THE VIBRATIONAL SPECTRUM OF GASEOUS TELLURIUM DIOXIDE

R.J.M. KONINGS, E.H.P. CORDFUNKE and A.S. BOOIJ

Netherlands Energy Research Foundation ECN, 1755 ZG Petten, The Netherlands

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The vibrational spectrum of the vapour over solid TeO₂ has been measured from 75 to 3400 cm⁻¹ in a high-temperature gas cell at 1250 K. Seven absorption bands have been recorded which were interpreted as the three fundamental vibrational modes and four overtone/combination bands of gaseous TeO₂.

1. Introduction

The geometry and spectroscopic parameters of the gaseous TeO_2 molecule have been studied by various techniques. However, only the internuclear distance has been measured directly in the gas phase by electron diffraction [1]. The bent ground-state geometry and values for the bond angle have been obtained from ab initio calculations [2–4] only, whereas the vibrational spectrum has been reported for TeO_2 isolated in matrices of argon, neon [5] and nitrogen [6].

Muenow et al. [5] as well as Spoliti et al. [6] derived the vibrational frequencies of gas-phase TeO_2 by applying empirical corrections to the matrix isolation data and the results of the latter authors are generally used for statistical thermodynamic calculation of the heat capacity and entropy [7]. Matrix shifts can affect the statistical thermodynamic calculation considerably, especially for low wave numbers. The present study reports the infrared spectrum of gas-phase TeO_2 , from which possible matrix shifts can be studied.

2. Experimental

The TeO₂ sample was prepared by dissolving tellurium (CERAC) in nitric acid at room temperature. The precipitate was washed with water and heated in oxygen at 775 K overnight.

The spectrum was recorded with a BOMEM

DA3.02 Fourier transform spectrometer, which was equipped with a high-temperature gas cell [8]. The cell essentially consists of a silica tube (95 cm long and 6 cm in diameter) which is heated in a 62.5 cm long furnace. The furnace is divided in three independently controllable sections by which a zone of constant temperature (approximately 20 cm) can be created in the centre of the furnace by heating the outer sections to a higher temperature. The temperature is determined by a chromel-alumel thermocouple placed at the winding of the central zone, and corrected to the actual temperature in the tube via calibration. The windows are mounted in watercooled flanges at both ends of the tube.

The following experimental set-ups were used: for the 450-3400 cm⁻¹ range a globar light source, KRS5 windows and a silicon-boron detector; for the 75 to 350 cm⁻¹ range a Hg light source, Si windows and a Ge bolometer operating at 4.2 K. The spectrum was recorded at 0.5 cm⁻¹ resolution; 128 scans were coadded. The cell was loaded in an argon-filled glove box. For the present experiments approximately 1 g of TeO₂ was heated in a platinum boat in the centre of the cell at about 1250 K, and 10 mbar at room temperature of oxygen buffer gas was added to the cell.

3. Results and discussion

Seven distinct bands were observed in the spectrum (fig. 1): three prominent bands at 593.4, 821.7



Fig. 1. The IR spectrum of $TeO_2(g)$ in the 150 to 1500 cm⁻¹ range. The 350 to 450 cm⁻¹ range was not covered by the experiments. Note that due to differences in experimental conditions and the absence of overlap, the intensities in the two wavenumber ranges are not comparable.

Table 1 Observed infrared bands of TeO₂(g)

Value (cm ⁻¹)	Assignment	Nature	
260.3		"hot band"	
303.3	V ₂	fundamental bending mode	
593.4	$2\nu_2$	overtone band	
821.7	ν_1	fundamental symmetric mode	
853.3	v ₃	fundamental asymmetric mode	
1119.2	$v_1 + v_2$	combination band	
1337.1	$2\nu_1 - \nu_2$	difference band	

and 853.3 cm⁻¹, and two weak bands at 1119.2 and 1337.1 cm⁻¹ in the 450–3400 cm⁻¹ range as well as two strong absorptions at 303.3 and 260.3 cm⁻¹ in the 75 to 350 cm⁻¹ range (table 1). However, in view of the bent C_{2v} structure of the molecule, only three infrared active modes are expected.

The two absorption maxima around 840 cm⁻¹ are undoubtedly the normal vibrations ν_1 and ν_3 . The absorption at 303.3 cm⁻¹ is concluded to be the bending frequency ν_3 , rather than the one at 260.3 cm⁻¹. This choice has been directed by the fact that with this assignment the absorptions at 593.4, 1119.2 and 1337.1 cm⁻¹ can be considered to be $2\nu_2$, $\nu_1 + \nu_2$ and $2\nu_1 - \nu_2$, respectively, whereas the absorption at 260.3 can be interpreted as a hot band (transition from an excited vibrational level). A different choice (i.e. $v_2 = 260.3 \text{ cm}^{-1}$) leaves the nature of two of the remaining four absorption bands unexplained.

The present data are in reasonable agreement with the results of previous investigations (table 2). Muenow et al. [5] studied the infrared spectrum of TeO₂ isolated in matrices of argon and neon and found v_1 at 822.6 and 826.4 cm⁻¹ and v_3 at 839.4 and 844.8 cm⁻¹. Additional absorptions were attributed to TeO(g), $(TeO)_n$ and $(TeO_2)_n$, which were also identified by mass spectrometry. However, these mass spectrometric results are suspicious in view of the poor agreement with various other literature sources [7]. Piacente et al. [9] showed that the vapour over solid TeO₂ in vacuum consists of the molecules $TeO_2(g)$, TeO(g) and $(TeO_2)_2$ with approximate concentrations of 100:9:9. The presence of TeO(g) in the present experiments is suppressed by the oxygen buffer gas, but the shoulder at ≈ 800 cm⁻¹ may suggest some monoxide. However, in view of the low concentrations, species other than TeO₂ are excluded from the assignment of the present results.

Spoliti et al. [6] studied the spectrum of TeO₂ isolated in a nitrogen matrix and found ν_1 and ν_3 at 821.7 and 848.3 cm⁻¹, respectively. In addition, the latter authors observed the bending frequency ν_2 at 294 cm⁻¹. From these data Spoliti et al. [6] "calculated" the vibrational frequencies of gas-phase TeO₂ to be 830, 292 and 849 cm⁻¹ using the empirical relation $\nu_{gas} = \nu_{Ne} + 0.8(\nu_{Ne} - \nu_{Ar})$, as reported by Hastie et al. [10]. Although these calculated gas-phase data reasonably agree with the actual values for TeO₂(g), the above relationship is not confirmed since the matrix shifts for ν_1 and ν_2 are opposite to the calculated ones.

The shifts in the wavenumbers of $TeO_2(g)$ have

Table 2			
The fundamental	vibrational	frequencies o	f TeO ₂ (g)

Ref.	State	<i>v</i> ₁	<i>v</i> ₂	V ₃
[5]	Ar matrix	822.6	-	839.4
	Ne matrix	826.4	-	844.8
[6]	N_2 matrix	831.7	294	848.3
	gas *)	830	292	849
this work	gas	821.7	303.3	853.3

*) Extrapolated from matrix data.

only little effect on the vibrational contribution to thermodynamic functions: using a harmonic oscillator approximation, the difference with the data obtained from the values recommended by Spoliti et al. is calculated to be $-0.253 \text{ J mol}^{-1} \text{ K}^{-1}$ at 298.15 K and 0.274 J mol⁻¹ K⁻¹ at 3000 K in the entropy; the difference in the heat capacity is even less significant, ranging from $-0.067 \text{ J mol}^{-1} \text{ K}^{-1}$ at 298.15 K to 0 at 3000 K.

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