The $X_2^2\Pi_{1/2} \rightarrow X_1^2\Pi_{3/2}$ electronic transitions of tellurium monohalides in the near infrared \bigstar

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Emission spectra of the 0–0 bands of the transitions $X_2 {}^2\Pi_{1/2} \rightarrow X_1 {}^2\Pi_{3/2}$ between the fine-structure components of the $X {}^2\Pi_1$ ground states of TeF, TeCl, TeBr and Tel have been observed in the near-infrared spectral region between 2.35 and 2.5 µm. The $X_2 {}^2\Pi_{1/2}$ states of the radicals were excited by addition of halogens to the reaction system of microwave-discharged H₂ with tellurium powder in a fast-flow system. The fine-structure splittings of the $X {}^2\Pi_1$ ground states were found to be $4187 \pm 1 \text{ cm}^{-1}$ (TeF), $4022.5 \pm 1 \text{ cm}^{-1}$ (TeCl), $4067 \pm 3 \text{ cm}^{-1}$ (TeBr) and $4130 \pm 10 \text{ cm}^{-1}$ (TeI).

1. Introduction

Knowledge about the spectroscopic properties of the diatomic tellurium halides is quite limited [1]. The molecules are expected to have ${}^{2}\Pi_{i}$ ground states as have TeH and the lighter group VI hydrides and halides, but no reliable data for the fine-structure splittings of the ground states are known for any of them. UV absorption spectra of TeCl, TeBr and TeI have been studied by Oldershaw and Robinson [2-4] during the flash photolysis of the corresponding polyhalides. They assigned most of the observed bands to transitions $B \rightarrow X_1^2 \Pi_{3/2}$ and $B \rightarrow X_2^2 \Pi_{1/2}$. Assuming that there is no fine-structure splitting in the B states, Huber and Herzberg [1] report the doublet splittings of the ground states to be 1674 (TeCl). 1719 (TeBr), and 1815 (TeI) cm⁻¹. In chemiluminescence studies of the reaction of TeH_2 with F_2 , Newlin et al. [5] observed two band systems in the visible and near-infrared regions which they attributed to $A^2\Pi_i \rightarrow X^2\Pi_i$ and $B^2\Sigma^+ \rightarrow X^2\Pi_i$ transitions

of TeF. From their analysis, they estimated the ground-state splitting of TeF to be 531 cm⁻¹. The same band systems were observed by Thorpe et al. [6] from the reaction system of tellurium vapour with F₂. They assigned the bands to transitions $B^{2}\Sigma^{+} \rightarrow X_{1}^{2}\Pi_{3/2}$, $B^{2}\Sigma^{+} \rightarrow X_{2}^{2}\Pi_{1/2}$, $A^{2}\Pi_{3/2} \rightarrow X_{1}^{2}\Pi_{3/2}$ and $A^{2}\Pi_{1/2} \rightarrow X_{2}^{2}\Pi_{1/2}$, and deduced a ground-state splitting of 497 cm⁻¹ for TeF.

Recently, we have reported the observation and analysis of the 0-0 bands of the $X_2 {}^2\Pi_{1/2} \rightarrow X_1 {}^2\Pi_{3/2}$ transitions between the fine-structure components of the ${}^2\Pi_i$ ground states of TeH and TeD near 2.6 µm [7]. In the present work, we report on the observation of the 0-0 bands of the analogous $X_2 {}^2\Pi_{1/2}$ $\rightarrow X_1 {}^2\Pi_{3/2}$ transitions of TeF, TeCl, TeBr and TeI in the same wavelength region from which the finestructure splittings of the ground states of these molecules are found to be much larger than those deduced from the previous work.

2. Experimental

The experimental setup was nearly identical to that used for measuring the spectra of TeH and TeD [7]. The flow system was made of pyrex glass and con-

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sisted mainly of a tube, 100 cm long and 12 cm in diameter, with quartz windows at both ends and equipped with a pumping port and two side arms for gas inlet. In one side arm, a flow of H₂ was passed through a microwave discharge and reacted with tellurium powder in a small glass bulb before entering the main tube. The halogens mixed with helium carrier gas could be added to this gas flow through the second side arm. The tube was pumped at the other end with a 500 m³ h⁻¹ roots pump in series with a 40 m³ h⁻¹ forepump resulting in flow velocities of around 5 m s⁻¹ in the large tube and ≈ 20 m s⁻¹ in the inlet systems. The total pressure in the tube was measured with a Baratron capacitance manometer and was in the range 0.5-2 Torr (1 Torr \approx 133 Pa). It consisted of about equal partial pressures of H_2 and He, some mTorr of the halogens and unknown traces of tellurium compounds. The tellurium metal and the gases were research grade and were used without further purification.

In first experiments, emissions from the tube were measured with a small grating monochromator (McPherson model 218) equipped with a grating blazed for 2 μ m and a liquid-nitrogen-cooled InSb detector/preamplifier hybrid (Cincinnati Electronics model IDH-100) equipped with a cooled color glass filter (Schott BG 24) which absorbed all radiation above 2.9 μ m. The experiments were started by flowing 0.2–1 Torr of microwave-discharged H₂ over tellurium powder and optimizing the intensity



Fig. 1. Low-resolution (10 cm⁻¹) Fourier-transform spectra of the $X_2^2\Pi_{1/2} \rightarrow X_1^2\Pi_{3/2}$, 0–0 bands of TeH, TeF, TeCl and TeBr.

of the TeH band at 2.61 μ m by slightly heating the tellurium ($\approx 50^{\circ}$ C) and regulating the H₂ gas flow [7]. When the halogens mixed with He carrier gas were added to this system, single bands of similar intensities as the TeH band showed up at somewhat shorter wavelengths. The spectral resolution in these experiments was up to $\approx 10 \text{ cm}^{-1}$ which was sufficient to see that the width of the bands decreased with increasing mass of the halogen. Later, the emissions from the F₂-, Cl₂- and Br₂-containing systems were

measured with a Bomem DA3.002 high-resolution Fourier-transform spectrometer. Details of the experimental setup for these measurements have been given previously [7].

3. Results and discussion

Fig. 1 shows sections of Fourier-transform spectra measured at a resolution of 10 cm^{-1} in the wave-

Table 1

Fine-structure splittings of the X ² Π ground states of diatomic group IV and group VI hydrides and halides (in cm⁻¹). The spin-orbit constants of the ground states of the group IV and group VI atoms are given for comparison (for the accuracy of these data see ref. [8])

Group IV species $(X^2\Pi_r)$			Group VI species (X ${}^{2}\Pi_{i}$)		
atom/molecule	splitting *>	ref.	atom/molecule-	splitting ")	ref.
с	29.0	[8]	0	151	[8]
СН	27.95	[1]	ОН	-139.21	[1]
CF	77.12	[1]	OF	-193.28	[9]
CC1	134.92	[1]	OCI	- 321.8	[10]
CBr	466	[1]	OBr	967.98	[11]
CI	b)		OI	(-2330) °)	[1]
Si	148.9	[8]	S	382.4	[8]
SiH	142.83	[1]	SH	- 376.96	[1]
SiF	161.88	[1]	SF	(-401)	[1]
SiCl	207.21	[1]	SC1	b)	
SiBr	423.1	[1]	SBr	b)	
Sil	(700)	[1]	SI	b)	
Ge	940	[8]	Se	1690	[8]
GeH	892.52	[1]	SeH	-1764.02	[12]
GeF	934 .33	[1]	SeF	$(-1790)^{d}$	[1]
GeCl	975	[1]	SeCl	b)	
GeBr	1150	[1]	SeBr	b)	
Gel	(1413)	[1]	SeI	b)	
Sn	2097.3	[8]	Te	(3383) ^{d)}	[8]
SnH	2178.88	[1]	TeH	-3816.39	[7]
SnF	2316.9	[1]	TeF	-4187	this work
SnCl	2356.6	[1]	TeCl	-4022.5	this work
SnBr	(2463)	[1]	TeBr	- 4067	this work
SnI	b)		TeI	-4130	this work
РЪ	7294	[8]			
РЬН	(8000)	[1]			
PbF	8263.5	[1]			
PbCl	8272.2	[1]			
PbBr	b)				
РЫ	b)				

*) Spin-orbit splitting parameter A₀ if available. b) Not known yet.

^{c)} Numbers in parentheses are estimated values. ^{d)} Calculated value.

number range 3400-10000 cm⁻¹. Besides the bands assigned to TeF, TeCl and TeBr, the fundamental and/or first overtones of HF and HCl and the TeH band were observed. Preliminary measurements of the TeF and TeCl bands at spectral resolutions up to 0.02 cm^{-1} showed that the bands have a similar structure to the TeH band [7] consisting of two R. Q and P branches, each due to large doublings in the $X_2^2 \Pi_{1/2}$ excited states. These findings confirm the identification of the bands as the 0-0 bands of the $X_2^2\Pi_{1/2} \rightarrow X_1^2\Pi_{3/2}$ transitions of the TeX molecules. From the high-resolution spectra, the band origins of the TeF and TeCl bands are estimated to lie at 4187 \pm 1 and 4022.5 \pm 1 cm⁻¹, respectively. The band maxima of the TeBr and TeI bands were found from low-resolution spectra to be at 4067 ± 3 and 4130 ± 10 cm⁻¹. The TeI band has been measured with the monochromator only.

Little is known about the ground-state splittings of the isovalent selenium and sulfur halides, somewhat more about the splittings of the analogous ${}^{2}\Pi_{r}$ groundstates of group IV hydrides and halides [1]. Table 1 shows a comparison of the fine-structure splittings in the ${}^{2}\Pi$ ground states of these two groups of molecules. The relative and absolute size of the splittings in TeH and TeX is in line with what has been found for the other molecules. The spin-orbit constants of the molecules are closely correlated with those of the ground states of the corresponding atoms [8] which are given in table 1 for comparison. Our results show that the $A \rightarrow X$ and $B \rightarrow X$ systems of the tellurium halides [2-6] need some re-investigation and reinterpretation. Moreover, quantum-mechanical calculations of the corresponding energy levels and transition moments are desirable.

As in the case of TeH [7], excitation of the $X_2^2\Pi_{1/2}$ states of the TeX molecules possibly proceeds by V-E energy transfer from vibrationally excited hydrogen,

More detailed kinetic studies are needed to prove this excitation mechanism.

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References

- K.P. Huber and G. Herzberg, Molecular structure and molecular spectra, Vol. 4. Constants of diatomic molecules (Van Nostrand Reinhold, New York, 1979).
- [2] G.A. Oldershaw and K. Robinson, Chem. Commun. (1970) 540.
- [3] G.A. Oldershaw and K. Robinson, Trans. Faraday Soc. 67 (1971) 907.
- [4] G.A. Oldershaw and K. Robinson, J. Mol. Spectry. 37 (1971) 314.
- [5] D.E. Newlin, G.W. Stewart and J.L. Gole, Can. J. Phys. 57 (1979) 2217; 59 (1981) 441.
- [6] W.G. Thorpe, W.R. Carper and S.J. Davis, J. Chem. Phys. 83 (1985) 5007.
- [7] E.H. Fink, K.D. Setzer, D.A. Ramsay and M. Vervloet, J. Mol. Spectry. 138 (1989) 19.
- [8] H. Lefebvre-Brion and R.W. Field, Perturbations in the spectra of diatomic molecules (Academic Press, New York, 1986) p. 214.
- [9] P.D. Hammer, A. Sinha, J.B. Burkholder and C.J. Howard, J. Mol. Spectry. 129 (1988) 99.
- [10] J.A. Coxon, Can. J. Phys. 57 (1979) 1538.
- [11] A.R.W. McKellar, J. Mol. Spectry. 86 (1981) 43.
- [12] J.M. Brown, A. Carrington and T.J. Sears, Mol. Phys. 37 (1979) 1837.