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Nonequilibrium product distributions observed in the multiple collision chemiluminescent reaction of Sc with NO₂. Perturbations, rapid energy transfer routes and evidence for a low-lying reservoir state

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Nitrogen dioxide reacts with scandium to yield the $B^2\Sigma^+ - X^2\Sigma^+$ spectrum of ScO. This reaction has been characterized from 10^{-5} to 1 Torr in order to study relaxation and rapid intramolecular E-E transfer among ScO excited states. At the lowest pressures, a ground state metal atom interacts with a tenuous atmosphere of oxidant gas (beam-gas configuration). These "single collision" studies are extended in a controlled manner to higher pressure by entraining the metal atoms in argon and subsequently carrying out the oxidation of this mixture. At all pressures, the measured $B^2\Sigma^+$ vibrational populations follow a markedly non-Boltzmann distribution. At the lowest pressures, the formation of ScO $B^{2}\Sigma^{+}$ results directly from the reaction $Sc + NO_2 \rightarrow ScO^* + NO$. At higher pressures, the $B^2\Sigma^+$ state is also populated via rapid intramolecular energy transfer from long-lived, weakly emitting "reservoir" states via the sequence $Sc + NO_2 + Ar \rightarrow ScO(res) + NO + Ar$ and $ScO(res) + Ar \rightarrow ScO(B^2\Sigma^+) + Ar$. Spin orbit and Coriolis interactions in ScO connect rovibronic levels of $B^2\Sigma^+$ and low-lying ${}^4\Pi_r$ or ${}^2\Pi_i$ reservoir states resulting in the observation of substantial perturbations in $B^2\Sigma^+$. Collisional energy transfer is particularly efficient for the most strongly perturbed levels of the $B^2\Sigma^+$ state. This energy transfer is manifest by the appearance of "extra" band heads representing normally forbidden (small electronic transition moment or Franck-Condon factor) "reservoir state"- ground state transitions which become allowed because of a small admixture of $B^2 \Sigma^+$ character. The relative intensities of the extra and "main" $B^{2}\Sigma^{+}-X^{2}\Sigma^{+}$ transitions are strongly dependent on argon buffer gas pressure. A quantitative description of this dependence gives an estimate for the amount of mixing between the reservoir state and $B^{2}\Sigma^{+}$ and for the rate of energy transfer between these two states. Collisional transfer to ScO B $^{2}\Sigma^{+}$ v' = 3-9 is found to proceed at rates which for certain levels approach 100 times gas kinetic. The effects observed in ScO demonstrate that the excited states of this molecule interact in the presence of a collision partner as if they were large diffuse entities. These effects are not pathological. This behavior may have important implications for the modeling of energy systems as well as the ability to create population inversions requisite for the construction of visible chemical laser systems.

INTRODUCTION

Recently,^{1,2} we have been concerned with the analysis of rapid intramolecular energy transfer routes among the excited states of molecules important at high temperatures. The energy transfer with which we are concerned is particularly efficient for the most strongly interacting excited state levels and hence the most strongly perturbed levels of each state. The magnitude of the perturbations which we observe in diatomic high temperature molecules can be comparable to that normally associated with polyatomics. While the analysis of these effects may, at first, seem impracticable, it is possible to employ the strength of the perturbations to advantage in order to obtain information at lower resolution which normally is obtained only in an exhaustive high resolution perturbation analysis.

In order to characterize rapid energy transfer in high temperature systems, we focus on highly exothermic chemiluminescent reactions involving the oxidation of refractory metals over the pressure range 10^{-6} to $\approx 10^2$ Torr. At the lowest pressures a metal atom intersects and interacts with a tenuous atmosphere of oxidant gas (beam-gas configuration)³ forming product molecules in both ground and excited electronic states. Those excited states which are connected via an allowed transition to the ground electronic state usually emit a photon before undergoing subsequent collisions. Longer-lived "reservoir" states may also be formed in the reaction. These states may not be connected to the ground state via an allowed transition. They will emit photons at a much slower rate and may easily undergo collision before the emission of a photon. It is primarily these states with which we are concerned as we extend "single collision" studies in a controlled manner to higher pressure by entraining the metal atoms in the noble gases argon or helium and subsequently carrying out the oxidation of this mixture.

In two previous studies, ^{1,2} we have investigated the pressure dependence of the chemiluminescent emission from the aluminum-ozone reaction. The observed chemiluminescent spectrum is characterized by emission from both the $B^2\Sigma^*$ and $A^2\Pi$ states of AlO. At pressures in excess of 1 Torr (primarily argon buffer gas pressure) where collisional deactivation might be expected to lead to significant thermalization of nascent vibrational and rotational distributions, the measured AlO $B^2\Sigma^*$ vibrational populations follow a markedly non-Boltzmann distribution, exhibiting local maxima at vibrational level v' = 6, 8, 12, and 14. This behavior can be attributed to an initial chemical reaction $Al + O_3$ $+ AlO(A^2\Pi) + O_2$ followed by the collision induced rearrangement $AlO(A^2\Pi) + Ar + AlO(B^2\Sigma^*) + Ar$. Spin-orbit interactions in AlO connect rovibronic levels of the $A^2\Pi$ and $B^2\Sigma^*$ states and collisional energy transfer is particularly efficient for the most strongly perturbed levels of the $B^2\Sigma^*$ state. Consistent with the proposed mechanism for AlO $B^2\Sigma^*$ formation is the appearance of "extra" satellite band heads representing normally "Franck-Condon forbidden" A-X transitions which become allowed because of a small admixture of $B^2\Sigma^*$ character. These features are observed concurrently with the main $B^{2}\Sigma^{+}-X^{2}\Sigma^{+}$ emission bands. In contrast to perturbations which affect only a few rotational levels in a given vibrational band or can lead to the appearance of certain extra rotational transitions,⁴ the satellite bands arise from much larger perturbations which affect a range of rotational levels in the vicinity of the B-XRbranch heads. These observed features in AlO have now been found to be characteristic of several high temperature systems where collisional transfer analogous to that from the AlO A^2 II state is observed and appears to emanate from long-lived reservoir states. Here we focus on the analysis of these effects in scandium oxide. More specifically, we investigate the pressure dependence of the chemiluminescent emission from the ScO $B^{2}\Sigma^{*}$ state. Formation of this state occurs directly^{5,6} via the chemical reaction

$$Sc(^{2}D) + NO_{2}(^{2}B_{1}) - ScO(A'^{2}\Delta, A^{2}\Pi, \underline{B^{2}\Sigma^{*}}, C^{2}\Pi \cdots$$

+ \cdot reservoir) + NO(²Π)

or as a result of rapid E-E transfer from long-lived reservoir states which may be connected to the $B^{2}\Sigma^{*}$ state via a spin-orbit $A(\hat{L} \cdot \hat{S})$ or coriolis $B(\hat{L} \cdot \hat{J})$ interaction. In the present study the Sc-NO₂ reaction has been investigated over the pressure range 10⁻⁵ to 1 Torr. At the higher pressures an argon buffer gas was used.

As in AlO, extra satellite features are found to accompany the main ScO $B^{2}\Sigma^{*} - X^{2}\Sigma^{*}$ emission bands. In both AlO and ScO the relative intensities of the satellite and main transitions are strongly pressure dependent (argon buffer gas). The dependence may be expressed by a set of rate equations. For AlO a quantitative description of this dependence gives an estimate of the amount of mixing between the $A^2\Pi$ and $B^2\Sigma^*$ states and the rate of energy transfer between these two states. The measured rate constant (K_{AB}) for the collisional energy transfer AlO($A^2\Pi$, v=53)+Ar - AlO($B^2\Sigma^*$, v=14) +Ar is found to be ~ 7×10^6 Torr⁻¹ sec⁻¹ comparable with a rate constant 9×10^{6} Torr⁻¹ sec⁻¹ estimated for "hard sphere" collisions between Ar ($T \sim 300$ °K) and AlO $(T \sim 3000 \,^{\circ}\text{K})$. This indicates that energy transfer occurs at every "hard sphere" collision on a time scale, K_{AB}^{-1} $\sim 2 \times 10^{-10}$ sec at 1 atm, similar to that generally associated with rotational relaxation (R-R process). In the present study, we will examine much more pronounced effects observed in ScO. In contrast to AlO where pressure dependent effects are observed from 1 to 5 Torr, they are observed in ScO from 10 to 400 μ m. Collisional transfer to ScO $B^2\Sigma^*$, v'=3-9 from long-lived reservoir states is observed to proceed at rates which for certain levels (v' = 6, 8) approach 100 times gas kinetic, the time scale K_{RB}^{-1} being 3×10^{-12} sec at 1 atm for the most perturbed levels.

The effects which we have observed and analyzed in ScO are significant since they demonstrate that the excited states of this molecule interact in the presence of a collision partner as if they were large diffuse entities. Effectively one deals with "pseudomacromolecules" which display many of the characteristics of Rydberg states. This behavior may have important implications for the modeling of energy systems as well as the ability to create population inversions requisite for the construction of chemical laser systems. Based upon preliminary studies of potassium hydroxide as well as yttrium, lanthanum, and boron oxide formation, the effects we observe in ScO are not pathological but rather are indicative of a broad class of compounds.

EXPERIMENTAL

The burner systems used in these experiments are similar in design to those described previously.⁸⁻⁸ The single collision experimental studies have been described in detail.⁶ For multiple collision work, scandium metal (Alfa products 99.98%) is evaporated in a vacuum chamber from a resistively heated vapor deposited tungsten crucible (Ultramet, Pacoima, Calif.). The metal vapor is collimated by an argon or helium carrier gas (Matheson 99.9995%) and transported to the reaction zone where mixing with the oxidant gas occurs. The scandium is oxidized with NO₂ as supplied by Matheson Corp. (99. 5%minimum purity). Typical operating pressures ranged from 2 to 20 μ m of oxidant and from 10 to 1000 μ m of argon or helium. Pressures were measured with a capacitance manometer (MKS Baratron Type 170). The sampling orifice to the manometer input head was made mobile so that pressure gradients in the chamber could be readily determined. In all cases the gas concentration in the multiple collision studies is dominated by the argon or helium carrier. For experiments run at the higher buffer gas pressures, flames were conical in shape with a base diameter of approximately 12 mm and heights ranging from 1 to 3 cm. At lower buffer gas pressures ($P_{ox} \sim 2-5 \ \mu m$, $P_{argon} \sim 10-50 \ \mu m$) flame definition decreased and a more diffuse glow was observed.

Fortunately scandium is one of the less corrosive and reactive high temperature metals. We have found that vapor deposited tungsten crucibles are ideally suited for long term experimental studies. These crucibles are placed in a machined carbon (Micromechanisms-99.95%) sheath which fits inside a commercial basket heater (R. D. Mathis, Long Beach, Calif.), the entire assembly being wrapped with several layers of zirconia (ZrO₂) cloth (Zircar Products, Florida, N. Y.). The zirconia insulation significantly reduces heat loss due to black-body radiative processes and, at the higher pressures, gas conduction⁸; its use permitted an upper operating temperature close to 1800 °C. The entire assembly was surrounded by a water cooled brass shield which was placed inside the vacuum chamber. This arrangement also provided an effective "light" baffle against black-body radiation from the crucible and heater. Under typical operating conditions (80 A at 12 V giving ~1600 $^{\circ}$ C), this crucible system continues to last indefinitely.

The chemiluminescent flame was focused onto the slit of a Spex 1 m monochromator, equipped with an RCA 4840 photomultiplier tube. The photomultiplier signal was detected with a Keithley 417 fast picoammeter whose output signal (partially damped) drove a Leeds and Northrop strip chart recorder. The spectrometer was periodically calibrated with a mercury resonance lamp. The entire optical system was calibrated for relative spectral response employing a quartz iodine standard lamp (EG and G #B 115 A).

ANALYSIS OF PERTURBATIONS AND RAPID TRANSFER ROUTES

In the following discussions, we focus on the nature of strong interactions between the $B^{2}\Sigma^{*}$ state of ScO and either previously unobserved long-lived electronic "reservoir" states or the high vibrational levels of known lower-lying electronic states from which transition may be "forbidden" primarily by virtue of the Franck-Condon principle. The reservoir states to which we refer are characterized by very small electronic transition moments connecting these states and the ground electronic state. Traditionally, emission from these states is seldom observed and, when detected, most frequently involves the lower energy state of an emission band system.

The Sc-NO₂ reaction is known to produce the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states of ScO.⁹ Very weak emission may be observed from the $A'^2\Delta$ (Ref. 10) and $C^2\Pi$ states,¹¹ the emission from $A'^2\Delta$ being over an order of magnitude weaker than that from $A^2\Pi$. In the present study, we are concerned with the sequence which involves the initial reaction step

$$Sc(^{2}D) + NO_{2}(^{2}B_{1}) \rightarrow ScO(X^{2}\Sigma^{*}, A^{2}\Pi, B^{2}\Sigma^{*}A'^{2}\Delta, C^{2}\Pi,$$

Reservoir States) + NO (1)

followed by collision induced transition to the $B^{2}\Sigma^{*}$ state:

$$ScO(initial) + Ar \rightarrow ScO(B^{2}\Sigma^{*}) + Ar$$
 (2)

The nature of expected reservoir states will be discussed in a following section.

In the presence of intramolecular perturbations, neither the $B^{2}\Sigma^{*}$ state nor the states from which energy transfer occurs may be considered as pure states. Rovibronic levels of these initially populated states contain a small admixture of $B^{2}\Sigma^{*}$ character. Hence transitions from these reservoir levels, which are forbidden or very weak in the absence of perturbations, may "borrow intensity" from the B-X spectrum and become allowed.¹² These features appear as satellite bands slightly shifted from the observed B-X transitions. Figure 1(b) exemplifies one of these satellite features in the ScO $B^{2}\Sigma^{*} - X^{2}\Sigma^{*}$ spectrum taken at a pressure of 400 μ m. Here we find a dominant (8, 5) band with a satellite observed ~ 50 $\rm cm^{-1}$ to the red. As we will demonstrate shortly, the energy separation $(\Delta \nu)$ between the main and satellite bands is dependent on the vibrational level v' in $B^{2}\Sigma^{*}$ and is invariant (within experimental error) to v'', the vibrational quantum number in the ground (lower) state.



FIG. 1. Scan over portion of ScO $B^2\Sigma^*-X^2\Sigma^*$ emission spectrum (res = 1.5 Å) resulting from the Sc + NO₂ reaction. Band heads are denoted (v', v''). The upper trace was taken at a total pressure $P_{tot} = 10 \ \mu m$; the lower trace corresponds to $P_{tot} = 400 \ \mu m \ P_{NO_2} = 4 \ \mu m$ for both traces, the remaining pressure corresponding to argon. As the argon pressure is raised an extra satellite feature becomes apparent to the red of the main (v', v'') = (8, 5) band.

The magnitude of $\Delta \nu$ depends upon the "strength" of the perturbation (w) which usually involves a spin-orbit or coriolis interaction and the energy separation of the unperturbed states (δ) . The eigenfunctions (Ψ) and eigenvalues (E) of the perturbed levels are¹²

$$\Psi_{+} = c\Psi_{1} - d\Psi_{2}, \quad \Psi_{-} = d\Psi_{1} + c\Psi_{2} , \qquad (3)$$

where

$$c^{2}/d^{2} = (\Delta \nu + \delta)/(\Delta \nu - \delta)$$
(4)

and

$$(E_{-} - E_{-}) = \Delta \nu = (4w^{2} + \delta^{2})^{1/2} \quad . \tag{5}$$

The subscripts 1, 2, and \pm pertain to unperturbed and perturbed levels, respectively. An independent evaluation of both w and $\delta = E_1 - E_2$ is not possible from a measure of $\Delta \nu$ alone; however, sufficient additional information may be obtained from the pressure dependence of the relative intensities for the main (Ψ_{\star}) and satellite (Ψ_{\star}) transitions. In Fig. 2, we depict two mutually perturbed levels in the $B^{2}\Sigma^{+}$ state and that state formed initially via Reaction (1) which interacts strongly with $B^{2}\Sigma^{*}$ and from which energy transfer occurs. The initial chemical Reaction (1) with rate constant k populates a range of levels in a given reservoir state or Franck-Condon "forbidden" levels of a known electronic state. The vibrational dependence of this rate, even if known, is not required for the description given here. Strongly perturbed levels may be depopulated by spontaneous emission to the ground $X^{2}\Sigma^{*}$ state giving rise to the satellite feature observed in Fig. 1 or by nonradiative collisional transfer to the $B^{2}\Sigma^{*}$ state. The rate of this latter pro-

J. Chem. Phys., Vol. 73, No. 2, 15 July 1980

838



FIG. 2. Schematic representation of the competing transfer and depopulation processes, collisional redistribution (k_{RB}) from "reservoir state" levels and radiative emission $(k_{\star}$ and k_{\star}) from $B^{2}\Sigma^{+}$ and reservoir states. The vibrational relaxation rates are denoted by k_{v} , and k_{v} . Transfer follows initial formation (k) of the reservoir state.

cess, intramolecular energy transfer which we denote by k_{RB} , is dependent on collisions between Ar and ScO and is therefore proportional to the argon pressure [Ar]. As a result of microscopic reversibility, there is a near equal probability of collisional transfer out of $B^{2}\Sigma^{+}$. i.e., $k_{BR} = k_{RB}$. k_B , the rate constant for direct ScO $B^{2}\Sigma^{*}$ formation [Reaction (1)] can be compared to the rate $k_{RB}(Ar)$ for collisional population of the $B^{2}\Sigma^{*}$ state [Reaction (2)] by evaluating the $Sc - NO_2$ reaction from 10⁻⁵ Torr, where emission results from nascent product formation, through the pressure range where collisional transfer increases in importance and begins to dominate. The radiative rate constants k_{\perp} for Ψ_{\perp} and k_{\perp} for Ψ_{\perp} pertain to transitions from a single vibrational level in the upper state to all vibrational levels v'' of $X^2\Sigma^*$. k_{\perp} and $k_{\rm a}$ are primarily dependent upon the upper state quantum number and to a much lesser extent on v''. The collisional rate constant is a function of both $v'(B^2\Sigma^*)$ and v(reservoir). k_{RB} and k_* are purely phenomenological. They contain an implicit vibrational dependence which will be considered in a later section. k_v and k_v , correspond to rate constants for radiative or nonradiative processes leading to vibrational relaxation in the reservoir or $B^{2}\Sigma^{*}$ states. As we will demonstrate in a following section, vibrational relaxation effects in either the $B^{2}\Sigma^{*}$ or reservoir states may safely be ignored.¹³

With the provisos indicated above, the elementary steps described in Fig. 2 which are pertinent to collisional transfer may be represented by a set of rate equations describing the time-dependent population of the $B^{2}\Sigma^{*}$ levels,

$$\frac{d}{dt[N_*]} = k_{RB}[N_-][\mathbf{Ar}] - k_{RB}[N_*][\mathbf{Ar}] - k_*[N_*] , \qquad (6)$$

where $[N_{\star}]$ and $[N_{\star}]$ are the population densities for the levels Ψ_{\star} and Ψ_{\star} , respectively. The steady state solution¹⁴ for Eq. (6) yields

$$[N_{\star}]/[N_{-}] = k_{RB}[Ar]/(k_{RB}[Ar] + k_{\star})$$
(7)

The two limiting cases can be envisioned:

$$\lim_{[A_{\Gamma}] \to 0} \left[\frac{[N_{\star}]}{[N_{\star}]} = 0 , \quad \lim_{[A_{\Gamma}] \to \infty} \frac{[N_{\star}]}{[N_{\star}]} = 1 .$$
 (8)

The first corresponds to a low pressure extremum where the dominant population resides in those levels corresponding to Ψ_{-} and emission from perturbed levels of the reservoir state may dominate the observed emission spectrum² (given a sufficiently large transition moment). The second correspond to a high pressure limit in which the populations of Ψ_{+} and Ψ_{-} become equal (saturation) and further increases in pressure have no effect on the relative intensities of the main and satellite features. The pressure at which the saturation point is reached is a function of the balance between the efficiency of collisional transfer (collisional transfer rate) and the radiative lifetime of the $B^{2}\Sigma^{*}$ state.¹⁵

The intensities of the main and extra transitions, $I^*(v', v'')$ and $I_{\bullet}(v', v'')$, respectively, are related to the excited state populations $[N_{\star}]$ by

$$I_{\pm}(v', v'') \propto A_{\pm}(v', v'') [N_{\pm}] , \qquad (9)$$

where $A_{\pm}(v', v'')$ represents the electronic and vibrational transition probability for emission from Ψ_{\pm} . Since the pertinent transitions are nearly coincident in frequency, phototube and frequency corrections are of minimal importance when considering relative intensities and we combine Eqs. (7) and (9) to yield

$$\frac{L(v', v'')}{I_{\star}(v', v'')} = \frac{A_{\star}(v', v'')}{A_{\star}(v', v'')} \left(1 + \frac{k_{\star}}{k_{RB}[Ar]}\right) .$$
(10)

A plot of relative intensity versus reciprocal pressure will be a straight line with an intercept $A_{\star}(v', v'')/A_{\star}(v', v'')$ and a slope which is a measure of k_{\star}/k_{RB} . In a later section we will consider more specifically the analysis of the terms in Eq. (10) and its application to the solution of Eqs. (4) and (5).

RESULTS

We will demonstrate in this section that collisional transfer to the $B^{2}\Sigma^{*}$ state of ScO occurs much more efficiently than previously observed in AlO. In order to characterize this energy transfer, the strong interactions from which it results, and its effect on the relative population distribution in the $B^{2}\Sigma^{*}$ state, we have analyzed the B-X emission spectrum from 10^{-5} to 1 Torr.

A. Vibrational populations in $B^2\Sigma^+$

Figures 3, 4, and 5 depict representative scans of the ScO $B^{2}\Sigma^{*}-X^{2}\Sigma^{*}$ emission spectrum taken at 10⁻⁵, 10⁻², and 1 Torr, respectively. Each spectrum is comprised of red-degraded bands falling into the sequence groupings



FIG. 3. Chemiluminescent spectrum obtained under single collision conditions from the reaction $\text{Sc} + \text{NO}_2 \rightarrow \text{ScO}^* + \text{NO}$. Bandheads in the ScO $B^2\Sigma^* - X^2\Sigma^*$ band system are denoted (v', v''). The lower trace corresponds to the experimental spectrum, while the upper trace is a computer simulation. Perturbations are apparent for levels with v' = 3-7. Spectral resolution is 1.5 Å. See text for discussion.

 $0 \le \Delta v \le 2$. (The notation $\Delta v = v' - v''$ pertains to the transitions connecting vibrational levels v' of $B^2 \Sigma^*$ and v'' of $X^2 \Sigma^*$.) The experimental spectra were taken at a resolution of 1.5 Å and a scan speed of 0.2 Å/sec. The spectra were assigned by comparison with previous-ly reported data.⁶ All spectra were calibrated using mercury and neon resonance lamps.

In each figure, the experimental spectra are compared to computer synthesized spectra calculated with the aid of Franck-Condon factors¹⁸ and RKR curves¹⁷ generated using available high resolution data. ¹⁸ The computer simulation assumes no level perturbations. The comparison of experimental and calculated spectra allows the rapid assessment of strong perturbations in the $B^{2}\Sigma^{*}$ state. Upon analysis of the spectra, it became apparent that the v' = 3-9 vibrational levels of the $B^{2}\Sigma^{*}$ state were all significantly perturbed, and that some modification of previous wavelength assignments^{9,15} was necessary. These revised level positions are listed in Table I where the error estimate (± 0.2 Å) represents one standard deviation in the wavelength calibration.

Taking into account the maximum temperature of the scandium metal undergoing reaction¹⁹ and all other factors in addition to reaction excergicity which contribute to the available energy for formation of ScO product, the Sc-NO₂ reaction can result in the population of 16 vibrational levels in the $B^{2}\Sigma^{*}$ state.

The relative intensities $I_{v',v'}$, of vibronic transition (v', v'') in emission are related to the excited state



FIG. 4. Chemiluminescent spectrum obtained at $P_{tot} = 14 \ \mu m$ for the process Sc + NO₂ ($P \approx 4 \ \mu m$) + Ar ($P \approx 10^{+} \ \mu m$) \rightarrow SeO* + NO + Ar. Bandheads in the ScO $B^{2}\Sigma^{+}_{-}X^{2}\Sigma^{+}$ band system are denoted (v', v''). The upper trace corresponds to the experimental spectrum; the lower trace is a computer simulation. Perturbations are apparent for levels with v' = 3-7. A dual satellite structure accompanies the (6, 4) band. Spectral resolution is 1.5 Å. See text for discussion.



FIG. 5. Chemiluminescent spectra (a) and (b) obtained at $P_{tot} \approx 1000 \ \mu m$ for the process Sc + NO₂ ($P \approx 30 \ \mu m$) + Ar ($P \approx 1000 \ \mu m$) \rightarrow ScO^{*} + NO + Ar. Bandheads in the ScO $B^2 \Sigma^* - X^2 \Sigma^*$ band system are denoted (v', v''). The upper traces correspond to the experimental spectrum; the lower traces are computer simulations. Perturbations and satellite structure are apparent for levels v' = 3 - 9. The computed spectrum corresponding to the (6, 6) inset in (b) (dashed line) merely indicates the expected location of the (6, 6) band and does not correspond to any attempted intensity match. Spectral resolution is 1.5 Å. See text for discussion.

populations N_{v} , by

$$I_{v',v''} = \xi(v) v^4 q_{v',v''} R_e^2(\vec{r}_{v',v''})$$
(11)

where $\xi(\nu)$ is a proportionality constant defined to include the variation of instrumental (spectrometer and

TABLE I. Modified parametrization for ScO $B^{2}\Sigma^{*}-X^{2}\Sigma^{*}$ transitions—bands observed in Figs. 3, 4, and 5.^a

Band (v', v'')	λ (Å) ^b	Ob served frequency	C alculated frequency ^e	Δ (cm ⁻¹) (obs-calc)
(0,0)	4859.3	20 573	20 573	• • •
(1, 0)	4674.0	21 389	21 389	• • •
(2,1)	4709.1	21 230	21228	2
(3,2)	4743.4	21076	21068	8
(4,3)	4780.0	20 914	20 907	7
(5,4)	4817.5	20752	20746	6
(6,4)	4644.6	21525	21518	7
(7,5)	4681.7	21354	21346	8
(8,6)	4719.1	21 185	21176	9
(9,7)	4759.2	21 006	21 002	4

^aBands listed are representative of $v' = 0 - 9 B^2 \Sigma^+$ perturbations. From analysis of several transitions to v'' = 0 - 7, no measurable perturbations of these ground state levels are found. ^bOnly (0,0), (1,0), and (2,1) bands agree with calculated bandhead positions. All other levels are shifted.

^cCalculated from $T_e(B^{2}\Sigma^*-X^2\Sigma^*) = 20640.2$, $w_e^* = 825.47$, $w_ex'_e = 4.21$, $w_e^{**} = 964.95$, $w_ex'_e^* = 3.95$. See A. Adams, W. Klemperer, and T. M. Dunn, Can. J. Phys. 46, 2213 (1968); L. Akerlind, Ark. Fys. 22, 41 (1962); and Refs. 9 and 15.



FIG. 6. $B^{2}\Sigma^{+}$ vibrational populations $(N_{v'})$ for (a) single collision conditions—Fig. 3; and (b) $P_{tot} = 14 \ \mu m$ —Fig. 4. Relative populations are determined on the basis of the computer simulations in Figs. 3 and 4 for v' = 0-9. Populations denoted with an asterisk represent upper bound estimates.

photomultiplier tube) response with frequency; $q_{v',v''}$ and $\overline{r}_{n',n''}$ are, respectively, the Franck-Condon factor and r centroid for the (v', v'') transition. The electronic transition moment $R_{\theta}(\vec{r}_{v',v'})$ is written as an explicit function of the r centroid in accordance with the Fraser approximation.²⁰ This information is incorporated into the computer program to calculate the spectrum corresponding to a ${}^{2}\Sigma^{*} - {}^{2}\Sigma^{*}$ transition. Once a fit is made to a given spectrum as in Figs. 3, 4, and 5, a rotational temperature is determined for each individual vibrational band and relative vibrational level populations are evaluated. For those spectra obtained at the lowest pressures where only nascent product formation is monitored, the rotational temperature of each vibrational band can differ²¹; however, at higher pressures rotational distributions are found to equilibrate rapidly and the entire spectrum is characterized by one rotational temperature.22

In Figs. 6 and 7 we compare $B^{2}\Sigma^{*}$ vibrational populations determined for 10⁻⁵, 10⁻¹, and 1 Torr chemilumines cent flames. Only those vibrational levels (v'=0-9)which play a dominant role in the spectra presented in Figs. 3, 4, and 5 are considered; however, emission

is also observed corresponding to those transitions from v' = 10-13 having the largest Franck-Condon overlap with the ground electronic state.

The single collision spectrum (Fig. 3) is characterized closely by a single rotational temperature, $T_{rot} \sim 6000$ °K. This result is consistent with a previous analysis of rotational structure in the (0, 0) band and with temperature dependence studies which demonstrate that the Sc-NO₂ reaction to form ScO $B^{2}\Sigma^{*}$ proceeds with a substantial activation energy.²² Not surprisingly, the vibrational distribution observed under single collision conditions is non-Boltzmann.

The population distribution observed at $P_{total} = 14 \ \mu m$ $(P_{NO_2} = 4 \ \mu m)$ is presented in Fig. 6(b). Within experimental error the vibrational distribution for levels v'=0-5 has changed only slightly. If present, vibrational relaxation is minimal. There is a notable change in the relative populations for vibrational levels v' = 6, 7. Two choices can be envisioned to explain this phenomenon: (i) the population in vibrational levels v' = 6 and 7 results in part from collisional transfer via an initially formed long-lived reservoir state or (ii) there is rapid vibrational relaxation in levels v' = 8-15, a bottleneck being encountered for levels v' = 6, 7. Based upon observations over the pressure range 10–1000 μm and comparison with previous studies,²³ the former mechanism is



FIG. 7. $B^{2}\Sigma^{+}$ vibrational population $(N_{v'})$ as a function of the vibrational energy term G(v') for vibrational levels v' = 0-9. Relative populations for $P_{tot} = 1000 \ \mu m$ are determined on the basis of the computer simulations in Figs. 5(a) and 5(b).

by far the more likely possibility. For a selection of confirming evidence, we focus on the spectra in Fig. 1. At a pressure of 10 μ m, it is apparent that there is substantial population in v' = 13 relative to v' = 8 or 3 [the FC factor for the (13, 9) transition exceeds those for all other transitions from $v' = 13 B^2 \Sigma^*$ but does not greatly exceed those for the (8, 5) and (3, 1) transitions]. In addition, a fit of the 400 μ m data taking into account overlap with the (8, 5) and satellite bands indicates that v' = 13is not drastically diminished with respect to v' = 3, as one would expect if unusually rapid vibrational relaxation were present. As a further demonstration of the presence of a collisional transfer process at 10 μ m (Fig. 4) we observe the first clear indication of satellite structure. The (6, 4) band is accompanied by both long and short wavelength satellite features. As we will demonstrate shortly, collisional transfer is most efficient for the v' = 6 level.

The vibrational bands observed at 10 μ m are well fit by a rotational temperature $T_{rot} = 4500$ °K. Although some rotational relaxation has taken place relative to the single collision spectrum, R-R transfer is not yet pronounced at 10 μ m. This result also casts doubt on the possibility of significant V-V transfer for levels v'=0-13 since this process is expected to proceed on a time scale two orders of magnitude slower than R-R relaxation.²⁴

At $P_{\text{total}} = 100 \ \mu \text{m}$ [Figs. 5(a) and 5(b)], we find significant spectral changes as well as a substantial modification of the population distribution observed at lower pressures. In Fig. 5(a), satellite bands are apparent for the transitions emanating from v' = 3, 4, 5, 8, and 9 $(B^{2}\Sigma^{*})$. In Fig. 5(b), the dual satellite features encompassing the main v' = 6 emission feature are emphasized. Because the v' = 6 and 8 levels and their satellites are the most amenable to characterization over a wide pressure range, we will focus on the pressure dependence of these satellite and main features in a following section. Figure 7 depicts the population distribution at 1000 μ m (1 Torr). This distribution is virtually identical to that observed at 400 μ m. The observed population distribution which peaks strongly at v' = 8 provides definitive evidence for efficient collisional transfer and casts strong doubt on the possibility of a bottleneck for vibrational relaxation at v'=6, 7.

The bands observed at P=1 Torr are well fit by a rotational temperature, $T_{\rm rot} = 800$ °K. Not surprisingly, significant rotational relaxation has occurred at this pressure. The observation of pronounced rotational relaxation focuses attention on the possibility of significant vibrational relaxation. While there are substantial changes in the observed population distribution, these changes do not indicate pronounced vibrational relaxation concomitant with the buildup of emission intensity for the lower (v'=0-3) vibrational levels. Rather, one observes a shift in population to higher v' levels indicative of rapid collisional transfer from initially populated states to the $B^{2}\Sigma^{*}$ state. More specifically, we observe pronounced transfer for v' = 6, 7, 8 and somewhat lesser effects for v' = 4, 5, 9. Note that while the population in v' = 9 is substantially less than that in v' = 8, the relative popula-

TABLE II. Main and extra transitions (v', v'') in the $B^2 \Sigma^* - X^2 \Sigma^*$ spectrum of ScO.

Assign-	Wavelength in air (Å)		Vacuum wa	Separation	
ment	Main	Extra	Main	Extra	$\Delta \nu \ (\text{cm}^{-1})$
(8,9)	5416.9	5432.4	18 455	18 403	52
(8,8)	5164.6	5178.8	19357	19304	53
(8,7)	4932.8	4945.9	$20\ 267$	20 213	54
(8,6)	4719.1	4730.8	21 185	21 1 32	53
(8,5)	4521.7	4532.7	22 109	22 056	53
(8,4)	4338.4	4348.3	23043	22 991	52
(8,3)	4167.9	4177.2	2 3 9 86	23 933	53
(6,6)	5084.0	5080.6	19664	19677	13
	5084.0	5088.1	19664	19648	16
(6,4)	4644.6	4641.9	21 525	21 537	12
	4644.6	4647.9	$21\ 525$	21 509	16
(6,3)	4450.1	4447.3	22465	22 479	14
	4450.1	4453.1	22 465	22 4 50	15

tion of this level has increased significantly relative to levels $v' \leq 4$. The observed population distribution is clearly non-Boltzmann. There is also a clear trend away from a Boltzmann distribution as pressure increases. Vibrational relaxation cannot play a significant role in any explanation of the pressure dependent effects observed in this study.

As we will discuss in a later section, the peaking in the $B^{2}\Sigma^{*}$ population distribution at $P = 1000 \ \mu m$ results primarily from the inherent population of that level which feeds v' = 8 upon collisional transfer. The peaking is *not* related to any bottlenecks in the $B^{2}\Sigma^{*}$ state but can result in part from any process including vibrational relaxation which populates the "feeder" level of the reservoir state from which transfer occurs.

B. Perturbations and satellite structure

In the previous section we have considered the non-Boltzmann distribution induced in the ScO $B^2\Sigma^*$ state as a result of collisional transfer. In a future section we will consider the possible states from which this transfer can occur. Here, we focus primarily on those bands corresponding to transitions which originate in the v'= 6 and 8 levels of the ScO $B^2\Sigma^*$ state. Because these bands and their satellites are the most amenable to study, they have been the most extensively investigated.

The satellite structure which accompanies the intense emission from $v' = 8 B^2 \Sigma^*$ is evident in Figs. 1(b) and 5(a) where we depict the (8, 5) and (8, 6) emission bands at 400 and 1000 μ m, respectively. In both cases, adjacent to each of these strongest features is a weaker and red shifted satellite band. A similar but somewhat more complicated satellite structure is observed for v' = 6transitions in Figs. 4 and 5(b). Here the (6, 4) and (6, 6) bands are accompanied by both a blue and red shifted satellite. As indicated in Table II, several other transitions involving the v' = 6 and 8 bands have been observed throughout the visible region. A scan of the data in Table II indicates that the energy separation (Δv) between the main and satellite bands depends on the vibrational level v' in $B^{2}\Sigma^{*}$ and is invariant (within experimental error) to v'', the vibrational quantum number of the lower state. The average separations are (Table II) $\Delta v = 53 \pm 1.6 \text{ cm}^{-1}$ for v' = 8 and $\Delta v = 16 \pm 1.4 \text{ cm}^{-1}$ (red feature) and $13 \pm 1.2 \text{ cm}^{-1}$ (blue feature) for v' = 6. Here the uncertainties represent one standard deviation in the mean.

It is the v'=6, 8 satellite features which have been the focus of our pressure dependent studies; however, further satellite features are clearly apparent at P_{tot} = 1000 μ m in Fig. 5(a). A weak satellite is associated with the (9, 7) band, its separation being 58 ± 2 cm⁻¹. As we will demonstrate, the location of this satellite can be predicted on the basis of v'=6, 8 perturbations. The red shifted satellite features which accompany the (5,4), (4,3), and (3,2) bands appear to emanate from a band system differing from that which perturbs the v'=6-9 levels. The satellite and main features are separated by 25 ± 2 , 22 ± 2 , and 20 ± 2 cm⁻¹ for v'=5,4,3, respectively. The nature of these satellites will be considered further in the following sections.



FIG. 8. (a) Variation of relative intensity of main (I_{\star}) and satellite (I_{-}) bands with reciprocal argon pressure for red shifted satellite associated with $v' = 6 \text{ ScO } B^2 \Sigma^*$. The full line represents a linear least-squares fit to all data points [(0) (6,6); (0) (6,4); (Δ) (6,3) band—see Table II]. (b) Similar plot for v' = 6 blue satellite (see Table II).



FIG. 9. Variation of relative intensity for main (I_{\star}) and satellite (I_{-}) bands with reciprocal argon pressure for red shifted satellite associated with $v' = 8 \text{ ScO } B^2 \Sigma^*$. The full line represents a linear least-squares fit to all data points [(0) (8,5); (0) (8,6); (Δ) (8,7) band—see Table II].

C. Pressure dependence of relative intensities

In Figs. 8 and 9, we plot the intensity ratio I(v', v'')/ $I_{i}(v', v'')$ versus reciprocal argon pressure [Ar]⁻¹ for the dual satellites associated with $v' = 6 \operatorname{ScO} B^2 \Sigma^*$ and the single satellite associated with $v' = 8 \operatorname{ScO} B^2 \Sigma^*$. Total argon pressures were measured with a calibrated capacitance manometer and are judged accurate to $\pm 10\%$. Relative band intensities were measured using both peak heights and peak areas (spectra taken at a resolution of 0.8 Å and scan speed of 0.1 Å/sec), the majority of data involving peak area measurement; however, the comparative variations obtained for a given datum point in all cases were less than 20%. The data points in Figs. 8 and 9 were taken for a series of bands corresponding to transitions originating in v' = 6.8 $B^{2}\Sigma^{*}$ and terminating in several vibrational levels $v^{\prime\prime}$ of the ground state. The full lines in Figs. 8 and 9 depict least squares fits in accord with the predictions of Eq. (10). Table III lists the corresponding least squares parameters A(v', v'')/A(v', v'') from the intercept and k_{\star}/k_{RB} from the slope. The error estimates result from one standard deviation uncertainty in the measured slope and intercept. The data points taken at lower pressure all display a negative deviation from the least squares fit. As we will discuss shortly, this is not surprising since the collisional transfer process and the corresponding interaction potential may be strongly influenced by significant dipole-dipole forces [ScO(res) +ScO \rightarrow ScO($B^{2}\Sigma^{+}$)+ScO] versus the very much more prevalent dipole-induced dipole interaction [ScO+Ar $- \operatorname{ScO}(B^{2}\Sigma^{*}) + \operatorname{Ar}]$ at higher pressures.

TABLE III. Kinetic and spectroscopic parameters (defined in text) for vibrational levels v' = 6, 7, 8, 9 of the ScO $B^2\Sigma^*$ state. Estimated errors arise from one standard deviation uncertainty in the experimentally determined parameters.

v '	$\Delta \nu$ (cm ⁻¹)	k ₊ ∕k _{RB} (Torr)	A_{-}/A_{+}	d^2	δ (cm ⁻¹)	$w ({\rm cm}^{-1})$	$\frac{k_{AB} \times 10^{-6}}{(\text{Torr}^{-1} \text{ sec}^{-1})}$
6 ^a	16±1.4 ^b	0.05	0.78	0.44	2±0.6	15.9 ± 2.5	500
	16 ± 1.4	0.04	0.77	0.44	2 ± 0.6	15.9 ± 2.5	600
	13 ± 1.2^{b}	29.75	0.040	0.038	12 ± 1.8	2.5 ± 1.2	0.84
	13 ± 1.2	31.25	0.037	0.036	13 ± 1.8	2.6 ± 1.2	0.80
7°	34.9 ± 2.4	•••	0.297	0.23	18.9±2.6	14.7 ± 4	•••
8 ^a	53 ± 1.6	0.12	0.20	0.17	35.8 ± 2.4	19.5 ± 2.4	210
	53	0.11	0.19	0.16	35.8	19.5 ± 2.4	230
9	58 ± 2^{d}	•••	(0.086) ^e	0.08	$(48.8 \pm 3.2)^{f}$	14.4 ± 2.8	•••
	56.7 ± 1.2^8	•••	0.076	0.08	48.7 ± 3.2	14.5 ± 2.8	• • •

^aThe first value represents the results of pressure dependence plots (Figs. 8 and 9) while the second corresponds to data obtained upon measurement of level shifts relative to unperturbed levels.

^bThe feature separated by 16 cm⁻¹ appears at longer wavelength while the feature separated by 13 cm⁻¹ appears at shorter wavelength.

^cCalculated through analysis of v' = 6, 8 perturbations.

^dMeasured perturbed level separation [Fig. 5(a)].

^eEstimated from ratio I^{-}/I^{+} (see text for discussion).

^fLower bound based on measured ratio I^{-}/I^{+} (see text for discussion).

^gCalculated through analysis of v' - 6, 8 perturbations, and measurement of level shifts relative to unperturbed levels (see text for discussion).

The application of the data obtained from Figs. 8 and 9 to the solution of the perturbation relation (4) and (5) necessitates several approximations in the microscopic interpretation of $A_{\star}(v', v'')$. For electric dipole radiation,

$$A_{\pm}(v', v'') = \left| \left\langle \Psi_{\pm} \right| \tilde{M}_{e}(r_{e}) \left| \Psi'' \right\rangle \right|^{2} , \qquad (12)$$

where the Ψ_{\star} are the same as in Eq. (3) and Fig. 2 and $M_{e}(r_{e})$ is the electric dipole moment operator dependent upon the electronic coordinates r_{e} .¹² The wave function Ψ'' represents the $X^{2}\Sigma^{*}$ ground state. The wave functions for the ground state and the pure $B^{2}\Sigma^{*}$ and reservoir states may be written as the product of an electronic and vibronic term. Following the notation of Eqs. (3)-(5) and Fig. 2,

$$|\Psi''\rangle = |X^{2}\Sigma^{*}\rangle |v''\rangle, \quad \Psi_{1} = |B^{2}\Sigma^{*}\rangle |v'\rangle, \quad \Psi_{2} = |\operatorname{res}\rangle |v\rangle.$$
(13)

Substituting for Ψ_{\bullet} and Ψ'' in Eq. (12),

$$A_{*}(v', v'') = \left| c \langle B^{2}\Sigma^{*} | \tilde{M}_{e}(r_{e}) | X^{2}\Sigma^{*} \rangle \langle v' | v'' \rangle - d \langle \operatorname{res} | \tilde{M}_{e}(r_{e}) | X^{2}\Sigma^{*} \rangle \langle v | v'' \rangle \right|^{2}, \qquad (14)$$

$$A_{\bullet}(v', v'') = \left| d \langle B^{2} \Sigma^{\star} \right| \tilde{M}_{\theta}(r_{\theta}) \left| X^{2} \Sigma^{\star} \rangle \langle v' \left| v'' \right\rangle \\ + c \langle \operatorname{res} \left| \tilde{M}_{\theta}(r_{\theta}) \right| X^{2} \Sigma^{\star} \rangle \langle v \left| v'' \right\rangle \right|^{2} .$$
(15)

Here "res" denotes a reservoir state or Franck-Condon forbidden high vibrational levels of a known electronic state. Because we have only a small amount of information on the source states from which collisional transfer occurs, it is difficult to estimate the magnitude of the vibrational overlap factors $\langle v | v'' \rangle$ which appear in Eqs. (14) and (15). Since intensity measurements are limited to the strongest B-X features, it is reasonable to expect $\langle v | v'' \rangle \leq \langle v' | v'' \rangle$. Using $c \geq d$, we have, to good approximation,

$$A_{\star}(v', v'') \sim c^2 |\langle B^2 \Sigma^{\star} | \tilde{M}_{e}(\gamma_{e}) | X^2 \Sigma^{\star} \rangle |^2 |\langle v' | v'' \rangle|^2 \quad (16)$$

A similar approximation for $A_{-}(v', v'')$ is less satisfactory since the smaller coefficient multiplies the larger transition moment and vice versa. The cross interference term obtained upon expanding expression (15) is the most troublesome since it is proportional to $\langle v | v'' \rangle$ and $\langle v' | v'' \rangle$ and should therefore produce a v'' dependence in the measured intercepts. Since this effect is not observed experimentally, we feel confident that such terms may be ignored and that we are justified in the approximation

$$A_{\bullet}(v', v'') \sim d^2 \left| \left\langle B^2 \Sigma^{\bullet} \middle| \tilde{M}_e(r_e) \right| X^2 \Sigma^{\bullet} \right\rangle \left|^2 \left| \left\langle v' \middle| v'' \right\rangle \right|^2, \quad (17)$$

so that

$$A_{(v', v'')}/A_{(v', v'')} \simeq d^2/c^2$$
 (18)

Figures 8(a) and 8(b) comprise intensity measurements for transitions (v', v'') = (6, 4), (6, 6), and (6, 3). Since all three sets of data points fall very close to a straight line plot, these measurements indicate no v''. dependence in the parameter $A_{-}(v', v'')/A_{+}(v', v'')$. Similar results are obtained for transitions (v', v'')= (8, 5), (8, 6), and (8, 7) in Fig. 9. Consequently, the fractional admixture of "reservoir" state character (column 5 of Table III) may be estimated from Eq. (18) and the normalization condition $c^{2} + d^{2} = 1$. The data in columns 6 and 7 give [from Eqs. (4) and (5)] the energy separation between unperturbed levels (δ) and the perturbation matrix elements (w), which will be dealt with more thoroughly in a later section.

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FIG. 10. Comparison of $B^2\Sigma^*$ and deperturbed "reservoir state" vibrational energy level spacing on the basis of the perturbation parameters given in Table III. The energy level spacings determined for the unperturbed reservoir state are indicated at the left-hand side. The location of the ScO $A^{*2}\Delta_{3/2}$ level is also indicated $(\frac{3}{2})$ in the figure. It would appear that the vibrational spacings for the reservoir state are slightly smaller than those for $B^2\Sigma^*$, indicating the possible interaction with a low-lying ${}^{2}\Pi_{i}$ state corresponding to configuration (29) in the text.

The rate constant k_{i} (Table III, column 3) pertains to emission from a single vibrational level v' in $B^2\Sigma^*$ to all vibrational levels v'' in $X^2\Sigma^*$. The reciprocal of this parameter may be approximated by the radiative lifetime of the level v'. The last column in Table III gives values for k_{RB} estimated from $k_{*}^{-1} \sim 4 \times 10^{-8}$ sec, the radiative lifetime for the first four vibrational levels of $B^{2}\Sigma^{+}$.²⁵ Intramolecular energy transfer is most efficient for those $B^{2}\Sigma^{*}$ levels which contain the largest admixture of "reservoir" state character. For v' = 6, an analysis of the long-wavelength satellite indicates $k_{RR} \sim 5 \times 10^8$ Torr⁻¹ sec⁻¹, which corresponds to a time period $\tau \sim 3$ $\times 10^{-12}$ sec at 1 atm pressure. A second comparable value $(k_{RB} \sim 6 \times 10^8 \text{ Torr}^{-1} \text{ sec}^{-1})$ is obtained by noting the frequency shift of the v' = 8 level relative to its frequency in the computer synthesized spectrum and combining this data with the I^{-}/I^{+} ratio at a given pressure. A similar analysis has been carried out for v' = 8 using both the data analysis from Fig. 9 and level shifts measured from Figs. 1 and 5(a). The time scale which characterizes the energy transfer is considerably shorter than the typical rotational relaxation time for R-R transfer processes.

The data obtained for the v' = 6, 8 levels of the ScO $B^{2}\Sigma^{*}$ state indicates extremely strong mixing with an initially populated diffuse reservoir state (see also following sections). The observed transfer rates should be contrasted to that for the v' = 6 short-wavelength satellite, where $k_{RB} \sim 8 \times 10^{5}$ Torr⁻¹ sec⁻¹ corresponds to $\tau \sim 5 \times 10^{-9}$ sec at 1 atm pressure. Unfortunately, the regions of v' = 7 emission are substantially overlapped prohibiting a quantitative pressure dependence analysis (Figs. 8 and 9) at present. It does appear that transfer into v' = 7 is comparable to that into v' = 6 and 8 (Figs. 6

and 7); however, two overlapping levels involving more than one reservoir state appear to be involved (see following sections). Despite these problems, we were able to obtain some information on the v' = 7 level using the results for v' = 6 and 8. Assuming that the same reservoir state leads to the rapid transfer into v' = 6 and 8 and using the deperturbed level separations (δ), we can estimate the vibrational level spacing in the perturbing reservoir state and the separation of the v' = 7 level from its corresponding perturbing level. The results of this analysis are indicated in Fig. 10. Having obtained the deperturbed level separation $\delta = 18.9 \pm 2.6$ cm⁻¹ we measure the shift of the v' = 7 level from its calculated position (~8 cm⁻¹) to deduce $\Delta \nu \sim 34.9 \pm 2.6$ cm⁻¹. A similar calculation for v' = 9 (shift ~4 cm⁻¹) yields the data given in the second column of Table III. The agreement between predicted (56.7±1.2) and observed $(58\pm2)\Delta\nu$ values is excellent lending credence to the validity of our approach for v' = 7. The values of (A_A) for the two measurements involving v' = 9 are not in strong agreement; however, the first value corresponds to the measured ratio I_{-}/I_{+} and therefore represents an upper bound to (A_{μ}/A_{μ}) . Given the determination of δ and $\Delta \nu$, it is possible to determine w (Table III, column 7) from relation (5).

We have not carried out extensive pressure dependent studies for the v'=3, 4, 5 levels of the $B^{2}\Sigma^{*}$ state. We can, however, obtain some estimate of the parameters for these levels and the states by which they are perturbed. Again, the level shifts for the main spectral features from their positions in the computer synthesized spectrum are determined. These shifts when combined with measured satellite-main feature separations $(\Delta \nu)$ yield the data given in Table IV. From Δv and δ a value of d^2/c^2 was estimated from Eq. (5). The determined δ values indicate that the perturbing levels must be correlated with a different perturbing reservoir state and do not correspond to an extension of those levels interacting with v' = 6-9. The emission characterizing the v' = 3, 4 satellites is quite broad and therefore it is difficult to estimate Δv and to determine readily the relative intensities of satellite and main features. The v'= 5 satellite is more defined and, using intensity data from Fig. 5(a), $I_{(v', v'')}/I_{(v', v'')}$ was deduced and combined with d^2/c^2 and the known radiative lifetimes [Eq. (10)] to estimate the transfer rate given in the last column of Table IV. It appears that collisional transfer to v' = 5 is approximately an order of magnitude less efficient than that to v' = 6, 8.

In summary, our pressure dependence studies indicate that there must be at least one-low-lying long-lived reservoir state interacting strongly with the $B^2\Sigma^*$ state. In the following section, we focus on the nature of those possible metastable states which one might correlate with the satellite levels. The number of candidates appears to be quite limited.

D. Perturbation matrix elements—possible interacting excited states

In order to assess the possible reservoir states which interact strongly with ScO $B^{2}\Sigma^{+}$, we consider the molecular orbital configurations associated with the low-lying

v'	$\Delta \nu$ (cm ⁻¹)	v [*] Level shift (cm ⁻¹)	δ (cm ⁻¹)	d^2/c^2	d ²	$w (cm^{-1})$	I_/I_	$\frac{K_{RB} \times 10^{-6}}{(\text{Torr}^{-1} \text{ sec}^{-1})}$
3	20 ± 2 ^b	8±1	4 ± 3°	0,67±0,17°	0.4 ± 0.07^{c}	9.8±2.2 ^c	>0.54 ^d	
4	22 ± 2^{b}	7 ± 1	8 ± 3 ^c	0.47±0.15°	0.32 ± 0.07	10.3±2.2°	>0,44 ^d	•••
5	25 ± 2	6 ± 1	12 ± 3	0.35 ± 0.12	$\textbf{0.26} \pm \textbf{0.06}$	11 ± 2	0.75 ± 0.06	55 ± 40

TABLE IV. Spectroscopic and kinetic parameters for vibrational levels v'=3, 4, 5 of the ScO $B^{2}\Sigma^{+}$ state.^a Uncertainties correspond to one standard deviation in the mean.

^aParameters quoted in this table obtained from spectrum taken at $P_{tot} = 1000 \ \mu m$ [Fig. 5(a)].

^bBand is broad and $\Delta \nu$ value must represent a lower bound to the appropriate value—see text for discussion. ^cLower bound due to $\Delta \nu$ measurement—see text for discussion.

^dObtained from peak height measurements. Broad nature of band makes quantitative measurement prohibitive—see text for discussion.

electronic states of ScO and the possibility of their spinorbit or Coriolis interaction with the $B^{2}\Sigma^{+}$ state.

To date the only *ab initio* calculations carried out on any of the Group III*b* metal monoxides are those by Carlosn, Ludena, and Moser.²⁶ Their calculations correctly predicted the ground state to be ${}^{2}\Sigma^{*}$. In addition, they predicted the first excited state to be ${}^{2}\Delta_{*}$ with an energy of 2.0±0.5 eV. Their work has since been verified experimentally.⁵ The ground state configuration used in these calculations is

$$1\sigma^{2} 2\sigma^{2} 3\sigma^{2} 1\pi^{4} 4\sigma^{2} 5\sigma^{2} 6\sigma^{2} 2\pi^{4} 7\sigma^{2} 8\sigma^{2} 3\pi^{4} 9, X^{2} \Sigma^{*} .$$
(19)

The low-lying ${}^{2}\Delta_{r}$ state arises from the configuration

$$\cdots 8\sigma^2 3\pi^4 1\delta, \ ^2\Delta_r \ . \tag{20}$$

The $A^2\Pi$ state arises predominantly from

$$\cdots 8\sigma^2 3\pi^4 4\pi, A^2\Pi$$
 (21)

while the $B^{2}\Sigma^{*}$ state arises from the configuration

$$\cdots 8\sigma 3\pi^4 9\sigma^2, \ B^2\Sigma^+ \ . \tag{22}$$

The predominant terms in the 9σ , 1δ , and 4π LCAO-MO's are $4s\sigma(Sc)$, $3d\delta(Sc)$, and $4p\pi(Sc)$, respectively. There is also significant $np\sigma(Sc)$ contribution to the 9σ orbital. The 8σ orbital is predominantly $2p\sigma$ on oxygen. The four configurations (19)-(22) represent first order descriptions of the lowest lying states from which emission has been observed in ScO.

In order to assess possible interactions with the $B^{2}\Sigma^{*}$ state we adopt a simplified microscopic form of the spin-orbit operator commonly used in semiempirical calculations

$$H_{\rm SO} = \sum_{i,k,\alpha} \xi_k(\gamma_{ki}) l^{\alpha}_{ik} S^{\alpha}_i , \qquad (23)$$

where the sum is over electrons *i* and nuclei *k*, l_{ik}^{α} , and S_i^{α} are the $\alpha = x$, y, or z components of the orbital and electron spin angular momentum, respectively, and $\xi_k(r_{kl})$ is the spin-orbit constant, proportional to the inverse cube distance r_{kl}^{-3} between electron *i* and nucleus *k*. Coriolis operators expressed in terms of one- and two-electron operators are

$$-B(J_{\star} L_{\star} + J_{\star} L_{\star}) = -\left(\frac{\hbar}{4\pi c \mu r^2}\right) \left[J_{\star}\left(\sum_{i} l_{i-}\right) + J_{\star}\left(\sum_{i} l_{i+}\right)\right],$$
(24)

$$B(L_{\star} S_{\bullet} + L_{\bullet} S_{\star}) = \left(\frac{\hbar}{4\pi c \mu \gamma^2}\right) \left[\left(\sum_{i} l_{i\star}\right) \cdot \left(\sum_{j} s_{j\star}\right) + \left(\sum_{i} l_{i\star}\right) \cdot \left(\sum_{j} s_{j\star}\right) \right] .$$

$$(25)$$

Matrix elements of these operators between several lowlying configurations and the $B^{2}\Sigma^{*}$ state have been evaluated to determine the extent of the possible interactions which can lead to the previously discussed satellite structure. In these calculations, we have assumed that each electronic state arises from a different single configuration, each of which is analogous to those used by Carlson *et al.* for ScO. The following low-lying configurations can couple with the $B^{2}\Sigma^{*}$ state

$$\cdots (8\sigma)(3\pi)^4 (9\sigma)(10\sigma)^2 \Sigma^*, \ ^4\Sigma^* , \qquad (26)$$

$$\cdots (8\sigma) (3\pi)^4 (9\sigma) (4\pi)^2 \Pi'_r, {}^4 \Pi_r , \qquad (27)$$

$$\cdots (8\sigma) (3\pi)^4 (9\sigma) (\pi')^2 \Pi'_r, {}^4 \Pi_r , \qquad (28)$$

$$\cdots (8\sigma)^2 (3\pi)^3 (9\sigma)^2, \, {}^2\Pi_i , \qquad (29)$$

where the 10 σ and π' LCAO-MO's are $(4s + 4p)\sigma$ and $3 d\pi$ on scandium, respectively. There are also a small number of additional low-lying configurations which involve promotions among the $n\sigma$ (n=8-10) and $n\pi$ (n=3,4) orbitals; however, these configurations will not couple (within the approximations used here²⁷) with the $B^{2}\Sigma^{+}$ state.

In constructing appropriate wavefunctions, we recall that parity represents a good quantum number. Therefore, the wave functions corresponding to configurations (19)-(22) and (26)-(28) are written in a parity basis. Linear combinations which transform as eigenfunctions of the parity operator are given in Table V. Methods for evaluating these matrix elements have been described elsewhere.^{5,28}

The evaluation of nonzero matrix elements for the spin-orbit and Coriolis operators leads to a surprisingly simple result. Only matrix elements connecting the $B^{2}\Sigma^{*}$ state with the ${}^{2}\Pi_{i}$ configuration (29) and one component of the ${}^{4}\Pi_{r}$ states, specifically ${}^{4}\Pi_{r-1/2}$, are nonzero. The ${}^{2}\Pi_{i}$ components interact through both spinorbit and coriolis coupling whereas ${}^{4}\Pi_{r-1/2}$ interacts only through spin-orbit coupling. All other matrix elements connecting the $B^{2}\Sigma^{*}$ state to those states arising from the configurations (26), (27), and (28) vanish. Because spin-orbit coupling strongly dominates the coriolis in-

J. Chem. Phys., Vol. 73, No. 2, 15 July 1980

TABLE V. Determinantal wave functions.

 $|X^{2}\Sigma^{4\pm},v\rangle = (1/\sqrt{2}) \left[|\Lambda=0, S=\frac{1}{2}, \Sigma=\frac{1}{2} \right] |\Omega=\frac{1}{2}, J\rangle \pm (-1)^{J-1/2} |\Lambda=0, S=\frac{1}{2}, \Sigma=-\frac{1}{2} |\Omega=-\frac{1}{2}, J\rangle |v\rangle^{a}$ $|A'^{2}\Delta_{\frac{1}{2}/2}^{\frac{1}{2}},v\rangle = (1/\sqrt{2})\left[|2\frac{1}{2}-\frac{1}{2}\rangle|\frac{3}{2}J\rangle \mp (-1)^{J-3/2}|-2\frac{1}{2}\frac{1}{2}\rangle|-\frac{3}{2}J\rangle|v\rangle$ $|A'^{2}\Delta_{5/2}^{\pm}, v\rangle = (1/\sqrt{2}) \left\{ |2\frac{1}{2}\frac{1}{2}\rangle |\frac{5}{2}J\rangle \pm (-1)^{J-5/2} |-2\frac{1}{2}-\frac{1}{2}\rangle |-\frac{5}{2}J\rangle |v\rangle \right\}$ $|A^{2}\Pi^{\pm}_{1/2}, v\rangle = (1/\sqrt{2}) \left[|1\frac{1}{2} - \frac{1}{2}\rangle |\frac{1}{2}J\rangle \pm (-1)^{J-1/2} |-1\frac{1}{2}\frac{1}{2}\rangle |-\frac{1}{2}J\rangle |v\rangle^{a} \right]$ $|A^{2}\Pi_{3/2}^{*}, v\rangle = (1/\sqrt{2}) \left[|1\frac{1}{2}\frac{1}{2}\rangle |\frac{3}{2}J\rangle \mp (-1)^{J-3/2} |-1\frac{1}{2}-\frac{1}{2}\rangle |-\frac{3}{2}J\rangle |v\rangle^{a} \right]$ $|{}^{4}\Sigma_{3}^{++}2, v\rangle = (1/\sqrt{2}) \left[|0\frac{3}{2}\frac{3}{2}\rangle |\frac{3}{2}J\rangle \pm (-1)^{J-3/2} |0\frac{3}{2}-\frac{3}{2}\rangle |-\frac{3}{2}J\rangle |v\rangle$ $|{}^{4}\Sigma_{1}^{**}, v\rangle = (1/\sqrt{6}) [|a\rangle + |b\rangle + |c\rangle \pm (-1)^{J-1/2} (|a^{*}\rangle + |b^{-}\rangle + |c^{-}\rangle)]v\rangle^{b_{1}c}$ $|{}^{4}\Pi_{5/2}^{\pm}, v\rangle = (1/\sqrt{2}) \left[|1\frac{3}{2}\frac{3}{2}\rangle |\frac{5}{2}J\rangle \pm (-1)^{J-5/2} |-1\frac{3}{2}-\frac{3}{2}\rangle |-\frac{5}{2}J\rangle \right] |v\rangle^{d}$ $|{}^{4}\Pi_{3/2}^{\pm}, v\rangle = (1/\sqrt{6}) \left[|d\rangle + |e\rangle + |f\rangle \pm (-1)^{J-3/2} (|d^{-}\rangle + |e^{-}\rangle + |f^{-}\rangle) \right] |v\rangle^{b_{s}c_{s}d}$ $|{}^{4}\Pi_{1/2}, v\rangle = (1/\sqrt{6}) [|g\rangle + |h\rangle + |i\rangle \pm (-1)^{J-1/2} (|g^{-}\rangle + |h^{-}\rangle + |i^{-}\rangle)] |v\rangle^{b,c}$ $|{}^{4}\Pi_{-1/2}, v\rangle = (1/\sqrt{2}) \left[|1\frac{3}{2} - \frac{3}{2}\rangle | -\frac{1}{2}J\rangle \pm (-1)^{J+1/2} | -1\frac{3}{2}\frac{3}{2}\rangle | \frac{1}{2}J\rangle \right] |v\rangle$ $|^{2}\Pi_{j=1/2}^{j\pm}, v\rangle = (1/\sqrt{6}) [|j\rangle + |k\rangle + |l\rangle \pm (-1)^{J-1/2} (|j^{+}\rangle + |k^{-}\rangle + |l^{-}\rangle)]v\rangle$ $|^{2}\Pi_{r,3/2}^{\prime\pm},v\rangle = (1/\sqrt{6})[|m\rangle + |n\rangle + |o\rangle (-1)^{J-3/2}(|m^{-}\rangle + |n^{-}\rangle + |o^{-}\rangle)]v\rangle$ $|a\rangle$, $|b\rangle$, $|c\rangle$; $|\Lambda=0$, $S=\frac{3}{2}$, $\Sigma=\frac{1}{2}\rangle^{c}$ $|a^{\circ}\rangle$, $|b^{\circ}\rangle$, $|c^{\circ}\rangle$; $|\Lambda=0$, $S=\frac{3}{2}$, $\Sigma=-\frac{1}{2}\rangle^{c}$ $|d\rangle, |e\rangle, |f\rangle, |\Lambda=1, S=\frac{3}{2}, \Sigma=\frac{1}{2}\rangle^{c}$ $|d^{-}\rangle$, $|e^{-}\rangle$, $|f^{-}\rangle$; $|\Lambda = -1$, $S = \frac{3}{2}$, $\Sigma = -\frac{1}{2}\rangle^{\circ}$ $|g\rangle$, $|h\rangle$, $|i\rangle$; $|\Lambda=1$, $S=\frac{3}{2}$, $\Sigma=-\frac{1}{2}\rangle^{c}$ $|g^{*}\rangle$, $|h^{*}\rangle$, $|i^{*}\rangle$; $|\Lambda = -1$, $S = \frac{3}{2}$, $\Sigma = \frac{1}{2}\rangle^{c}$ $|j\rangle$, $|k\rangle$, $|l\rangle$; $|\Lambda=1$, $s=\frac{1}{2}$, $\Sigma=-\frac{1}{2}\rangle$ $|j^{\prime}\rangle, |k^{\prime}\rangle, |l^{\prime}\rangle; |\Lambda = -1, s = \frac{1}{2}, \Sigma = \frac{1}{2}\rangle$ $|m\rangle$, $|n\rangle$, $|o\rangle$; $|\Lambda=1$, $s=\frac{1}{2}$, $\Sigma=\frac{1}{2}$ $|m^{-}\rangle, |n^{-}\rangle, |o^{-}\rangle; |\Lambda = -1, s = \frac{1}{2}, \Sigma = -\frac{1}{2}\rangle$

^aThe determinantal wave function for ScO $B^{2}\Sigma^{*}$ is virtually identical to that for $X^{2}\Sigma^{*}$; however, the electron configurations for the $X^{2}\Sigma^{*}$ and $B^{2}\Sigma^{*}$ states differ. The ${}^{2}\Pi_{i}$ configuration (29) is represented by a determinantal wave function virtually identical to that for $A^{2}\Pi_{i}$; however, the configurations differ. See text for discussion.

^bSlater determinants are symbolized by $|\Lambda S\Sigma\rangle$ when only one Slater determinant can be constructed with the specified values of Λ , S, Σ . Otherwise, letters are used as labels. ^cSpecific determinants are defined with respect to the configurations given in the text for ${}^{4}\Sigma^{+}$ and ${}^{4}\Pi_{r}$.

teraction we will consider only matrix elements of the spin-orbit operator. Using the determinantal wavefunctions in Table V, the matrix element connecting ${}^{4}\Pi_{r-1/2}$ and $B^{2}\Sigma^{*}$ is of the form

$$w = \langle v, {}^{4}\Pi_{\tau-1/2}^{+} | H_{SO} | B^{2}\Sigma_{1/2}^{+}, v' \rangle$$

= $\frac{1}{4} \langle v | v' \rangle \{ \pm [(-1)^{J+1/2} \langle -1 \frac{3}{2} \frac{3}{2} | H_{SO} | 0 \frac{1}{2} \frac{1}{2} \rangle$
+ $(-1)^{J-1/2} \langle 1 \frac{3}{2} - \frac{3}{2} | H_{SO} | 0 \frac{1}{2} - \frac{1}{2} \rangle] \},$ (30)

where the notation is that used in Table V, $|v\rangle$ and $|v'\rangle$ represent, respectively, vibrational wave functions for the ⁴II, and $B^{2}\Sigma^{*}$ states and we have noted that

$$\langle 1 \frac{3}{2} - \frac{3}{2} | H_{so} | 0 \frac{1}{2} \frac{1}{2} \rangle = \langle -1 \frac{3}{2} \frac{3}{2} | H_{so} | 0 \frac{1}{2} - \frac{1}{2} \rangle = 0$$
.

Expression (30) can be simplified by re-expressing the basis functions $|\Lambda S\Sigma\rangle$ in terms of antisymmetrized products of one electron molecular orbitals.^{1,2} Considering the interaction between the ⁴ Π_{τ} [Eq. (27)] and $B^{2}\Sigma^{*}$ states and omitting the 3π orbital which remains fully occupied in both $B^{2}\Sigma^{*}$ and ⁴ Π_{τ} [Eq. (27)],

$$\begin{vmatrix} -1\frac{3}{2}\frac{3}{2} \rangle = |A(\cdots -1\frac{1}{4}0^{*}_{6}0^{*}_{9})\rangle, \\ |0\frac{1}{2}\frac{1}{2} \rangle = |A(\cdots -0^{*}_{6}0^{*}_{0}0^{*}_{0})\rangle,$$
(31)

where numerals 0 and ± 1 identify the z component of the orbital angular momenta l_i , and superscripts \pm specify the corresponding projection of s_i . A is the antisymmetrizing operator and the subscripts 4, 8, and 9 pertain to molecular orbitals 4π , 8σ , and 9σ , respectively. Expressions similar to Eq. (30) may be written for $|1\frac{3}{2}-\frac{3}{2}\rangle$ and $|0\frac{1}{2}-\frac{1}{2}\rangle$. The many-electron integrals which appear in Eq. (30) may now be reduced to tractable sums over one electron integrals noting

$$\langle -1\frac{3}{2}\frac{3}{2} | H_{\rm SO} | 0\frac{1}{2}\frac{1}{2} \rangle = -\langle 1\frac{3}{2}-\frac{3}{2} | H_{\rm SO} | 0\frac{1}{2}-\frac{1}{2} \rangle$$

we have

$$w = \pm \left(\frac{1}{2} \langle v | v' \rangle (-1)^{J+1/2} \langle -1_4 | \sum_{k} \epsilon_k(r_k) l_k^- | 0_9 \rangle \right) . \tag{32a}$$

Through a very similar approach to that already applied to the treatment of $B^{2}\Sigma_{1/2}^{*}-A^{2}\Pi_{1/2}$ interactions in

AlO, ¹ the appropriate matrix element for ${}^{2}\Pi_{i_{1/2}} - B {}^{2}\Sigma^{+}$ spin-orbit coupling is

$$\omega = \frac{1}{2} \langle v' | v \rangle \langle -\mathbf{1}_{3} | \sum_{k} \epsilon_{k}(r_{k}) l_{k}^{-} | \mathbf{0}_{8} \rangle .$$
 (32b)

The presence of $\epsilon_k(r_k) \sim r_k^{-3}$ assures that only one center integrals will make a significant contribution to the Eqs. (32). A complete evaluation of the matrix elements ω requires knowledge of the molecular orbitals $|-1_4\rangle = 4\pi$, $|-1_3\rangle = 3\pi$, $|0_6\rangle = 2p\sigma$, and $|0_9\rangle = 9\sigma$. In order to evaluate the matrix elements (32), we note that the ${}^4\Pi_r$, ${}^2\Pi_i$, $B \, {}^2\Sigma^+$, and $A \, {}^2\Pi$ states can be represented to reasonable approximation by the charge distribution Sc⁺O⁻.²⁶

To evaluate the ${}^{4}\Pi_{-1/2} - B {}^{2}\Sigma^{*}$ interaction, we represent the 4π orbital as an atomic *p* orbital centered on scandium and take into account the (Sc) $p\sigma$ orbital character of the 9σ orbital (using the population analysis given in Ref. 26) to determine

$$w \cong \pm 0.25 / \sqrt{2} (-1)^{J+1/2} a_0 \langle v | v' \rangle$$
,

where we have taken advantage of the transformation property²⁹ $l_0^* | P_0 \rangle = \sqrt{2} | P_{\pm} \rangle$. The radial integral

$$a_0 = \langle p\Pi | \epsilon_0(r_0) | p\Pi \rangle$$

may be evaluated by considering the spin-orbit splitting of the ScO $A^{2}\Pi$ state which is 120 cm⁻¹ (Ref. 30) giving

$$w \approx 20 \langle v | v' \rangle \,\mathrm{cm}^{-1} \tag{33}$$

A matrix element of similar magnitude can be estimated for the interaction between $B^{2}\Sigma^{*}$ and the ${}^{4}\Pi_{r}$ state corresponding to configuration (28).

The evaluation of the ${}^{2}\Pi_{t} - B {}^{2}\Sigma^{*}$ interaction follows from previous studies¹ in which we represent the molecular orbitals as atomic p orbitals

 $|-1_3\rangle \sim P_{-}(O^{-})$ and $|0_8\rangle \sim P_{0}(O^{-})$

centered on the oxygen ion (O⁻). Again using the appropriate transformation properties

$$\omega \sim (1/\sqrt{2}) a_0 \langle v' \mid v \rangle$$

where the radial integral

$$a_0 = \langle P(\mathbf{O}) | \epsilon_0(r_0) | P(\mathbf{O}) \rangle \sim 121 \text{ cm}^{-1}$$

(Ref. 31). We arrive at the final result

$$\omega \sim 86 \langle v' \mid v \rangle \quad . \tag{34}$$

Equalities (33) and (34) are clearly not exact because approximate representations have been used for the 3π , 4π , 8σ , and 9σ orbitals, respectively. In addition the spin-orbit coupling constant $a_0 \sim 121 \text{ cm}^{-1}$ is strictly appropriate to O⁻ and not Sc⁺O⁻.

It would appear that the significant energy transfer observed for the v' = 6, 8 levels of the ScO $B^{2}\Sigma^{*}$ state is related to the presence of ${}^{4}\Pi_{r}$ or ${}^{2}\Pi_{i}$ reservoir states and more specifically to the location of levels with substantial ${}^{4}\Pi_{r-1/2}$ or ${}^{2}\Pi_{i1/2}$ character is close proximity to v' = 6, 8. There is also the possibility of second-order coupling effects associated either with ${}^{4}\Pi_{r-1/2}$ mixing (small admixture of ${}^{4}\Pi_{r-1/2}$) with other components of the ${}^{4}\Pi_{r}$ state or other low-lying configurations which do

not couple directly with $B^{2}\Sigma^{*}$. Similar comments apply to ${}^{2}\Pi_{i}$. The representation of the ScO electronic states through more appropriate multiconfigurational descriptions will introduce further weak couplings. If we consider the long-range interactions (following section) which should characterize the weakly interacting v' = 6satellite and those satellites associated with v' = 3, 4, 5. second order coupling effects and higher order descriptions of the interacting states may play a significant role. A similar comment applies to the multiple complicated spectral features associated with v' = 7 [Fig. 5(b)]. The relatively strong interactions associated with v' = 3, 4, 5 (Table IV) appear to emanate from a different source than v' = 6, 8. In view of the magnitude of the matrix elements (33) and (34) and the data in Tables III and IV, we favor an interaction with levels which are primarily ${}^{2}\Pi_{i_{1}/2}$ for $v' = 6-9 B {}^{2}\Sigma^{*}$ and levels which are primarily ${}^{4}\Pi_{r-1/2}$ for v' = 3, 4, 5. The confirmation of the exact nature of the interacting levels awaits further analysis. It is somewhat surprising that strong emission from the ${}^{2}\Pi_{i}$ state [configuration (29)] has not been observed; however, no information has been obtained for this state. Similarly surprising effects have been noted in ICl.³² Finally, we should note that there appears to be a close correlation between the location of the weakly interacting v' = 6 satellite level and the v = 14 level of the ScO $A^{2}\Delta_{3/2}$ state. This correlation is drawn on the basis of our analysis of the A' $^{2}\Delta_{3/2}$ state for which we find $T_0 = 14\,966 \text{ cm}^{-1}$, $w_e = 843.6 \text{ cm}^{-1}$, $w_e x_e = 4.8 \text{ cm}^{-1}$. The agreement between calculated and observed level positions (3 cm^{-1}) is quite enticing. If the weak satellite is associated with ${}^{2}\Delta_{3/2}$, this interaction must result from secondary coupling effects.

SUMMARY AND DISCUSSION

The primary emphasis of the current study has been the analysis of rapid energy transfer routes connecting certain long-lived electronically excited reservoir states in ScO with ScO $B^{2}\Sigma^{*}$. As Table III demonstrates, the observed energy transfer rates from levels which would appear to possess substantial ${}^{4}\Pi_{r-1/2}$ and ${}^{2}\Pi_{i_{1/2}}$ character (Sec. IVD) are unusually fast for the most highly perturbed and hence most strongly interacting levels of the $B^{2}\Sigma^{*}$ state. Intramolecular energy transfer is most efficient for those levels of $B^{2}\Sigma^{+}$ which contain the largest admixture of "reservoir state" character. For both v' = 6 and $v' = 8 B^2 \Sigma^*$, the observed bimolecular transfer rate constant is significantly larger than 10⁸ Torr \times sec⁻¹ corresponding to a time period of 10⁻¹² sec at 1 atm pressure. This is approximately two orders of magnitude faster than a typical relaxation time for rotation-rotation energy transfer.²⁴

It is instructive to compare the rates observed in this study with appropriate rate constants for "hard sphere" collisions between Ar and ScO. In order to make this comparison, we assume that the ScO translational temperature will equilibrate more rapidly than the rotational temperature.^{24,33} Therefore, based on previously computed rotational temperatures (Sec. IVA), we consider hard sphere collisions between Ar (300 °K) and ScO (1000 °K), ³⁴ and compute a bimolecular rate constant $k \sim (5-6) \times 10^6$ Torr⁻¹ sec⁻¹. Hence, the transfer

848

rates to $v' = 8 \text{ ScO } B^2 \Sigma^*$ approach 50 and 100 times gas kinetic. This is not surprising for we expect long range forces to be the most efficient in causing the observed transitions. Collisions with argon³⁵ may be viewed as time dependent perturbations which cause transitions between states (mixing via spin-orbit coupling)

$$|+\rangle = c | B^{2}\Sigma^{+}\rangle | v'\rangle | J'\rangle - d | \operatorname{res}\rangle | v\rangle | J'\rangle$$

and
$$|-\rangle = d | B^{2}\Sigma^{+}\rangle | v'\rangle | J\rangle + c | \operatorname{res}\rangle | v\rangle | J\rangle$$
(35)

of ScO. The selection rule³⁸ dictates that the two components of $|+\rangle$ and $|-\rangle$ contain the same rotational basis functions $|J\rangle$ and $|J'\rangle$. The perturbing Hamiltonian is the the time dependent intermolecular potential between Ar and ScO. For a particular trajectory, the rate constant k_{RB} is proportional to the squared matrix elements of the amplitude V of this interaction

$$k_{RB} \propto \left| \left\langle + \left| V \right| - \right\rangle \right|^2 . \tag{36}$$

Here, the interaction V arises primarily from the dipoleinduced dipole and dispersion forces between the approaching atom and diatomic; however, at the lowest pressures characterizing the current experiments dipole-dipole interactions between ScO molecules as well as inelastic collisions with NO₂ may play a significant role.³⁷ The long or short range nature of the interaction causing transitions depends upon the time scale of the collision versus the frequency of the transition (arguments analogous to radiation-adsorption process). If V acts over a "range" L, energy transfer will be most efficient for those collisions having a relative velocity v such that

$$v/L \sim c \Delta \nu \quad . \tag{37}$$

For a typical root-mean-square velocity of 5×10^4 cm/ sec, L corresponds to 3.1 Å for the perturbed v' = 8level and 10.3 Å for the red shifted and most strongly interacting v' = 6 satellite. Indeed, this simple model agrees reasonably with the relative magnitude of observed transfer rates to the v'=6 and 8 levels. Because the v' = 6 transitions are expected to occur at much longer range, it is not surprising that they proceed at a faster rate. This result indicates that the observation of a population maximum at v' = 8 at $P_{\text{total}} = 1000 \ \mu\text{m}$ (Fig. 7) must result primarily from the nature of the relative populations in those feeder levels associated with the transferring reservoir state. The value of L associated with the weakly interacting shorter wavelength v' = 6satellite is 12.6 Å. Therefore, even this weakly interacting level would be expected to exhibit observable interactions and manifest itself readily in the observed emission spectra.

If we substitute Eq. (35) into (36), we have

$$k_{BB}^{1/2} \propto c^{2} \langle J' | \langle v' | \langle B^{2}\Sigma^{*} | V | \operatorname{res} \rangle | v \rangle | J \rangle$$

$$- d^{2} \langle J' | \langle v | \langle \operatorname{res} | V | B^{2}\Sigma^{*} \rangle | v' \rangle | J \rangle$$

$$+ cd \{ \langle J' | \langle v' | \langle B^{2}\Sigma^{*} | V | B^{2}\Sigma^{*} \rangle | v' \rangle | J \rangle$$

$$- \langle J' | \langle v | \langle \operatorname{res} | V | \operatorname{res} \rangle | v \rangle | J \rangle \}, \qquad (38)$$

where the terms in brackets are off diagonal in J alone and correspond to R-R processes within the manifolds $|B|^{2}\Sigma^{*}\rangle |v'\rangle$ and $|res\rangle |v\rangle$. The remaining matrix elements (off diagonal in three variables) correspond to electronic quenching processes, all of which are expected to proceed at a relatively slow rate. The nature of relationship (38) indicates that we have observed the equivalent of an unusually fast $R \rightarrow R$ process. The magnitude of the effects which characterize these systems may not be surprising. In retrospect our observation may be intimately connected with the large dipole moments which characterize the ground and excited states of most refractory high temperature molecules. There may, however, be other more subtle factors operative.

The enhanced transfer cross sections observed in the present study are reminiscent of the large cross sections now being associated with energy transfer involving highly excited Rydberg states.³⁸ One may view a highly excited Rydberg state as an electron circulating in wide orbit about a positive ionic core.³⁹ If we consider collisions with a neutral molecule, the interaction potential for this Rydberg state is dominated by the electronneutral interaction, the ionic core-neutral interaction contributing much less to the cross section. This result leads one to believe that effects observed in the present study might be correlated with an increasingly diffuse electron density associated with molecular excitation (electronically excited states or high vibrational levels of the ground electronic state); however, it is not clear what the extent of long range electron density must be in order to facilitate the observed energy transfer. In other words, the observed energy transfer may require only a small "tickle" as opposed to substantial electron density.

Effects similar to those described here for ScO have now been observed in YO and LaO where E-E energy transfer is even more pronounced. In a related study V-E energy transfer has been observed in BO at pressures as low as 10^{-5} Torr.

As more data are collected it should be possible to ascertain interesting correlations regarding the nature of these "time dependent" collisional transfers and the intermolecular potentials which characterize the processes leading to efficient transfer. We are now investigating the effects of polarizability variation in the collisional partner versus Ar using He, N₂, CO, and CO₂. There appear to be several distinct playoffs between level separation, range of interaction, and mean free path at a given pressure.

In the current studies, we have utilized the strong perturbations among the excited electronic states of high temperature molecules. Although a complete perturbation analysis of the emission spectra (all rotational levels) may be prohibitive if not impossible, ⁴⁰ the appearance of the satellite features allows us to achieve a good quantitative description of those "super highways" connecting various electronic states. If one wishes to understand efficient energy deposition processes, this is a valuable tool.

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