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Citation: The Journal of Chemical Physics **74**, 5595 (1981); doi: 10.1063/1.440922 View online: http://dx.doi.org/10.1063/1.440922 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/74/10?ver=pdfcov Published by the AIP Publishing

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# Crossed-beam chemiluminescent reactions of titanium and vanadium with $O_2$

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Titanium and vanadium have been reacted with  $O_2$  under crossed-beam conditions to form the TiO  $A^{3}\Phi$ ,  $B^{3}\Pi$ ,  $C^{3}\Delta$ , and  $E^{3}\Pi$  states and the VO  $B^{4}\Pi$  state. By heating and seeding the  $O_2$  nozzle beam the Ti reaction has been studied at relative collision energies of 4.0, 7.6, and 13.3 kcal/mol, and the V reaction at 3.9, 6.9, 7.6, and 13.1 kcal/mol. Computer simulations of the spectra yield relative rates for formation of TiO(A) and VO(B) vibrational states, which are slightly more excited than the "prior" model predictions. Increasing the relative collision energy does increase the production of all the electronically excited states, but the VO B state population does not increase as quickly as expected from the prior model. The dependence of the chemiluminescent signals on the metal source temperature suggests reaction of ground state Ti to form TiO(A), but metastable V to form VO (B).

# INTRODUCTION

The methods of beam-gas and crossed-beam chemiluminescence (CL) have been sucessfully used for studying various metal plus oxidant reactions.<sup>1</sup> The high sensitivity of the techniques allows one to obtain information about energy partitioning in product internal states as well as the dependence of the cross sections on initial internal states and translational energy. Recent spectroscopic work<sup>2</sup> on the TiO and VO molecules has made them good candidates for CL studies by providing vibrational and rotational constants for a number of electronic systems. Gole and co-workers have observed CL from the reactions of V with  $NO_2^3$  and of Ti with  $O_2$ ,  $NO_2$ , and  $N_2O^4$  in a beam-gas arrangement. They reported emission from the  $C^{4}\Sigma$  state of VO and the D,  $c^{1}\Phi$ ,  $C^{3}\Delta$ , and  $B^{3}\Pi$  states of TiO. Their studies did not extend to the wavelength region of emission of the lower lying  $B^{4}\Pi$  state of VO and the  $A^{3}\Phi$ ,  $E^{3}\Pi$ , and b <sup>1</sup> $\Pi$  states of TiO. In a spectroscopic study, Linton and Broida<sup>5</sup> reported CL flames produced by reactions of Ti with  $O_2$ ,  $N_2O$ ,  $NO_2$ , NO, and  $CO_2$  in argon. For O2 and N2O they observed all known TiO systems with considerably different electronic state distributions. Because of the high pressure in their experiments, some uncertainty exists regarding the mechanisms leading to formation of excited TiO, and the importance of collisional relaxation of excited states.

We have observed CL of VO and TiO formed in the reactions of V and Ti with  $O_2$  under crossed-beam conditions. We report here CL from the *B* state of VO and the *A*, *B*, *C*, and *E* states of TiO. Formation of VO(*B*) and TiO(*A*) has been studied as a function of the metal atom source temperature, in order to identify the primary reactant species, and as a function of the relative collision energy by variations in the oxygen beam conditions. Computer simulations of the emission from these electronic states have allowed us to extract information about the energy disposal in these systems, even though they are plagued by extensive overlapping.

## **EXPERIMENTAL**

The molecular beam and light detection systems have been described previously.<sup>6-8</sup> The metal atom source was heated by a resistively heated tungsten mesh radiator surrounded by a radiation shield pack consisting of three tungsten and three molybdenum shields. The oven and inner crucible were made of tungsten for generating the V beam, and tantalum for the Ti beam. Oven temperatures were determined by an optical pyrometer calibrated by the manufacturer.<sup>9</sup> This calibration proved to be good enough to give the expected metal atom oven temperature dependence for another reaction<sup>10</sup> Cu +  $F_2 \rightarrow CuF(A) + F$  based on independent measurements of CL as a function of Cu flight time.<sup>11</sup> The  $O_2$  beam or  $O_2$ /He seeded beam originated in an alumina nozzle, and the O<sub>2</sub> velocity and relative intensity were determined for various nozzle heating and seeding conditions using a time-of-flight method as previously.<sup>7</sup> As found by others,  $^{12}$  the  $O_2$  velocity distributions could be explained using essentially complete relaxation of rotational energy, but no relaxation of vibrational energy.

The CL spectra were measured using pulse counting techniques, and the data were processed by an on-line programmable calculator. The signal was corrected for background light (which varied smoothly) by periodically measuring the background with the  $O_2$  beam shuttered and interpolating the background between points. In order to correct for drifts in beam intensity and detector response, time normalization was performed by periodically measuring a reference-wavelength signal. Later the spectra were corrected for variations in the response of the detector system, which was calibrated using a standard lamp.

## RESULTS

Preliminary experiments involved varying the source conditions to determine the orders of CL reactions with respect to reactants. The VO CL signal due to the  $B^{4}\Pi - X^{4}\Sigma^{-}$  transition was observed to vary linearly with the O<sub>2</sub> pressure over the range  $2 \times 10^{-7}$  to  $1 \times 10^{-4}$  Torr, indicating that the reaction was first order in O<sub>2</sub> with

J. Chem. Phys. 74(10), 15 May 1981

0021-9606/81/105595-11\$01.00

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negligible attenuation of the V beam. The reaction was also concluded to be first order with respect to V from the observation that the CL signal variation with the V oven temperature was that expected for reaction of atomic rather than dimeric species. (See below for further discussion of the atomic states involved in the reactions based on the signal variation with metal oven temperature.)

The TiO CL signal due to the  $A^3 \Phi - X^3 \Delta$  transition was concluded to be first order with respect to Ti based on the signal variation with the Ti oven temperature. Dependence of TiO formation on O<sub>2</sub> pressure was not tested, but the similarity of the signal strength to the VO CL signal made anything but a reaction first order in O<sub>2</sub> very unlikely in the 10<sup>-5</sup> Torr pressure regime employed.

Wavelength scans of the CL were performed at a variety of O2 beam conditions, which gave different collision energies and O<sub>2</sub> vibrational excitation. The TiO spectra from 450-900 nm at a resolution of 0.6 nm taken with three  $O_2$  conditions are shown in Fig. 1 as relative photon count. These spectra have been corrected for detector response, as are all other spectra shown. The spectra have been normalized with respect to each other and divided by the relative  $O_2$  number density as found using a mass spectrometric detector. Emission in the  $\alpha$ ,  $\gamma'$ ,  $\gamma$ , and  $\epsilon$  systems due to the C, B, A, and E states, respectively, is evident. There may be some δ system emission due to the  $b^{1}\Pi - a^{1}\Delta$  transition at the long wavelength end of the spectra, but the noise there caused by the reduced PM tube response made it impossible to characterize. The  $\epsilon$  and  $\gamma$  systems are seen to predominate over the  $\gamma'$  and  $\alpha$  systems, although the latter increase faster with increasing average relative collision energy  $\overline{E}_{T}$ . The other changes with increasing collision energy, apparent for the A-X transition shown in greater detail in Figs. 2-4, are broadening of the sequences and increases in the off-diagonal sequences, reflecting increasing rotational and vibrational excitation of the products.



FIG. 1. Experimental wavelength scans of  $Ti + O_2$  chemiluminescence at three relative collision energies. These and other spectra shown are corrected for variations in beam intensity and detector response.



FIG. 2. Experimental and simulated (top) TiO A-X emission at  $\overline{E}_T = 4.0$  kcal/mol.

Table I gives the beam conditions and average energy change  $\Delta D_0$  for formation of the lowest level of the A, B, C, and E states from the lowest level of the reactants. A recently determined value of  $158.4 \pm 1.5$ kcal/mol for  $D_0^{\circ}(\text{TiO})^{13}$  has been used in calculating  $\Delta D_0$ . The relative rates for forming the different electronic states may be approximated by integrating the spectra between appropriate limits. Errors arise when there is overlap of the systems, or if some of the product states are metastable and do not radiate on a time scale less than the time needed to traverse the reaction zone. A detailed treatment of this excited state loss mechanism has been given elsewhere.<sup>10</sup> For our geometry, radiative lifetimes less than ~  $10^{-6}$  s will assure that radiation is much more likely than diffusional loss of the

TABLE I. Relative rate coefficients for production of TiO<sup>\*</sup> ( $E^{3}\Pi$ ,  $A^{3}\Phi$ ,  $B^{3}\Pi$ , and  $C^{3}\Delta$ ). Energies are in kcal/mol.

	Product			
Beam conditions	state	$\Delta D_0$	Exptl.	Prior
$T_{O_2} = 300 \text{ K}$	<i>Е</i> <sup>3</sup> П	-6.5	0.99	3.35
$T_{T_{1}} = 2390 \text{ K}$	$A^{3}\Phi$	-0.3	1.00	1.00
$\overline{E}_{T} = 4.0$	<b>в</b> <sup>3</sup> п	6.0	0.19	0.32
•	$C^{3}\Delta$	14.9	0.01	0.06
$T_{O_2} = 1215 \text{ K}$	<i>Е</i> <sup>3</sup> П	-6.5	2.02	6.68
$T_{T1} = 2330 \text{ K}$	$A^{3}\Phi$	-0.3	2.91	2.64
$\overline{E}_T = 7.6$	<b>В</b> <sup>3</sup> П	6.0	0.72	0.85
•	$C^{3}\Delta$	14.9	0.04	0,17
10% O <sub>2</sub> /90% He	<b>Е</b> <sup>3</sup> П	-6.5	2.76	12,69
$T_{O2} = 1215 \text{ K}$	$A^{3}\Phi$	-0.3	5.57	6.20
$T_{T_1} = 2390 \text{ K}$	<b>В</b> <sup>3</sup> П	6.0	1.90	2.49
$\overline{E}_T = 13.3$	$C^{3}\Delta$	14.9	0.16	0.46





excited states. Oscillator strength estimates<sup>14</sup> derived from absolute intensity measurements for the  $\alpha$  and  $\gamma$ systems indicate that radiative lifetimes for the C and A states are less than 50 ns. Also, unpublished measurements in our laboratory<sup>15</sup> using laser excited fluorescence gave a lifetime of 33 ns for the ground vibrational level of the C state. Absorption measurements of matrix isolated TiO<sup>16,17</sup> indicate that the  $\gamma$  and  $\gamma'$ systems have comparable oscillator strengths. Thus, the A, B, and C states are suitably short lived for detection without the problem of diffusional loss. The  $\epsilon$ system, on the other hand, appears to be significantly weaker in absorption, <sup>16,17</sup> and some diffusional loss of the E state may occur in our experiments.

Table I gives estimates of the relative rates for formation of excited electronic states of TiO for the three crossed beam experiments. Sequences included in the integration were  $\Delta v = 0$  and 1 for the  $\epsilon$  system,  $\Delta v = 0$ and  $\pm 1$  for the  $\gamma$  system,  $\Delta v = 0$  and 1 for the  $\gamma'$  system, and  $\Delta v = 0$  and -1 for the  $\alpha$  system. Because of the possibly longer lifetime of the E state and the cutoff in the spectra before the negative  $\Delta v$  sequences, its integrated emission provides only a lower bound on its relative rate of formation. For the other electronic states, the integrated emission gives the approximate relative rates of formation, subject to an uncertainty of about  $\pm 30\%$  due to missing sequences and uncertainty in spectral calibration. A simulation method described



FIG. 4. As Fig. 2 at  $\overline{E}_T$ 

TABLE II. Beam conditions for VO wavelength scans.

% O <sub>2</sub>	Т <sub>О2</sub> (К)	T <sub>V</sub> (K)	$\overline{E}_T$ (kcal/mol)
100	300	2315	3.9
100	1210	2315	7.6
10	370	2370	6,9
10	1180	2315	13.1

in the next section gave slightly larger B/A ratios, but the difference in the ratios was no more than 16%.

Wavelength scans were performed under the four different sets of beam conditions shown in Table II for the  $V+O_2$  reaction at 0.6 nm resolution. In agreement with the results of Jones and Gole, <sup>3</sup> no VO C-X emission was observed even at the highest reactant energy. Figures 5 and 6 show the scans obtained of VO B-X emission using a pure  $O_2$  beam at 300 and 1210 K. Only sequences with  $\Delta v \ge 0$  were included because the spectral response fell rapidly in the region of the  $\Delta v = -1$  sequence. To test the importance of the  $O_2$  vibrational energy in the higher temperature experiment, another spectrum was taken at about the same relative collision energy but with negligible  $O_2$  vibrational energy by using a mixture of 10% O<sub>2</sub> seeded in He at 370 K. In addition, a spectrum was taken with the same mixture at 1180 K. Here the vibrational energy was about the same as in the 1210 K pure  $O_2$  experiment but the relative collision energy was increased. These latter two spectra are shown in Figs. 7 and 8. Higher initial energy in translation or vibration is seen to give broader sequences and stronger off-diagonal sequences. This is



FIG. 5. Experimental and simulated (top) VD B –X emission at  $\overline{E}_T$  = 3.9 kcal/mol.



FIG. 6. As Fig. 5 at  $\overline{E}_T = 7.6$  kcal/mol.

expected since on the basis of a VO bond strength of  $D_0^0 = 148.8 \text{ kcal/mol}$ , <sup>18</sup> the reaction V + O<sub>2</sub> - VO ( $B^4\Pi$ ) + O is endoergic by 5.0 kcal/mol, and a larger fraction of reactants have enough energy to form higher vibrational states of VO ( $B^4\Pi$ ) as the initial energy is raised.

#### SPECTRAL SIMULATIONS

Due to severe overlap of bands in the TiO and VO CL spectra, it was difficult to derive relative rate coeffi-



FIG. 7. As Fig. 5 at  $\overline{E}_T = 6.9$  kcal/mol.



FIG. 8. As Fig. 5 at  $\overline{E}_T = 13.1$  kcal/mol.

cients for formation of product states directly from peak heights or areas. Instead, it was necessary to match calculated spectra to the experimental results by iteratively varying the distributions of product electronic, vibrational, and rotational energy. The accuracy of such simulations is limited by how well the states have been characterized spectroscopically. Table III gives spectroscopic constants available for the relevant states of TiO and VO which were used for generating spectral simulations.

Rotational intensity factors for the transitions were calculated assuming that the  $\Lambda \neq 0$  states were represented by the case (a) limit.<sup>19</sup> This approximation is expected to be reasonable for the A and X states of TiO, where  $A/B_0$  is ~114 and 95, respectively. Because the low resolution of the spectra made the product vibrational rather than rotational distribution of primary in-

terest, simulations using the much more complicated intermediate case intensity factors were not attempted. Extensive simulations of TiO spectra were made of only the A-X transition because the endoergicity of the reactions to form the B and C states makes the product energy distributions reflect largely just the distribution of energy available to the reactants, and the E state has not been rotationally analyzed. Case (a) intensity factors offer a reasonable approximation for the VO Bstate, where  $A/B_0$  is ~122. Furthermore, intermediate case intensity factors would not be obtainable without numerical diagonalization of a four-by-four matrix for every transition, and more extensive rotational analysis than available.

Franck-Condon factors (FCF) were calculated using standard methods.<sup>20</sup> The spectroscopic constants given in Table III were used to construct the RKR potentials for TiO, and the A-X FCF are given in Table IV. The rotational constants given in Table III for VO are only effective values which match the line positions, and do not have the mechanical meaning appropriate for calculating FCF. Instead, data from Richard's thesis<sup>21</sup> for the (0,0) band of the VO B-X transition were refit using a more appropriate representation of the energy levels provided by the LINFIT program of Zare et al. 22 By variations in seven parameters  $(T_0, A'_0, B'_0, D'_0, \epsilon'_0, B''_0)$ , and  $\epsilon_0^{\prime\prime}$ ) 585 lines given by Richards were fit to a standard deviation of the residuals of 0.9 cm<sup>-1</sup>. Better fits would be obtainable by including the effects of  $\lambda$  doubling, but information on the major perturbing states is lacking.  $D_0^{\prime\prime}$  was frozen at the value 6.472  $\times 10^{-7}$  cm<sup>-1</sup> determined by Richards from the better characterized C-X transition. Results for the varied parameters were  $T_0$ = 12 610.9 cm<sup>-1</sup>,  $A'_0 = 63.56$  cm<sup>-1</sup>,  $B'_0 = 0.50538$  cm<sup>-1</sup>,  $D'_0 = 6.514 \times 10^{-7}$  cm<sup>-1</sup>,  $\epsilon'_0 = 1.848$  cm<sup>-1</sup>,  $B'_0 = 0.53931$  cm<sup>-1</sup>, and  $\epsilon'_0 = 1.516$  cm<sup>-1</sup>. The value of  $B''_0 - B'_0 = 0.0339$  cm<sup>-1</sup> obtained was used for constructing Morse potentials based on the more accurately known  $B_e^{\prime\prime} = 0.54825 \text{ cm}^{-1}$ , and the resulting FCF obtained are given in Table V. A fit to the same rotational lines by Veseth<sup>23</sup> using a more extensive Hamiltonian gave  $B_0'' - B_0' = 0.0338$ , virtually

State	T <sub>e</sub>	ω <sub>e</sub>	ω <sub>e</sub> x <sub>e</sub>	Be	α <sub>e</sub>	D <sub>e</sub>	Spin splittings
TiO $X^{3}\Delta$	•••	1009.02	4,498	0.53541	0.00301	6.03×10 <sup>-7</sup>	96.4, 101.1
TiO <b>A</b> <sup>3</sup> Φ <sup>2</sup>	14089.9	867.78	3.942	0.50739	0.00314	$6.92 \times 10^{-7}$	172.9, 168.2
тіО <i>В</i> <sup>3</sup> П <sup>а</sup>	16 293.5	871.96	4.113	0.50781	0.00328	$6.86 \times 10^{-7}$	21.6, 16.2
VO X <sup>4</sup> Σ <sup>- b</sup>	•••	1012.36	5.26	0.54825	0.00352	$6.43 \times 10^{-7}$	
VO <i>B</i> <sup>4</sup> ∏ <sup>d</sup>	12 567	910.9	5.0	$\begin{pmatrix} 0.5247 \\ 0.5187 \\ 0.5127 \\ 0.5002 \end{pmatrix}^{c}$	0.0040	1.0×10 <sup>-6</sup>	71, 62, 55

TABLE III. Spectroscopic constants (in  $cm^{-1}$ ) used in the simulations. Constants are from Ref. 2 unless otherwise noted.

<sup>a</sup>Because of the low resolution of the CL Spectra, there was no need to include the effects of spin-spin and spin-rotational interactions.

<sup>b</sup>Additional constants used were  $\lambda = 1.371$ ,  $\gamma_1 = 0.0112$ , and  $\gamma_2 = 0.0111$ .

<sup>c</sup>Separate values are given for the spin-orbit states  $\Omega = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$ , and  $-\frac{1}{2}$ , respectively. <sup>d</sup>Reference 21.

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v'	<i>v</i> '' = 0	1	2	3	4	5	6	7
0	7.19-1	2.36 - 1	3.98-2	4.37-3	3.23-4	1.39 - 5	1.49-7	1.55-8
1	2.36 - 1	3.19 - 1	3.30 - 1	9.72 - 2	1.57 - 2	1,60-3	9.63-5	1.98-6
2	3.98 - 2	3.31 – 1	1.04 - 1	3.30 - 1	1.55 - 1	3.48 - 2	4.66 - 3	3.70 - 4
3	4.26 - 3	9.71 - 2	3.34 - 1	1.45 - 2	2.77 - 1	2.01 - 1	6.04 - 2	1.04 - 2
4	3.12 - 4	1.49 - 2	1.55 - 1	2.84 - 1	1,96 - 3	2.02 - 1	2.28 - 1	9.02 - 2
5	1.61 - 5	1.43 – 3	3.25 – 2	2.04 - 1	2.12 - 1	2.98 - 2	1.27 - 1	2.35 - 1
6	5.64 - 7	9.13-5	3.94 - 3	5.62 - 2	2.37 - 1	1.38 - 1	7.16 - 2	6.51 - 2
7	1.38-8	3.93-6	3.02-4	8.37 - 3	8.41-2	2.51-1	7.54 – 2	1.10-1

TABLE IV. Franck-Condon factors for TiO (A - X).

the same value we used. A simpler approach for determining a mechanical  $B'_0$  based on inverting Richard's effective  $B'_0$  values using the spin splittings in the case (a) limit [e.g.,  $B'_{0,eff}$  ( $\Omega = 5/2$ ) =  $B'_0$  (1 + 3 $B'_0/A$ ] gave a somewhat larger value for  $B'_0 - B'_0$  of 0.0356 cm<sup>-1</sup>. The electronic transition moment had to be assumed to be constant for each of the transitions in TiO and VO because no information was available on its variation.

Initial efforts at simulating the experimental spectra involved adjusting the vibrational, rotational, and spinorbit populations, but it was found that the results for these distributions were strongly coupled to each other because of the overlap of numerous branches. Since the rotational distributions in these preliminary fits were found to be similar to the distributions expected for a simple prior model<sup>24</sup> for energy disposal, this model was then adopted for the rotational distributions, with averaging in the simulation program over the collision energy distribution. The prior form used for the rotational distributions was

$$P(J') \sim (2J'+1)(E_T - \Delta D_0 - E'_v - E'_J)^{1/2}$$

where  $E_T$  is the relative collision energy,  $\Delta D_0$  is the endoergicity from reactants to the particular product electronic state involved,  $E'_{\nu}$  is the product vibrational energy, and  $E'_J$  is the product rotational energy. The form for the collision energy distribution has been given previously.<sup>6</sup> Because most of the spread in the collision energy distribution was caused by the high temperature of the metal effusive beam, the contribution of the nozzle beam to the distribution could be approximated as a delta function. The averaging over collision energy was essential in the simulation program because many of the product vibrational states observed involved endothermic reactions.

For the TiOA state, simulations were successful if the spin-orbit distribution was also calculated using the same prior model as was used for the rotational distribution. Thus, only the relative vibrational populations had to be adjusted. The simulations obtained by iteratively adjusting these populations are shown in Figs. 2-4 above the experimental spectra, and the normalized vibrational distributions are given in Fig. 9 in comparison with the prior model predictions. Included in the simulations is a small contribution from the  $\gamma'$  system which overlaps the  $\gamma$  system slightly. Simulation of the major part of the  $\gamma'$  system itself was not as successful, possibly because of breakdown of the case (a) representation for the B state, for which  $A/B_0$  is only ~39. Figure 10 shows that surprisal plots<sup>24</sup> for the TiOA state vibrational distributions are approximately linear when the fraction of average total product energy in vibration  $f_v$ is less than 0.9. Linear fits in this region give slopes of -0.95, -0.95, and -1.08 for the 4.0, 7.6, and 13.3 kcal/mol experiments, respectively. Points with larger  $f_{\rm m}$  were not included because of the greater uncertainty in the experimental values and an uncertainty in the bond strength which may lead to large errors in those prior values. We do not report here the average values of  $f_v$ because so many of the product states observed are above the average available product energy available. and there exists an ambiguity as to whether these states should be included in the average  $f_n$ .

Some differences between experimental and simulated spectra are apparent in Figs. 2-4. The  $\Delta v = -1$  sequence is predicted to be too high. Possible causes include incorrect FCF or a significant electronic transition moment dependence on the transitions involved. FCF were also calculated at rotational levels other than J=0, up to J=41, but changes were too small to account

TABLE V. Franck-Condon factors for VO (B-X).

v '	<i>v</i> ′′ = 0	1	2	3	4	5	6	7
0	6.19-1	3.10-1	6.35 - 2	7.00 - 3	4.54-4	1.80-5	4.39 - 7	6.88-9
1	2.82 - 1	1.66 - 1	3.80-1	1.46 - 1	2.39-2	2.08 - 3	1.04 - 4	3.06-6
2	7.77 - 2	3.05 - 1	1.33 - 2	3.28 - 1	2.20 - 1	5.06 - 2	5.66 - 3	3.47 - 4
3	1.71 - 2	1.53 – 1	2.23 - 1	1.03 - 2	2.29-1	2.70 - 1	8.49 - 2	1.19-2
4	3.34 - 3	4.94 - 2	1.94 - 1	1.22 - 1	6.34 - 2	1.30 - 1	2.91 - 1	1.24 - 1
5	6.10 - 4	1.28 - 2	8.72 - 2	1.94 - 1	4.56 - 2	1.20 - 1	5.49 - 2	2.84 - 1
6	1.08 - 4	2.91-3	2.88 - 2	1.20 - 1	1.64 - 1	6.40 - 3	1.54 – 1	1.20-2
7	1.86 - 5	6.15 - 4	7.99-3	<b>4.97</b> – 2	1.40 - 1	1.18 - 1	1.69 - 3	1.61 - 1

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FIG. 9. Experimental (shaded bars) and prior (open bars) probabilities for populating TiO(A) vibrational state v at three relative collision energies.



FIG. 10. Surprisal plots for TiO(A) vibrational distributions.



FIG. 11. Experimental (shaded bars) and prior (open bars) probabilities for populating VO(B) vibrational state v at four relative collision energies.

for the simulation differences. Also, the highest energy experiment (Fig. 4) gives somewhat broader peaks than achieved with the simulation, and this discrepancy suggests that the experimental rotational distribution is slightly more highly excited than the prior form.

For the VO spectra, simulations of the overall shapes were possible using the prior model for the rotational distributions of the VO B state provided both the spinorbit and vibrational distributions could be adjusted away from the prior distributions. It was necessary to make the vibrational distribution hotter than the prior form, as was found for the TiO A state, but the spinorbit distribution was found to be much colder than the prior prediction. Because the detailed structure of the branches was not well fit even if populations of all the spin-orbit states were varied, it was decided to represent the spin-orbit distribution simply by a temperature in order to match the general shapes of the sequences. This temperature was determined to be  $200 \pm 50$  K for the three higher energy spectra and  $180 \pm 50$  K for the lowest energy spectrum. The crudeness of the fit prevented any variation of the spin-orbit temperature with vibrational state from being detectable. These low temperatures found contrast with a range of 900-2300 K expected on the basis of the prior model applied to the four sets of beam conditions. The best fit simulations are shown in Figs. 5-8, and the vibrational distributions are compared in Fig. 11 with the prior results. Figure 12 gives surprisal plots<sup>24</sup> for the highest three energies. No surprisal plot is given for the lowest energy experi-



FIG. 12. Surprisal plots for VO(B) vibrational distributions.

ment, where only the ground vibrational level of the VO B state is accessible when the reactants have the average energy available. Linear fits of the surprisal in the region  $f_v < 0.9$  are shown, and slopes of -0.97, -0.44, and -0.31 are found for the 6.9, 7.6, and 13.1 kcal/ mol experiments, respectively. Thus, for all the energies used, slightly higher vibrational excitation of the products was found than predicted by the prior model, irrespective of whether the initial energy included vibration and translation, or just translation. The extent of deviation from the prior model does not change markedly with energy.

It should be noted that if the radiative lifetime of the VO B state were greater than 1  $\mu$ s, then corrections would have to be made to the observed vibrational distributions because faster product molecules would be more likely to escape before radiating. Such a long lifetime seems unlikely because the B-X transition is known from theoretical work<sup>25</sup> to involve the same types of molecular orbitals  $4\pi - 9\sigma$  as the strongly allowed A-X transition in ScO and TiO.<sup>26,27</sup>

# RELATIVE COLLISION ENERGY DEPENDENCE OF RATE COEFFICIENTS

The relative rate coefficients for forming TiO (A, v'=0) and VO (B, v'=0), were determined as functions of initial energy by changing the pure O<sub>2</sub> beam temperature between 300 and 1200 K with the spectrometer adjusted so as to transmit light from predominately one vibra-

tional state. Variation in the pure  $O_2$  beam number density was determined using a differential-pressure capacitance manometer with an entrance slit on the beam center. The reference pressure on the other side of the manometer was the ambient pressure in the collision chamber. For TiO a wavelength of 709.4 nm was used with a resolution of 3.0 nm FWHM. This was centered on the  $F_2$  component of the (0, 0) band, although some  $F_1$ and  $F_3$  emission was included. The v'=1 branches did not interfere since they are red degraded, and the nearest band head is at 712.5 nm. For VO the spectrometer was set at 789.9 nm with the same resolution. Mostly the  $F_3$  and  $F_4$  components of the (0,0) bands were included. The nearest v = 1 branch had a band head at 791.8 nm, and it is red degraded and not prominent. The low resolution was used in both cases to assure that a wide range of rotational states were observed, making the CL characteristic of the vibrational state as a whole. The relative rate coefficients are plotted vs  $\overline{E}_{T}$  in Figs. 13 and 14. A form given previously<sup>6</sup> for the relative collision energy distribution was used to calculate  $\overline{E}_{T}$ . Comparison is made with the simple prior model, in which the rate coefficients depend only on the product densities of states, with no other effect of changing the total energy. Agreement is generally good for the TiO case but poor for VO, where the prior model predicts a much more rapid increase in relative rate coefficient than observed. Figure 14 also shows that even when reaction from ground state V is excluded in the prior model, as suggested by measurements described in the next section, substantial disagreement remains with experiment.

# RATE COEFFICIENT DEPENDENCE ON METAL ATOM STATE POPULATIONS

In order to assess the importance of excited metal atoms in producing CL reactions, the dependence of the CL signal on the metal beam temperature was measured at the same wavelengths and resolution used in the collision energy studies. This method has been used ex-



FIG. 13. Relative collision energy dependence for formation of TiO (A, v'=0). The solid curve gives the energy dependence of the prior rate coefficient.



FIG. 14. Relative collision energy dependence for formation of VO (B, v'=0). The solid curve gives the energy dependence of the normal prior rate coefficient, and the dashed curve gives the prior prediction if reaction from ground state V(<sup>4</sup>F) is excluded.

tensively by Gole and co-workers,  $^{4,28}$  and in particular, they have shown that the reaction of Ti with O<sub>2</sub> to give the TiO C state involves overwhelmingly the excited  $^{5}F$  states of Ti.

If we consider reaction from each metal atom state iof energy  $E_i$  at a fixed O<sub>2</sub> temperature, then the observed CL intensity is proportional to the sum  $\sum_i k_i N_i$ , where  $k_i$  is the relative rate coefficient for the state i and  $N_i$ is the number density of the state. In a thermal beam as employed here





FIG. 15. Logarithmic plot of the chemiluminescence intensity from TiO (A, v'=0) vs the inverse of the Ti oven temperature. Solid curves show calculations based on two combinations of relative rates of reaction of Ti states (see text).



FIG. 16. Logarithmic plot of the chemiluminescence intensity from VO (B, v'=0) vs the inverse of the V oven temperature. Solid curves show calculations based on two combinations of relative rates of reaction of V states (see text).

 $\Delta H$  is either the heat of vaporization or the heat of sublimation, depending on the temperature. With various combinations for the relative values of  $k_i$ , which were assumed to be temperature independent, we constructed plots of  $\ln \sum k_i N_i$  vs 1/T for comparison with the logarithm of the observed CL intensity for TiO (A, v'=0)and VO (B, v'=0).  $\Delta H$  was taken from a compilation of Hultgren et al.<sup>29</sup> for Ti, and from measurements of Farber and Srivastava<sup>30</sup> for V. For Ti the four lowest manifolds of states were included with the assumption that the average energy and the same rate coefficient applies to all states within a manifold. For V the three lowest manifolds of states were included in the same The manifold average energies are given in Table way. VI.<sup>31</sup>

For Ti, good agreement with experiment is seen to occur in Fig. 15 with all four of the rate coefficients equal to each other. Comparison is also made with the temperature dependence obtained with no reaction of the ground  ${}^{3}F$  states and the other rate coefficients equal to each other. Good fits would also be provided if only the  ${}^{3}F$  states reacted, since the populations of the higher states are small.

For V, agreement with experiment is seen to be provided in Fig. 16 when  $k_0 = 0$  and  $k_1 = k_2$ . Again, the con-

TABLE VI. Major states present in the the metal beam with average energies.

Atom	States	i	$E_{i} ({\rm cm}^{-1})$
Ti	$^{3}F$	0	185.7
	<sup>5</sup> F	1	6686.5
	$^{1}D$	2	7255.3
	${}^{3}P$	3	8510.5
v	${}^{4}F$	0	253.5
	<sup>6</sup> D	1	2244.4
	$^{4}D$	2	8795.8

stants are not uniquely determined, but the fit suggests predominant reaction of excited V atoms. An activation energy in  $k_0$  could not be responsible for the larger slope observed since the relative collision energy changes only slighly over the temperature range covered and we know that the relative collision energy dependence is weak over the range covered.

### DISCUSSION

The large number of potential surfaces open to the reactants in these systems make it difficult to draw any inferences about the detailed dynamics from the product state distributions. Furthermore, the complexity of the diatomic product spectra hampers attempts to extract reliable energy distributions. Nevertheless, the CL spectra do contain a great deal of information for comparison with model calculations. A useful procedure has been to assume that rotational structure may be characterized by the simple prior model for energy disposal, and to determine the vibrational distributions which allow best-fit simulations of the spectra. If the product state distributions are not constrained in this or some other way, then there is too much flexibility in fitting the spectra because of the extensive overlap of bands.

Much better fits were possible in simulating the detailed structure of the TiO A-X transition than the VO B-X transition. This could be due to greater uncertainty in the VO rotational constants, the failure of a case (a) description for the VO B state, or even the presence of emission from an unknown electronic state. The latter possibility can be explored by performing experiments at higher pressures where relative populations in electronic states strongly perturbing each other may change dramatically because of collisional effects.<sup>32</sup>

As the initial energy is increased in both the Ti and V reactions, we have found that product excitation in rotational and vibrational degrees of freedom increases, irrespective of whether the added energy is translational or vibrational. This is the behavior expected for reactions proceeding by way of intermediate complexes which live long enough to randomize the energy among the various modes, although it certainly does not prove the existence of a long-lived complex. Slight deviations of the vibrational distributions from the prior predictions persist at all energies for both reactions, but the deviations are not sufficient to imply nonstatistical behavior, because of uncertainties in estimating product state distributions ( $\sim \pm 20\%$ ), and because the prior model is only one approximate scheme for quantifying the statistical phase space open to the products. Also, the large spread of relative collision energy for the nearly thermoneutral reactions studied causes the product distribution to be largely influenced by the distribution of total energy available, rather than just the dynamics at fixed total energy. Future experiments involving velocity selected metal atom beams promise to give more information about the dynamics of monoenergetic collisions.

More dramatic deviations occur between experimental relative rates for formation of product electronic states

TABLE VII. Symmetries of potential energy surfaces associated with reactants and products.

Asymptotic States	2S + 1	$C_s$ symmetry	$C_{\infty v}$ symmetry
$\mathrm{Ti}({}^{3}\boldsymbol{F}_{\boldsymbol{g}}) + \mathrm{O}_{2}({}^{3}\boldsymbol{\Sigma}_{\boldsymbol{g}}^{*})$	1,3,5	4A', 3A''	Σ¯, Π, Δ, Φ
$\mathrm{Ti}({}^{\boldsymbol{5}}\!F_{\boldsymbol{g}}) + \mathrm{O}_2({}^{\boldsymbol{3}}\boldsymbol{\Sigma}_{\boldsymbol{g}}^{-})$	3, 5, 7	4A ', 3A ''	Σ, Π, Δ, Φ
$\mathrm{TiO}(X^{3}\Delta) + \mathrm{O}(^{3}P_{g})$	1,3,5	3 <u>A</u> ', 3 <u>A</u> ''	$\underline{\Pi}$ , $\underline{\Delta}$ , $\underline{\Phi}$
$\mathrm{TiO}(a^{1}\Delta) + \mathrm{O}(^{3}P_{g})$	3	3 <u>4</u> ', 34''	Π, Δ, Φ
$\mathrm{TiO}(d^{1}\Sigma^{\star}) + \mathrm{O}(^{3}P_{g})$	3	A', 2A''	Σ*, П
$\mathrm{TiO}(E^{3}\Pi) + \mathrm{O}(^{3}P_{g})$	1,3,5	3 <u>4</u> ′, 34″	Σ*, <u>Σ</u> , Π, Δ
$\mathrm{TiO}(A^{3}\Phi) + \mathrm{O}(^{3}P_{g})$	1,3,5	3A', 3A''	Δ, Φ, Γ
$\mathrm{TiO}(b^{-1}\Pi) + \mathrm{O}({}^{3}P_{g})$	3	3A', 3A''	Σ*, Σ*, Π, Δ
$\mathrm{TiO}(X^{3}\Delta) + \mathrm{O}(^{1}D_{g})$	3	3A', 3A''	Σ*, Σ <sup>-</sup> , Π, Δ, Φ, Γ
$\mathrm{TiO}(B^{-3}\Pi) + \mathrm{O}(^{3}P_{\mathfrak{s}})$	1,3,5	3A', 3A''	Σ*, Σ*, Π, Δ
$\mathrm{TiO}(C^{3}\Delta) + \mathrm{O}(^{3}P_{g})$	1, 3, 5	3A', 3A''	Π, Δ, Φ
$\mathrm{TiO}(c^{1}\Phi)+\mathrm{O}(^{3}P_{g})$	3	3A', 3A''	Σ*, Σ-, Π, Δ
$\mathbf{V}({}^{4}\boldsymbol{F}_{\boldsymbol{g}}) + \mathbf{O}_{2}({}^{3}\boldsymbol{\Sigma}_{\boldsymbol{g}})$	2,4,6	4A ', 3A ''	Σ, Π, Δ, Φ
$\mathbf{V}({}^{6}D_{\boldsymbol{s}})+\mathbf{O}_{2}({}^{3}\boldsymbol{\Sigma}_{\boldsymbol{s}})$	4,6,8	2 <b>A</b> ', 3 <b>A</b> ''	Σ¯, Π, Δ
$\operatorname{VO}(X^4\Sigma^{-}) + O(^3P_s)$	2,4,6	<u>A</u> ', <u>A</u> ''	<u>Σ</u> , <u>Π</u> ,
$\frac{\operatorname{VO}(B^{4}\Pi) + \operatorname{O}({}^{3}P_{g})}{2}$	2,4,6	2 <u>A</u> ', 2 <u>A</u> ''	Σ*, Σ¯, Π, Δ

and prior model predictions. As seen in Table,I, the ratios of B/A and C/A TiO state formation are consistently lower than predicted. This could be due to reaction of predominately excited Ti states in the endothermic reactions to form the B and C states, as already shown by Dubois and Gole for the C state.<sup>4</sup> The E/A ratio is also lower than predicted, but this may be due to a significantly longer radiative lifetime for the E state. We did not observe the  $\beta$  system ( $c^1\Phi-a^1\Delta$ ) which was reported as appearing weakly by Dubois and Gole. Possibly it was populated in their experiments by secondary collisions of the C state products. Such collisions have been shown to occur effectively by Linton and Broida.<sup>33</sup>

Although a prior model distribution of spin-orbit states in the TiO A state gave good agreement with experiment, it was not acceptable for the VO B state, where the distribution was much colder. With increasing relative collision energy increases in the total VO B state production and the relative amount of higher spinorbit states were also markedly slower than predicted by the prior model.

An explanation for highly nonstatistical distributions of product electronic energy can sometimes be found using adiabatic correlation diagrams for reactions.<sup>34</sup> Table VII gives the symmetries of triatomic potential surfaces which arise from reactants and products in the  $C_{sv}$  and  $C_s$  point groups. Not shown are the VO  $^2\Sigma^-$ ,  $^2\Gamma$ , and  $^2\Sigma^+$  states predicted theoretically<sup>25</sup> to arise from the same molecular orbital configuration as the X state, but not observed experimentally. The column labeled 2S + 1gives all the allowed multiplicities of these surfaces. If adiabatic correlations are made including all the states shown, then ground state reactants can lead to only certain product states via the underlined surfaces, without any nonadiabatic surface changes. If the extended point groups appropriate for systems with strong spin-orbit coupling are used instead or the unobserved VO states are included, then even fewer of the excited product states observed correlate adiabatically with the reactants. It is seen that passage to the A state or higher in TiO requires a nonadiabatic surface change regardless of the point group symmetry of the triatomic surface. Exciting the Ti atom may then be expected to enhance reactivity to form these higher TiO states, although it may not be essential. The cold VO B state spin-orbit distribution may be explicable in terms of favored connections of the reactant surfaces with the lower spinorbit states. The dependence of the CL signal on the V oven temperature suggests greater reactivity of the excited V states than the ground  ${}^{4}F$  states, but in those measurements predominately the higher two spin-orbit states of VO (B, v'=0) were detected in order to exclude v'=1. Possibly the lower spin-orbit states are favored in the products because they can be formed directly from the more abundant  ${}^{4}F$  states.

In summary, the prior model is useful for characterizing product vibrational and rotational excitation of TiO and VO, but the detailed consideration of triatomic electronic surfaces will probably be necessary for understanding branching into product electronic states.

#### ACKNOWLEDGMENTS

Support of the National Science Foundation is gratefully acknowledged. We would like to thank Dr. D. M. Manos and Dr. K. Liu for assistance in this work. Computer time was provided by The Ohio State University Computation Center.

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