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Te_2 absorption spectrum from 19000 to 24000 cm^{-1}

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ABSTRACT

A Fourier-transform absorption spectrum of $^{130}Te_2$ has been recorded from 19000 to 24000 cm^{-1} at approximately 620 °C; a transmission spectrum is made available in ASCII format. The spectrum is intended to aid spectral calibration in the blue-violet region. It extends slightly beyond the paper version of the Tellurium atlas, published in 1980 (J. Cariou and P. Luc, 'Atlas du spectre d'absorption de la molécule de tellure', Laboratoire Aime-Cotton (1980)).

1. Introduction

This work was motivated by interest in having a digital record of the absorption spectrum of tellurium vapour, as a supplement to the paper atlas of Cariou and Luc [1] in order to simplify comparison and scaling between laboratory reference signals and this spectral atlas. The strong and crowded $A0_u^+$-$X0_g^+$ bands of Te_2 have been known for many years, and provide useful benchmarks for calibration beyond 20000 cm^{-1}, where room-temperature B-X I_2 absorption cuts off. Tellurium melts at around 450 °C and Te_2 is the dominant form in the vapour phase, giving saturated vapour pressures of 2 Torr at 550 °C and 10.5 Torr at 635 °C [2]. Barrow and du Parcq noted that isotopically pure tellurium was critical to analysis of the A-X and B-X systems [3], and this is equally important in obtaining a useable reference spectrum. There are 8 naturally occurring isotopes of tellurium, the most abundant of these are ^{130}Te (34.1%) ^{128}Te (31.7%), ^{126}Te(18.8%) and ^{125}Te(7.1%) [4]. The sample used in this work was a standard 10 cm sealed evacuated cell supplied by Ideal Vacuum Products, containing a small amount of ^{130}Te.

2. Experiment

The tellurium cell was placed in a purpose-built furnace, designed to maintain temperature to within ±7 °C. The furnace is resistively heated with a single zone ceramic fiber heating element. It is fitted with fused silica windows to produce better temperature homogeneity across the cell than an open furnace would allow; this also minimizes deposition of tellurium on the window faces of the sealed reference cell. The temperature is monitored by a type K thermocouple and stabilized by a PID control loop [5]. We worked at temperatures between 600 and 640 °C to provide significant absorption without saturation. Emission from a quartz halogen bulb (Osram) operated at up to 11 Amp, 22 Volts dc passed through the cell, and was focused on the 'emission port' aperture of a Fourier transform spectrometer (Bomem DA3). Optical filters were selected so that the spectrum (417–510 nm) could be recorded in overlapping ~2000 cm^{-1} pieces, to reduce problems related to detector saturation at zero optical path difference coupled with weak interference signals elsewhere – an issue associated with broadband input. This also allowed us to record spectra at instrumental resolution nominally better than Doppler width without exceeding the W2000 computer memory limit of 10^6 points in our interferograms. Between 200 and 600 interferograms were averaged in each segment of the spectrum to improve the signal/noise ratio. The quartz 'visible' beamsplitter performed well for wavelengths above 425 nm. Below this cut-off, it was replaced by the 'UV' beamsplitter. The short-wavelength limit was imposed by low signal levels in the tail of emission from the white light source. Interferograms were collected on a silicon avalanche photodiode, at an instrumental resolution varying from 0.02 cm^{-1} at the long wavelength end of the spectrum to 0.035 cm^{-1} in the violet. Interferograms were zero-padded by a factor of 2. A small part of the spectrum is illustrated in Fig. 1. We show a raw spectrum and a transmittance trace generated by dividing the experimental absorption spectrum by a baseline contour to create a dimensionless Y axis. The raw intensity scale is arbitrary and uncorrected for instrumental response. The baseline in the transmittance spectrum appears noisy, but is in fact reproducible, revealing many weak transitions not necessarily listed in ref. [1].

Although the Fourier transform spectrometer is in principle self-calibrated by reference to its internal stabilised HeNe laser, we further processed the wavenumber scales to match established reference data, including the Doppler-free measurements from Gillaspy and Sansonetti (using frequency modulation) [6], from Scholl and co-workers (via saturated absorption) [7] and three unblended lines at 444 nm from Coker and co-workers [8], in addition to some 500 reference peaks taken from the existing Doppler-limited atlas of ref. [1]. The choice of Doppler-limited reference lines was initially random, but severe outliers (clearly

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the result of trying to match blended lines) were discarded. We minimized the differences between the selected reference values and those returned by a 'peaks above threshold' algorithm, looking for upwards zero-crossings in a boxcar-smoothed first derivative in our 'transmittance' spectrum, fitting to a $\Delta\sigma = a + b\sigma$ linear expression. These corrections to the raw wavenumber scale were of the order of 0.03 cm^{-1} at 23000 cm^{-1}.

The measured FWHM linewidths of isolated peaks are between 0.04 and 0.09 cm^{-1}, and we would expect peak positions for resolved features to be determined with uncertainties about ten times smaller. Fig. 2 illustrates the deviations of peak positions determined from our composite spectrum with respect to our selection of transitions listed in the literature. The lines are wider than one would expect from considerations of Doppler broadening alone, and since ^{130}Te has zero nuclear spin, we assume this results from a degraded performance of the Fourier transform spectrometer at short wavelengths.

Once the calibration controls were complete, we spliced and concatenated the pieces of spectrum using cubic spline interpolation to accommodate successive segments with interleaving wavenumber scales. This also allowed us to impose the intervals between data points as multiples of 0.001 cm^{-1} in the Supplementary Data files.

Results: spectral atlas

The composite spectrum is available to download in ASCII format at https://data.mendeley.com/datasets/kmkbwtjhd3/1, or may be obtained from the authors on request. The combination of optics and sources available has restricted the spectral range we can record; the spectrum actually extends to higher wavenumbers. Our spectrum extends a short way beyond the tellurium atlas of Luc and Cariou, but the spectral resolution is clearly lower than theirs below 450 nm. Nevertheless, these data should still prove to be a convenient secondary standard for Doppler-limited applications. We became motivated to record this spectrum while investigating the blue $^4\Sigma^- - ^4\Sigma^-$ bands of AlC [9],

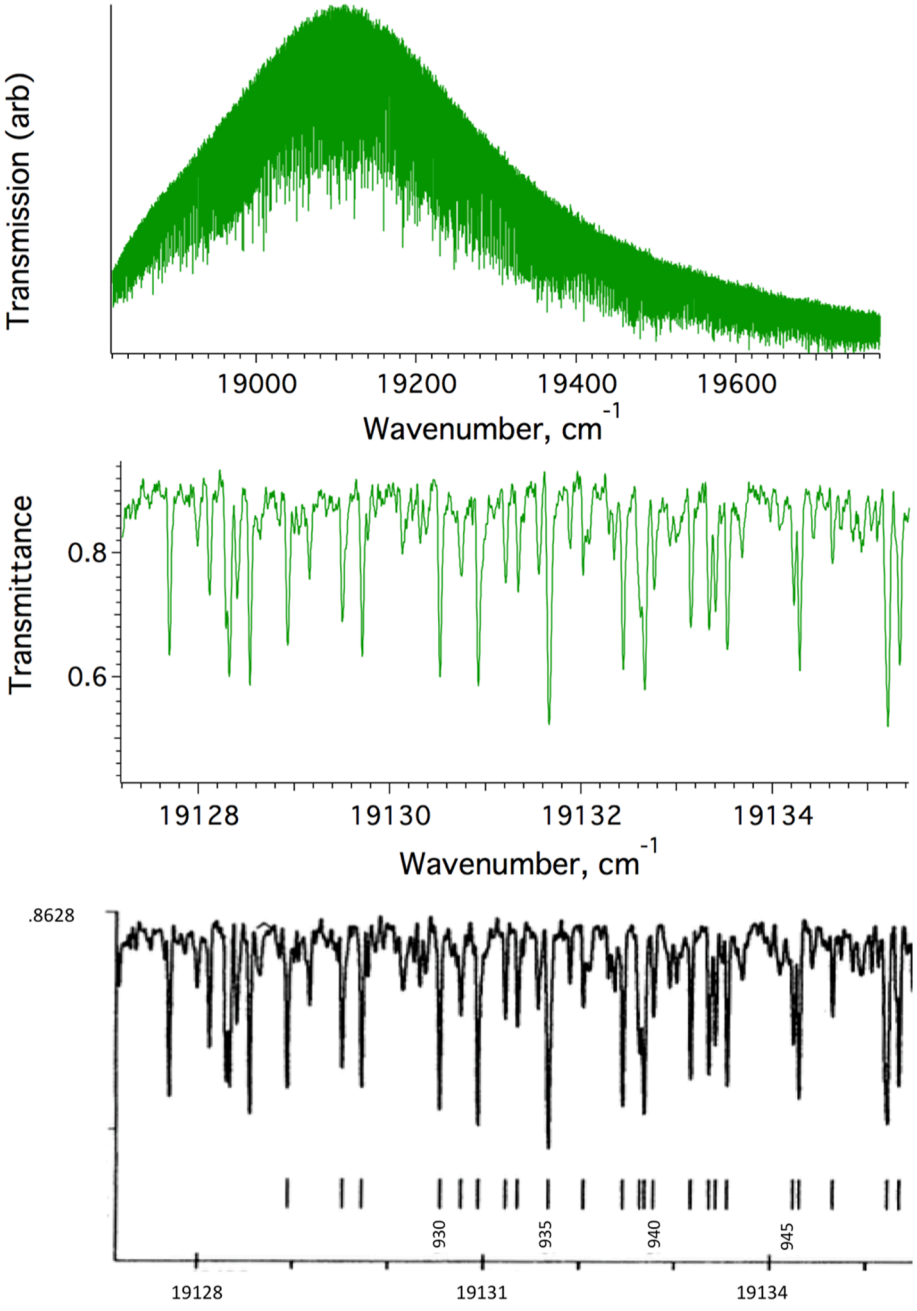

Fig. 1. Illustration of the portion of the Tellurium absorption spectrum recorded through a combination of a blue-green filter (Corning glass 5–61) and a narrow-pass filter centred at 506 nm. The upper trace shows the raw absorption spectrum. The middle trace shows an 8 cm^{-1} window in the corresponding transmittance spectrum. The lower trace displays a scan of the same region from the paper atlas of ref. [1] for comparison, reproduced with permission from Laboratoire Aimé Cotton.

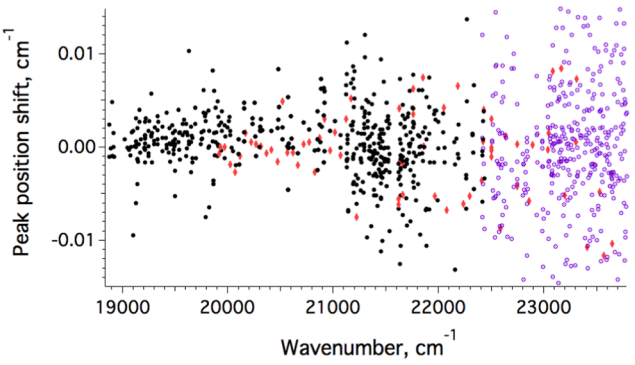

Fig. 2. Scatter plot showing differences in cm^{-1} between peak positions determined as zero derivatives in our spectrum minus reference peak positions. Circles refer to the Doppler limited atlas [1], diamonds (red) are shifts from the sub-Doppler values [6–8]. Open (violet) circles are from the lower-resolution spectra recorded with the UV beamsplitter.

where the sparser density of optogalvanic lines of Ar and Ne made calibration somewhat difficult, and we note that tellurium dimer is being used for calibration in other laboratories [10–13]. Although the optogalvanic spectrum of uranium [14,15] is also useful as a spectral reference in this wavelength range, the greater density of useful lines in the $^{130}Te_2$ absorption spectrum is advantageous for the calibration of smaller wavenumber intervals.

CRediT authorship contribution statement

Amanda J. Ross: Investigation, Data curation, Writing – original draft. **Joseph M. Cardon:** Methodology, Resources, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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