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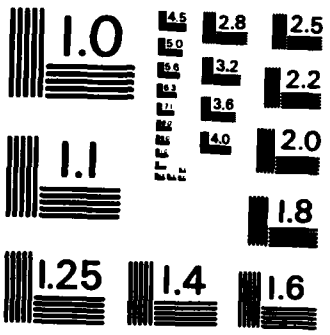

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Te_2 Chemiluminescence from Alkali Atom-$TeCl_4$ Reactions

by

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Te_2 Chemiluminescence from Alkali Atom-$TeCl_4$ Reactions*

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Abstract

The gas phase reaction between alkali atoms and $TeCl_4$ produces chemiluminescence from the $A(0_u^+)$ state of Te_2.

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In this Letter we report the observation of visible chemiluminescence from the $A(0_u^+) \rightarrow X(0_g^+)$ transitions of Te_2 produced in alkali atom-$TeCl_4$ reactions.

The reactions took place in a 500 ml Pyrex flask connected to a vacuum-gas-handling system. $TeCl_4$ crystals were contained in a sidearm connected to the cell. Alkali metal (K, Rb, or Cs) was distilled into the cell, the entire cell was heated to produce an alkali atom pressure in the range 10^{-3}-1 Torr, and then the $TeCl_4$ crystals were melted to produce a vapor pressure in the 1-10 Torr range. The resulting reaction produced a yellow flame which filled the entire volume of the cell. The addition of helium gas resulted in a red flame. The chemiluminescence was observed and recorded with an optical multichannel analyser (OMA) with a spectral range of 200-700 nm and a resolution of 0.5 nm per channel.

Fig. 1 shows the spectrum from the reaction of Cs with $TeCl_4$. The wavelengths for the vibrational bands correlate with transitions from the $A(0_u^+)$ state of Te_2. Fig. 2 shows the relevant potential energy curves for Te_2 [1]. These curves indicate the complexity of the Te_2 spectrum. Numerous transition wavelengths from both the A and B states [2] overlap to within the $\pm$0.5 nm resolution of the OMA. Using the RKR potential curves of Fig. 2 as a guide, the best fit to the spectral data appears to be transitions from $v'=0$-5 of the $A(0_u^+)$ state to $v''=3$-20 of the $X(0_g^+)$ ground state.

We reject the possibility of the chemiluminescence originating from $B(0_u^+) \rightarrow X(0_g^+)$ transitions because the observed spectrum cuts off at ~ 500 nm. $B(0_u^+) \rightarrow X(1_g)$ transitions are not ruled out directly, but one would not expect to see them without the $B(0_u^+) \rightarrow X(0_g^+)$ transitions as well.

The addition of 1-3 Torr of He to the reaction cell radically changed the character of the chemiluminescence. The flame became red, and the spectrum was a structureless continuum from 550-750 nm, with a peak at ~ 650 nm. This spectrum is similar to those observed in rare-gas matrices and attributed to $A'(^3\Sigma_u^+) \rightarrow X(1_g)$ transitions [3,4].

A similar change in chemiluminescence due to the addition of a buffer gas has been observed for alkali atom-SCl_2 reactions [5], which produce excited S_2 molecules, and we believe that similar mechanisms are responsible for the formation of excited Te_2. The $X(0_g^+)$, $X(1_g)$, and $A'(^3\Sigma_u^+)$ states of Te_2 correlate with two $Te(^3P_2)$ atoms, and the $A(0_u^+)$ state correlates with $Te(^3P_2)$ and $Te(^3P_0)$ atoms. The $^3P_0$ state is ~ 4750 cm^{-1} above the $^3P_2$ state. It is proposed that the following reaction is responsible for the formation of excited Te_2 in the absence of a buffer gas:

$$Te(^3P_0) + TeCl^* \rightarrow Te_2(AO_u^+) + Cl,$$

where the excited $Te(^3P_0)$ and vibrationally excited TeCl result from energy liberated in the alkali atom stripping reactions.

When helium gas is added to the reaction cell, the energy liberated from the stripping reactions is rapidly dissipated in collisions with the gas. In the absence of energy storage, the stripping reactions produce only ground state $Te(^3P_2)$ atoms. We therefore propose that the structureless red-shifted spectrum observed is a three-body recombination continuum:

$$Te(^3P_2) + Te(^3P_2) + He \longrightarrow Te_2(A') + He \longrightarrow Te_2(1_g) + He + h\nu.$$

We note, in conclusion, that the chemiluminescent reactions reported here might be applicable to the construction of a chemical electronic-transition laser. The excited-state potentials of Te_2 are displaced from the ground state potentials, as shown in Fig. 2, and continuous laser oscillation of optically pumped Te_2 has been achieved for $B(0_u^+) \longrightarrow X(0_g^+)$ transitions [6]. The Te_2 $A \longrightarrow X$ transitions observed in this experiment are to $v''=3-20$ of the X state and the v' levels of the A state have comparable, or longer, lifetimes than those of the B state [7,8], making this system a potential laser candidate.

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Figure Captions

Figure 1. Chemiluminescence spectrum of Te_2 from the reaction Cs + $TeCl_4$.

Figure 2. Energy level diagram for Te_2 (ref. [1]).

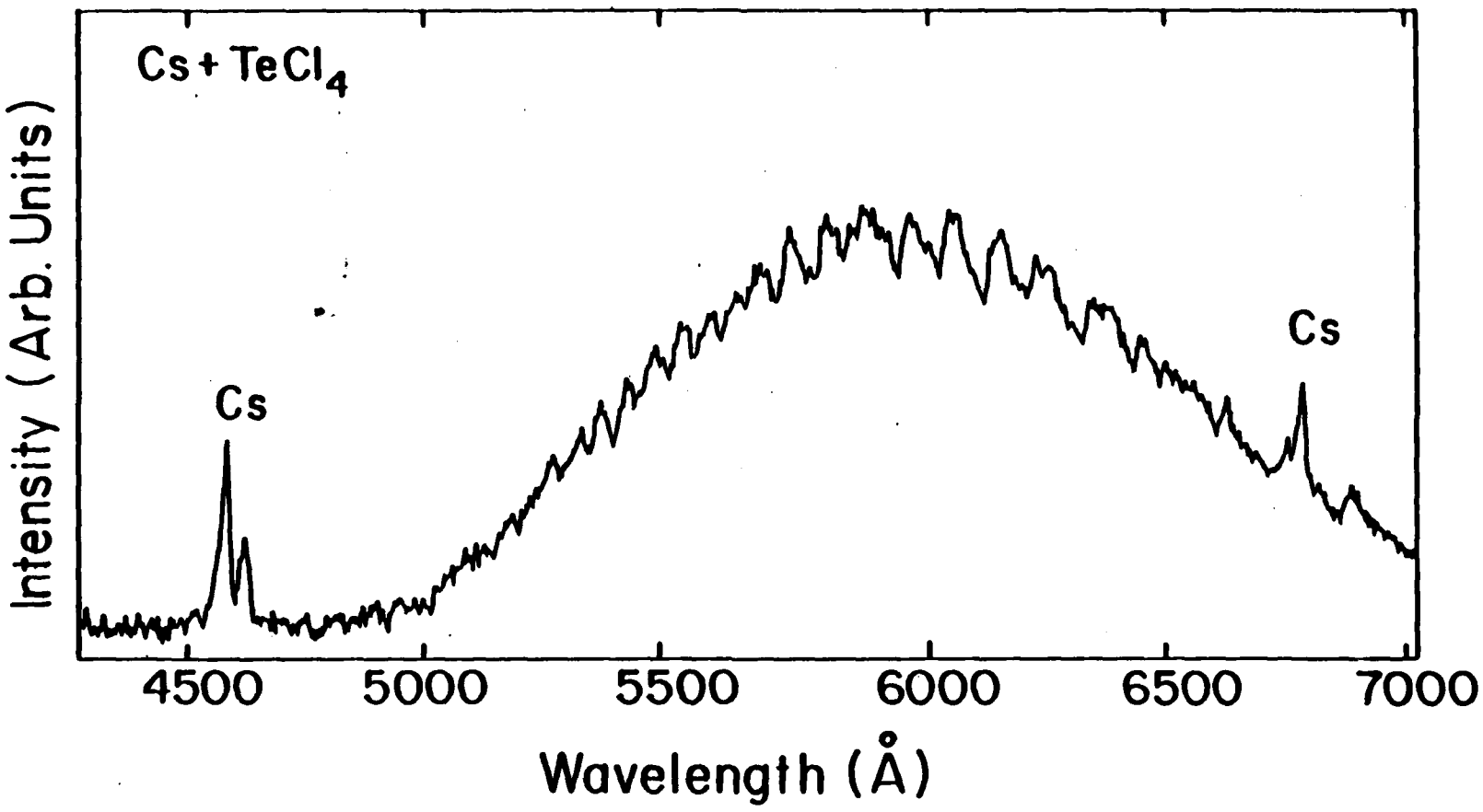
Cs + TeCl4
Intensity (Arb. Units)
Cs
Cs
4500
5000
5500
6000
6500
7000
Wavelength (Å)

Fig. 1

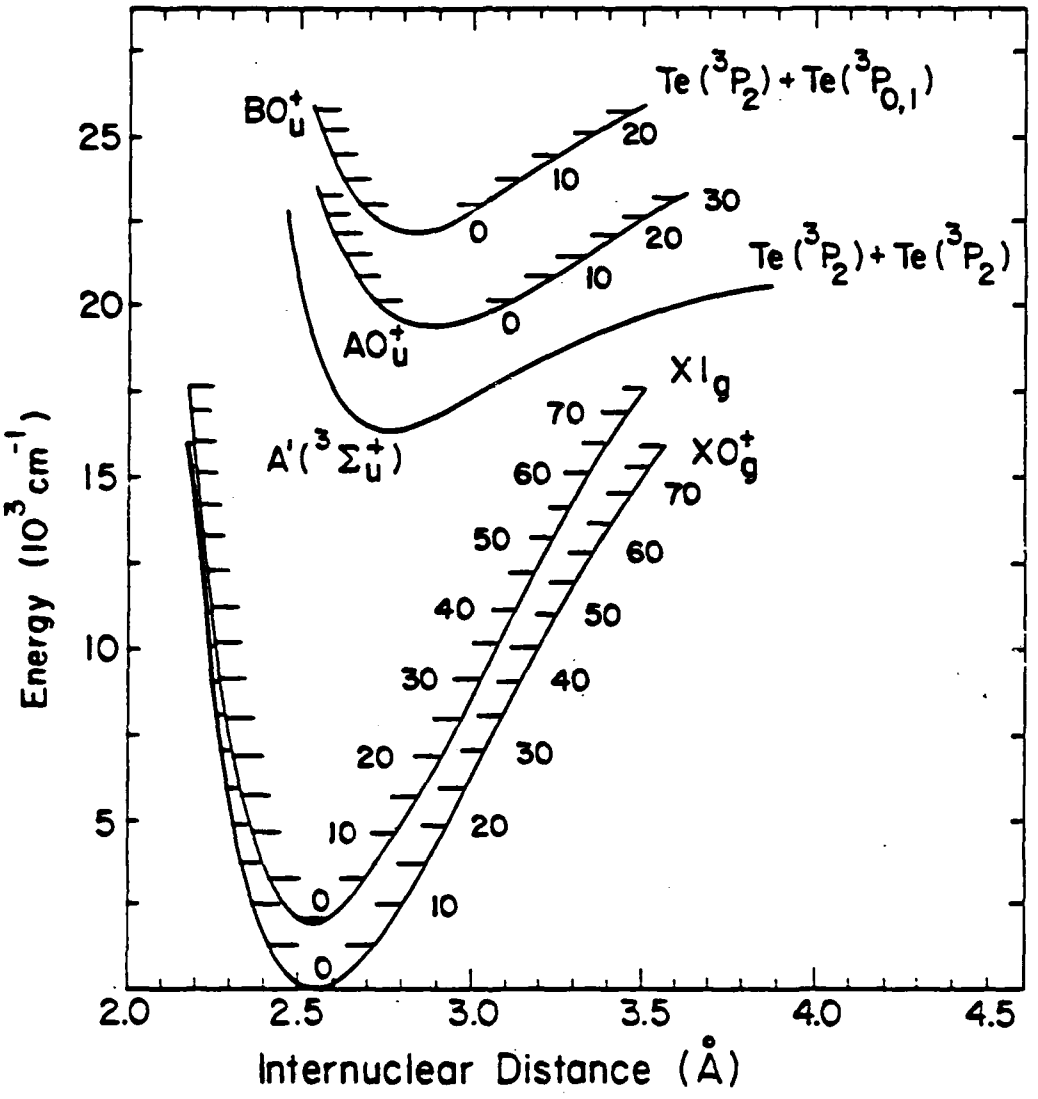
Energy (10^3 cm^{-1})
Internuclear Distance (Å)
BO_u^+
AO_u^+
$A'(^3\Sigma_u^+)$
XI_g
XO_g^+
Te ($^3P_2$) + Te ($^3P_{0,1}$)
Te ($^3P_2$) + Te ($^3P_2$)

Fig. 2

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