2$ for the $\tilde{X}$A$_1$ ($\approx 976$ cm$^{-1}$ and $321$ cm$^{-1}$) and $\tilde{A}$B$_2$ ($\approx 879$ cm$^{-1}$ and $185$ cm$^{-1}$) states produce:

$$F_{\text{sym}}(\tilde{X}A_1) = \begin{pmatrix} 7.3598 & 0 \\ 0 & 0.3549 \end{pmatrix}$$ (A3)

and

$$F_{\text{sym}}(\tilde{A}B_2) = \begin{pmatrix} 5.6922 & 0 \\ 0 & 0.1236 \end{pmatrix}.$$ (A4)

The units for $F_{\text{sym}}$ are mdyn Å$^{-1}$. The eigenvectors are obtained by a similarity transformation:

$$V^{-1}G_{\text{sym}}F_{\text{sym}}V = A$$ (A5)

In eqn (A5), $A$ is a diagonal matrix with elements proportional to the square of the harmonic vibrational frequencies $\nu_i$:

$$A_i = \frac{\nu_i^2}{5.8918 \times 10^{-7}}$$

where $\nu_i$ is given in cm$^{-1}$. The resulting eigenvectors are:

$$V(\tilde{X}A_1) = \begin{pmatrix} 0.9264 & 0.0196 \\ -0.3766 & 0.9998 \end{pmatrix}$$ (A6)

and

$$V(\tilde{A}B_2) = \begin{pmatrix} 0.9344 & 0.0083 \\ -0.35617 & 0.9999 \end{pmatrix}.$$ (A7)

The internal symmetry coordinates, $S$, are related to the normal coordinates, $Q$, by

$$S = LQ$$ (A8)

where $L$ and $V$ differ only by a normalization constant$^{23}$ chosen to assure that $LL^T = G$:

$$L = VN$$ (A9)

with

$$N = [V^{-1}G(V^T)^{-1}]^{1/2}.$$ (A10)

The results are:

$$L(\tilde{X}A_1) = \begin{pmatrix} 0.2750 & 0.0081 \\ -0.1118 & 0.4118 \end{pmatrix}$$ (A11)

and

$$L(\tilde{A}B_2) = \begin{pmatrix} 0.28233 & 0.0033 \\ -0.1076 & 0.4031 \end{pmatrix}.$$ (A12)

The one dimensional vibrational analysis for the asymmetric stretch is performed in a similar manner. The observed vibrational $\omega_3$ value for the $\tilde{A}$B$_2$ ($= 316(2)$ cm$^{-1}$) and MRCI predicted $\omega_3$ value for the $\tilde{X}$A$_1$ state ($= 946$ cm$^{-1}$) are used to predict the force constants for the asymmetric stretch normal mode of 5.790 mdyn Å$^{-1}$ and 0.6760 mdyn Å$^{-1}$, respectively.

Appendix B: two dimensional Franck–Condon factors

The goal is to use only experimentally derived information to assign the optical spectrum and predict the Franck–Condon factors (FCF) for the $\tilde{A}$B$_2$ ($\nu_1,\nu_2,\nu_3$)$\rightarrow\tilde{X}$A$_1$ (000) transitions. Under the assumption that the $\tilde{A}$B$_2$ and $\tilde{X}$A$_1$ potentials can be modeled as two displaced and distorted harmonic oscillators, the FCF for the $\tilde{A}$B$_2$ ($\nu_1,\nu_2,\nu_3$)$\rightarrow\tilde{X}$A$_1$ (000) transitions can be calculated using relatively simple analytical expressions,\textsuperscript{16–19} with the analytical expression from ref. 18 being particularly convenient. Due to the C$_2v$ symmetry, only the two totally symmetric modes need to be considered. The implementation of the analytical expressions requires expressing the normal coordinates of the $\tilde{X}$A$_1$ (000) state, $\mathbf{Q}(\tilde{X}A_1)$, in terms of those for the $\tilde{A}$B$_2$ ($\nu_1,\nu_2,\nu_3$) state, $\mathbf{Q}(\tilde{A}B_2)$. The transformation between the normal coordinates of the two states is given by:

$$\mathbf{Q}(\tilde{X}A_1) = \mathbf{JQ}(\tilde{A}B_2) + \mathbf{D},$$ (B1)

where $\mathbf{D}$ is the vector of geometry displacements given in terms of the normal coordinates of the ground state ($= \Delta Q_1, \Delta Q_2$) and $\mathbf{J}$ is the $2 \times 2$ Duschinsky rotation matrix. The results of a Wilson GF matrix method\textsuperscript{15} normal mode analysis and a knowledge of the change in equilibrium structure can be used to obtain $\mathbf{J}$ and $\mathbf{Q}$. Specifically:\textsuperscript{18}

$$\mathbf{J} = (L(\tilde{X}A_1))^{-1}L(\tilde{A}B_2)$$ (B2)

and

$$\mathbf{D} = (L(\tilde{X}A_1))^{-1}(\mathbf{R}_\text{eq} (\tilde{A}B_2) - \mathbf{R}_\text{eq} (\tilde{X}A_1)).$$ (B3)
Substitution of $A_{13}$ and the inverse of $A_{12}$ into eqn (B2) gives the Duschinsky rotation matrix
\[ J = \begin{pmatrix} 1.026 & -0.016 \\ 0.017 & 0.974 \end{pmatrix}. \] (B4)

The change in equilibrium geometry is:
\[ R_{eq}(\tilde{X}^1 A_1) - R_{eq}(\tilde{A}^1 B_2) = \begin{pmatrix} S_1(\tilde{X}^1 A_1) - S_1(\tilde{A}^1 B_2) \\ S_2(\tilde{X}^1 A_1) - S_2(\tilde{A}^1 B_2) \end{pmatrix} = \begin{pmatrix} 0.084 \\ 0.236 \end{pmatrix}. \] (B5)

with the resulting vector of geometry displacements, $D$, obtained using eqn (B3) is:
\[ D = \begin{pmatrix} 0.287 \\ 0.640 \end{pmatrix}. \] (B6)

Note that the $D_2$ element is about 3 times larger than $D_1$ stemming from the large change in bond angle ($\sim 11^\circ$) and therefore a long progression in $\nu_2$ is expected.

Acknowledgements

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