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W. J. Childs and T. C. Steimle

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A molecular-beam-optical and radio frequency-optical double-resonance study of the $A^2\Pi_r - X^2\Sigma^+$ band system of scandium monoxide^{a)}

W. J. Childs Physics Division, Argonne National Laboratory, Argonne, Illinois 60439

T.C. Steimle

Department of Chemistry, Arizona State University, Tempe, Arizona 85287-1604

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A molecular-beam-optical and rf-optical double-resonance study of the $A^{2}\Pi$ (v' = 0-2) $-X^{2}\Sigma^{+}$ (v'' = 0-2) band systems of gas phase scandium monoxide has been performed. No localized perturbations in the $X^{2}\Sigma^{+}$ state have been observed but strong perturbations in the $A^{2}\Pi$, (v = 1) state were detected. Quantum numbers for the optical spectrum could only be assigned assuming a negative value for the excited state Λ -doubling-type magnetic hyperfine parameter, contrary to current theoretical understanding of this interaction. The ground state magnetic hyperfine parameters can be interpreted in terms of *ab initio* models for the electronic states of ScO whereas the spin-rotation parameters cannot.

I. INTRODUCTION

Bonding in transition-metal-containing compounds is the theme of a vast number of modern quantum chemical computations. Transition metal oxide (TMO) bonding is of particular concern both because of the importance of oxygen chemisorption processes and the influence it has on bulk electronic properties of the new high-temperature superconducting materials.¹ Although of great interest, it is difficult to obtain quantitative information from current quantum chemical computations even for a simple isolated diatomic TMO molecule. The failing of ab initio calculations for TMO molecules can be traced, in part, to the inability of the theoretical method to correctly describe the state distribution of the transition metal atom. A difficulty with the first row TM atomic calculations is the near degeneracy of the low-lying states arising from the $3d^n 4s$, $3d^{n-1} 4s^2$, and $3d^{n-1} 4s4p$ configurations. Therefore, accurate wave functions for the first row transition metal atoms can only follow from an extensive configuration interaction (CI) treatment.^{2,3} In addition, there are surprisingly large relativistic effects for the TM atom⁴ which have to be taken into account. The problems are compounded when accurate transition metal atomcontaining molecular calculations are attempted.

The small number (three) of valence electrons and the low atomic number of scandium makes ScO an optimal TMO from a computational point of view. Accordingly, there are a large number of reported theoretical results, both all-electron SCF⁵ and all-electron SCF-CI^{2.6} as well as results from less rigorous theoretical treatments.⁸⁻¹⁰ The early *ab initio* calculations suggested that the bonding was nearly purely ionic with a charge distribution Sc $^{+2}O^{-2}$. The more recent calculations indicated that the charge distribution is Sc $^{+0.7}O^{-0.7}$ and that there is bond formation between the $3d\sigma$ and $3d\pi$ orbitals centered on the scandium and the $2p\sigma$ and $2p\pi$ orbitals of oxygen. This is consistent with the general view of bonding in the first row transition metal oxides.¹¹ Namely, at the right-hand side of the Periodic Table the TMO bonding is nearly purely ionic with a charge distribution TM $^{+0.7}O^{-0.7}$ while at the left-hand side the same ionic character is preserved and there is considerable bond formation.

The intensified theoretical interest in ScO has not been paralleled by the needed detailed experimental spectroscopic studies. There are four known electronic states¹²: the $X^{2}\Sigma^{+}$, $A'^{2}\Delta$ ($T_{e} = 15029 \text{ cm}^{-1}$), $A^{2}\Pi_{r}$ ($T_{e} = 16547$ cm⁻¹), and $B^{2}\Sigma^{+}$ ($T_{e} = 20.645 \text{ cm}^{-1}$), which in a simple one-electron model all have the same closed-shell molecular orbital core and a single unpaired electron in an orbital centered on the scandium nucleus. In the $X^2\Sigma^+$ state the unpaired electronic orbital is essentially the 4sp hybridized atomic orbital while the primary configurations for the $A'^{2}\Delta$, $A^{2}\Pi_{+}$ and $B^{2}\Sigma^{+}$ states correspond to a promotion into a $3d\delta$, $(3d + 4p)\pi$, and $(3d + 4p)\delta$ molecular orbital, respectively, all centered on scandium. The $A^{2}\Pi_{r}(v'=0)$ - $X^{2}\Sigma^{+}(v''=0)$ band system has been recorded in emission and rotationally analyzed.¹³ That analysis showed that the low rotational levels of the $X^2\Sigma^+$ state had an energy level pattern of a case $b_{\beta\beta}$ molecule with the nuclear spin (⁴⁵Sc, I = 7/2) and electron spin angular momenta coupled together (by Fermi contact interaction). Other optical studies include the low resolution laser induced fluorescence (LIF) of the numerous bands of the $A^{2}\Pi - X^{2}\Sigma^{+}$ system¹⁴ and the high resolution LIF measurements and perturbation analysis of the $A^2 \Pi_r (v'=1) - X^2 \Sigma (v''=0)$ band system.¹⁵ In addition, the $A^{2}\Pi_{r}(v=0 \text{ and } 1)$ permanent electric dipole moment has been determined¹⁶ and the ground state matrix isolated ESR spectrum recorded.¹⁷

In a continuation of our investigation of the bonding in Group IIIa TMO compounds, we report here on the molecular beam optical and radio frequency-optical double resonance measurements for gas phase scandium monoxide. Previous results on YO¹⁸⁻²⁰ indicate that the electronic state distribution for the Group IIIa TMO compounds is more complex than current spectroscopic data would indicate. Specifically, the strong vibrational dependence of the spinrotation parameter $\gamma(X^2\Sigma^+)$ for YO is proposed to arise from a perturbation of two as yet unobserved low-lying ² Π

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states. It is suggested that the primary configuration for these unobserved states has three unpaired electrons and they can be expected to have quite different chemical properties from the known electronic states. Therefore, the fine and magnetic hyperfine interactions of gas phase ScO were analyzed for the v = 0, 1, and 2 levels of the $X^2\Sigma^+$ state. The interpretation of these parameters in terms of possible electronic configurations is presented. In the process of these measurements a strong perturbation in the $A^2\Pi$ (v = 1) state was observed and an rf-optical labeling technique²¹ used to assign the quantum numbers associated with the perturbed features. The details of the perturbation are discussed separately.^{15,21}

II. EXPERIMENTAL DETAILS

The molecular beam laser-rf double-resonance method has been used for nearly 10 years²²⁻²⁵ to obtain high-precision measurements of level splittings in the lower states of electronic (optical) transitions. Because of the well-collimated nature of the molecular beam, the single frequency tunable dye laser produces excitation spectra that are nearly Doppler-free with the 15–20 MHz linewidth (FWHM) typically observed arising primarily from imperfect collimation. The molecular beam is orthogonally intersected twice by a single-frequency laser beam: once near the molecular beam source (the "pump" region), and once further downstream (the "probe" region). When the laser is tuned into resonance with a particular hfs component of an optical line, the number of molecules in the lower hfs level is severely depleted so that little fluorescence is induced by the probe beam. If the depleted lower level is repopulated (in the space between the pump and probe regions), by driving a suitable rf or microwave transition, the probe beam LIF is enhanced. The increase in LIF can be large, and, when combined with the typically 10 kHz linewidth seen for the rf transitions, makes this double resonance technique both sensitive and precise. Although the precise rf transition measurements are limited to the ground electronic state, upper-state splittings can then be inferred by combining the lower-state splittings with observation of the spacings between the hfs components in the optical lines.

In addition to providing high-resolution measurement of rf ground state transitions, the rf-optical double resonance technique provides a sensitive means by which quantum number assignments for optical transitions can be determined. The laser-rf double-resonance technique uniquely identifies the lower level associated with any optical line by precisely measuring the lower-state hfs splittings. The precisely determined ground state energy level spacings for an extensive range of quantum numbers can only be reproduced by a unique quantum number assignment consistent with the model Hamiltonian. The optical selection rules then dictate the quantum number assignment for the upper state. This technique was used in the past for the assignment of optical features in NO2^{26,27} and was used in the present study²¹ to assign the transitions in the $A^{2}\Pi_{r}$ (v' = 1, and 2)- $X^{2}\Sigma^{+}$ (v'' = 1, and 2) band system for which there was no previously published high-resolution optical analysis.

The ScO molecular beam is produced by electron-bom-

bardment heating of a tantalum oven, 1.7 cm tall and 0.8 cm in diameter containing Sc_2O_3 and some scandium metal chips. The beam effuses from a 1.5 mm hole in the oven lid. A Coherent Radiation 599-21 tunable single-frequency dye laser is used to induce fluorescence, which is detected (in the probe region) through an interference filter by a cooled, photon-counting photomultiplier. An ~100 Å pass-band filter centered at 6000 or 6100 Å was used to reduce the background of black-body radiation from the beam source. The remaining background consisted primarily of scattered laser photons.

The laser wavelength was measured by a Hall-type interferometric "lambda meter"²⁸ which had a reproducibility of about ± 0.002 Å. A portion of the laser light was passed through a 50 cm temperature-stabilized confocal Fabry– Perot étalon with a free spectral range of 150 MHz to provide markers for incremental laser frequency measurements. A precision of about 1 MHz in the separation between features in the optical spectrum could be achieved in this way. The radio frequencies were provided by a 0–1 GHz rf synthesizer, with suitable amplifiers and doublers, and rf frequency and power meters supplemented the setup. The precision of the rf transitions was typically ± 2 kHz.

III. OBSERVATIONS AND ANALYSIS

The present study was greatly facilitated by the published rotational analysis of the $A^{2}\Pi_{r}(v'=0)-X^{2}\Sigma^{+}(v''=0)$ band system¹³ and the optical assignments of numerous features in the $A^{2}\Pi_{r}(v'=1)-X^{2}\Sigma^{+}(v''=0)$ band system used in the electric dipole moment determinations.¹⁶ As in the previous optical studies, a modified ${}^{2}\Pi$ (case a) ${}^{2}\Sigma$ (case b) branch labeling scheme is adopted. In this scheme the F_{i} label (i = 1 or 2 for J = N + S or N - S), customarily used as a subscript in the branch designation, is replaced by G(=I + S) which is the approximately good intermediate quantum number for the $X^{2}\Sigma^{+}$ (case $b_{\beta S}$) state. Because of the large splitting between the G = 3 and G = 4 levels of the $X^{2}\Sigma^{+}$ state there are 16 branches: ${}^{S}R_{2G}$, ${}^{R}Q_{2G} + {}^{R}R_{2G}$, ${}^{Q}P_{2G}$ $+ {}^{Q}Q_{2G}$, ${}^{P}P_{2G}$ for the $A^{2}\Pi_{3/2} - X^{2}\Sigma^{+}$ subband and ${}^{R}R_{1G}$, ${}^{Q}Q_{1G} + {}^{Q}R_{1G}$, ${}^{P}P_{1G} + {}^{P}Q_{1G}$, ${}^{O}P_{1G}$ for the $A^{2}\Pi_{1/2} - X^{2}\Sigma^{+}$ subband with G = 3 and 4.

A portion of the molecular beam LIF spectrum for the ${}^{P}P_{1G} + {}^{P}Q_{1G}$ (40) branch features and the ${}^{Q}P_{2G} + {}^{Q}Q_{2G}$ (40) branch features are presented in Figs. 1 and 2, respectively, and are representitive of the LIF spectra for the two subbands. The large splitting ($\sim 8 \text{ GHz}$) between the G = 3and G = 4 branch features results from ground state magnetic hyperfine interaction and is nearly independent of the rotational quantum number because the $X^2\Sigma^+$ state remains a case $b_{\beta S}$ molecule even for high N values. The small splittings in each branch feature result from the splitting of each level in the $A^{2}\Pi_{-}$ state into eight (2I + 1) components by magnetic hyperfine interactions and splitting of the ground state levels into 2G + 1 components by spin-rotation interactions. Because the upper-state splitting is larger for the branch features associated with $A^2 \Pi_{1/2}$ substate, it is assumed that the $A^{2}\Pi_{1/2}$ hyperfine splitting comes primarily from the A-doubling-type magnetic hyperfine interaction.29

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FIG. 1. A section of the $A^{2}\Pi_{1/2}$ $(v' = 0)-X^{2}\Sigma^{+}$ (v'' = 0) subband in the ${}^{P}P_{1G} + {}^{P}Q_{1G}$ (N'' = 40) spectral region as recorded by molecular-beamlaser induced fluorescence.

All recorded rf transitions were magnetic dipole allowed either within the G=3 or G=4 set of levels (" $\Delta G = 0$ " transitions) or between the G = 3 and G = 4levels (" $\Delta G = 1$ " transitions) of a given rotational level of the $X^2\Sigma^+$ state. The latter set of transitions all occur at ~ 8 GHz. The $A^{2}\Pi_{3/2}$ $(v'=0)-X^{2}\Sigma^{+}$ (v''=0) subband was initially selected for the rf-optical double-resonance measurements because the overlap of the optical features assured that numerous hyperfine levels were simultaneously pumped, thereby reducing the search time. Initial observations were of the $\Delta G = 1$ type for $N'' \approx 40$. Attempts to assigns F and G quantum numbers for each rf transition made by assuming a set of quantum numbers and then seeking a least-squares fit to a ${}^{2}\Sigma^{+}$ Hamiltonian failed. The difficulty in assigning quantum numbers was partly a consequence of the laser pumping a feature made up of several unresolved hfs components. A switch from the ${}^{R}Q_{2G} + {}^{R}R_{2G}(N'')$ lines of $A^2\Pi_{3/2} \leftrightarrow X^2\Sigma_{1/2}^+$ to the ${}^{P}P_{1G}(N'')$ lines of $A^2\Pi_{1/2}$ $\leftrightarrow X^{2}\Sigma_{1/2}^{+}$, for which the optical hfs components are resolved, was made. Although $\Delta G = 0$ as well as $\Delta G = 1$ transitions were now observed it was still impossible to find a set of quantum numbers that led to a satisfactory least-squares fit to the observations.



FIG. 2. A section of the $A^{2}\Pi_{3/2}$ $(v'=0)-X^{2}\Sigma^{+}$ (v''=0) subband in the ${}^{0}P_{2G} + {}^{0}Q_{2G}$ (N''=40) spectral region as recorded by molecular-beamlaser induced fluorescence.

In this procedure, the optical hfs components of the $A^{2}\Pi_{1/2}$ $(v=0)-X^{2}\Sigma^{+}$ (v=0) subband were labeled assuming a positive value for "d," the parameter that describes the strength of the A-doubling-type magnetic hyperfine interaction of the excited electronic state. Current theoretical description³⁰ of this interaction requires that "d" be positive, although there are instances, particularly for excited electronic states, ³¹⁻³³ where it is experimentally determined to be negative. When, assuming a positive d value, the quantum number assignment for the features in Fig. 1 was made it was impossible to obtain a satisfactory fit to a ${}^{2}\Sigma^{+}$ Hamiltonian. The sign of d was then reversed and consequently the order of the $A^{2}\Pi_{1/2}$ hyperfine levels reversed and an excellent fit of all the ground state rf measurements was achieved.

The energy level pattern for the $X^2\Sigma^+$ state is irregular and a strong function of rotational quantum number. The N'' = 40 energy level pattern is presented in Fig. 3 where the labels *a*-*x* refer to the various types of transitions that were observed. Table I gives the *F* and *G* quantum numbers for all the types of transitions observed. The F = 26-27 transition for the N = 30, G = 4, $X^2\Sigma^+$ (v = 2) level is shown in Fig. 4 and is representative of the rf transitions measured by the rf-



FIG. 3. The energy level pattern for the hyperfine splitting of the N = 40 level of the $X^2\Sigma^+$ state as determined by rf-optical double-resonance spectroscopy. The measured rf transitions are labeled a-x.



FIG. 4. The *a* type of transition (see Fig. 3) for the $N = 30 X^2 \Sigma^+$ (v = 2) level as measured by rf-optical double-resonance spectroscopy.

optical double-resonance technique. The observed transition frequencies, quantum number assignments, and observation — calculated frequencies are presented in Table II. For v = 0, the table lists 39 $\Delta G = 0$ and 39 $\Delta G = 1$ transitions. The corresponding numbers of observations for v = 1 are 78 and 12, and for v = 2 they are 14 and 11, respectively.

There are no localized perturbations in the v = 0, 1, and 2 levels of the $X^{2}\Sigma^{+}$ state and therefore an effective Hamiltonian approach^{34,35} was used. The required terms of the effective Hamiltonian can be written as

TABLE I. The quantum numbers associated with radio frequency transitions listed in Table II (and depicted in Fig. 3). All transitions are characterized by $\Delta v = 0$ and $\Delta N = 0$ in the $X^2\Sigma^+$ state and are magnetic dipole allowed.

Transision	lowe	er state	upper state		
type	G	F-N	G	F-N	
a	4	- 4	4	- 3	
Ь	4	— 3	4	- 2	
с	4	- 2	4	- 1	
d	4	-1	4	0	
е	4	0	4	1	
f	4	1	4	2	
g	4	3	4	2	
ĥ	4	4	4	3	
i	3	- 2	3	- 3	
i	3	- 1	3	- 2	
k	3	0	3	- 1	
1	3	1	3	0	
m	3	2	3	1	
n	3	3	3	2	
0	3	3	4	2	
p	3	3	4	3	
q	3	3	4	4	
r	3	2	4	2	
\$	3	2	4	1	
t	3	2	4	3	
и	3	1	4	2	
U	3	1	4	1	
w	3	0	4	1	
x	3	- 3	4	- 2	

$$\hat{H}_{\text{eff}} = \gamma \hat{S} \cdot \hat{N} + b \hat{I} \cdot \hat{S} + c \hat{I}_z \hat{S}_z + C_I \hat{I} \cdot \hat{N} + \frac{eqQ}{4I(2I-1)} (3\hat{I}_z - \hat{I}^2) + \hat{H}_{cdsr} + \hat{H}_{cdhfs}.$$
(1)

In this expression, the quantities γ , b, c, C₁, and eqQ are the strengths of the spin-rotation, contact, dipolar, nuclear spinrotation, and electric quadrupole interaction. The operators \ddot{H}_{cdsr} and \ddot{H}_{cdhfs} represent higher-order terms which have been treated phenomenologically. Namely, b, c, and γ have been replaced by $b_0 + b_1 N^2 (N + 1)$, $c_0 + c_1 N (N + 1)$, and by $\gamma_0 + \gamma_1 N(N+1) + \gamma_2 N(N+1)^2$, respectively. The matrix representation of \hat{H}_{eff} was set up in terms of the adjustable parameters and diagonalized to produce eigenvalues from which rf transition frequencies were calculated. A least-squares procedure was used to minimize the observed-- calculated transition frequencies. The results of the fits are presented in Table III. The limited data for the $X^{2}\Sigma^{+}$ v = 2 level required that the higher-order terms γ_1 , b_1 , c_1 , and γ_2 , be held fixed to estimates based on the v = 0 and 1 results.

IV. DISCUSSION

As was the case for YO, the ground-state spin-rotation parameter is a strong function of the vibrational quantum number, whereas the magnetic hyperfine interactions are nearly independent of v. This indicates that the dominant contribution to γ corresponds to the second-order interaction and serves as a sensitive probe of the existence of perturbing electronic states. In contrast, the dominant contribution to the magnetic hyperfine interactions is from matrix elements within the Born–Oppenheimer description of the $X^2\Sigma^+$ state and is nearly independent of vibrational level. The determined value of 1.947 GHz for the Fermi contact parameter b_F (= b + 1/3 c), is close to the 2.01 GHz value established by ESR matrix isolation measurements¹⁷ and is interpreted in terms of electron density at the nuclei and the spatial distribution of the unpaired electrons.

The experimentally determined magnetic hyperfine parameters can be compared with theoretical predictions. The Fermi contact parameter b_F and the dipolar parameter c are related to the electronic wave functions through the expectation relationships

$$b_F = \frac{\mu_0}{h} \sum_i g_i \mu_B g_N \mu_N \langle \delta(r_i) \rangle \tag{2}$$

and

$$c = \frac{\mu_0}{4\pi h} \sum_i \frac{3}{2} g_i \mu_B g_N \mu_N \left\langle \frac{3\cos^2\theta_i - 1}{r_i^3} \right\rangle \tag{3}$$

in the usual notation. The results of the *ab initio* calculations⁶ indicate that the primary configuration for the $X^{2}\Sigma^{+}$ state of ScO is

$$(\text{core}) \ 3\pi^4 7\sigma^2 8\sigma^1, \tag{4a}$$

where

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$$3\pi \sim 3d\pi(\mathrm{Sc}) + 2p\pi(\mathrm{O}),$$
 (4b)

$$7\sigma \sim 3d\sigma(Sc) + 2p\sigma(O),$$
 (4c)

$$\sigma \sim 4sp(Sc).$$
 (4d)

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TABLE II. Experimental values for the rf transitions of gas phase ScO in its $X^2 \Sigma^+$ state.

			Obs.	Obs.				Obs.	Obs.				Obs.	Obs.
		Trans.*	freq.	calc.			Trans.	freq.	calc.			Trans.	freq.	calc.
v	N	type	(MHz)	(kHz)	v	N	type	(MHz)	(kHz)	v	N	type	(MHz)	(kHz)
									<u> </u>					-
0	10	h	42.010	-2	0	38	h	22.430	4	0	40	S	7875.921	1
0	12	h	39.865	0	0	38	p	7868.186	1	0	40	r	7880.293	0
0	15	h	37.207	0	0	38	q	7845.756	- 3	0	40	w	7852.215	- 2
0	18	a	40.542	0	0	38	t	/800.8//	1	0	40	v	/86/.098	1
0	20	h	33.343	0	0	38	S	/8/2.54/	2	0	40	u	78/1.4/3	3
0	20	P	/818.881	- 1	0	38	r	/8/5.919	-2	0	40	a	55.142	2
0	20	q	//85.338	1	0	38	w	7850.798	-1	0	40	b	46.241	-1
0	20	а	42.057	0	0	38	u	/868.088	1	0	40	C,	30.707	0
0	22	a	43.481	-1	0	38	a	53.836	-1	0	40	d	26.668	0
0	24	a	44.844	1	0	39	n	21.811	0	0	40	e	15.892	1
0	25	n	30.324	1	0	39	P	/8/1.409	1	0	40	J	4.3/4	1
0	25	a	45.508	1	0	39	9	/849.398	1	0	40	8	/.958	- 1
0	20	а	40.104	1	0	39	t	7809.384	2	0	40	1	31.133	3
0	27	a	40.811	-1	0	39	r	/8/8.088	1	0	40	J	25.985	1
0	28	a	4/.43/	1	0	39	w	7831.498	- 2	0	40	ĸ	20.582	0
0	29	a	48.095	0	0	39	v	7803.891	-1	0	40	1	14.8/9	1
0	30	n	27.209	- 1	0	39	u L	/809./04	2	0	40	m	0.024	1
0	30	a	48.731	- 1	0	40	n	21.190	- 2	0	40	n	2.331	1
0	24	a	49.308	0	0	40	P	70/4.001		0	40	x	7093.199	4
0	34	a	51.275	1	0	40	q	1833.493	3	0	41	9	7837.442	- 3
0	35	n	24.234	1	0	40	0	7872.043	0	0	41	r	78/3.140	5
0	30	a	32.330	1	0	40	1	1012.333	-2	1	41	r c	/882.339	- 1
0	41	w	7852.940	- 4	1	21	a 2	45.704	1	1	29	a	20.23/	1
0	41	v	7000.320	3	1	21	0	39.204		1	29	е ;	15.001	- 1
0	41	u	78/3.213	2	1	21	с d	31.301	1	1	29	:	29.032	2
0	42	9	7001.433	-1	1	21	4	22.319	5	1	29	J k	25.141	4
0	42	1	7071.903		1	21	;	24.713	2	1	29	ĸ	20.019	4
0	42	5	7994 979	- 1	1	21	ן ג	15 756	5	1	29	1	8 202	9
0	42	, r	7952 606	2	1	21	r 1	10 214	5	1	29	m	0.272	0 7
0	42	w	7850.578	- 3	1	21	<i>i</i>	3 876	3	1	29	и ,	7871 418	
0	42		7874 080	л Л	1	21	/// t	7848 561	ó	1	29	, r	7700 757	0
0	42	u	1014.909 57 124	4	1	21	ן ד	7770 006	0	1	29	х а	53 151	1
0	43 50	u L	14 734	1	1	21	х а	46 571	Ô	1	30	u a	53 956	- 1
1	30 11	n	19.503	-1	1	22	u a	40.371	0	1	31	u h	45 905	- 1
1	12	8	7850 280	10	1	23	u a	48 262	0	1	32	0	54 760	1
1	13	и ь	36 363	- 10	1	27	a	40.002	0	1	32	и Ь	46 593	_ 1
1	13	n 0	38 878	1	1	26	a	49.072	0	1	32	0	55 564	- 1
1	15	h	34 343	2	1	20	a	50 729	õ	1	34	u a	56 372	- 2
1	15	h	33 401	2	1	28	<u>a</u>	51 539	_ 1	1	35	a .	57 181	õ
1	17	" a	42 013	3	1	28	ц ,	43 869	_ 1	1	36	и а	57 991	_ 1
1	18	h	31 613	3	1	29		52 347	0	î	37	a	58 806	_ 1
1	10	" a	43 914	2	1	29	ц "	44 543	õ	1	38	a	59.627	1
1	20	и л	44,821	2	î	29	č	35.863	õ	1	38	b	50.863	-1
1	38	c u	41 505	-2	1	61	a	80.630	-1	2	22	t t	7873.125	- 5
1	38	đ	31.508	- 2	1	62	a	81.676	i	$\frac{1}{2}$	22	h	24.220	- 1
1	38	e	20.818	- ī	1	63	a	82.734	Ō	2	22	υ	7870.014	- 1
1	38	u u	7890.060	- 1	1	64	a	83.807	Ő	2	22	2	9.158	2
1	38	- t	7900.917	5	1	65	a	84.895	1	2	23	u	7876.335	- 3
- 1	39	a	60.451	1	1	65	h	- 6.642	- 10	2	23	t	7876.671	1
1	40	a	61.279	Ō	1	66	a	85.995	- 1	2	23	h	23.271	0
1	40	h	14.551	2	1	67	а	87.114	1	2	23	υ	7871.514	0
1	45	a	65.518	- 1	1	69	a	89.395	0	2	24	h	22.330	- 1
1	49	a	69.050	0	1	70	а	90.559	— 1	2	25	h	21.399	0
1	50	h	6.605	1	1	71	a	91.741	0	2	26	h	20.473	- 1
1	53	a	72.732	2	1	72	а	92.939	- 1	2	27	h	19.552	- 2
1	55	h	2.394	- 2	1	73	a	94.156	1	2	30	а	57.800	- 1
1	57	а	76.583	0	1	75	a	96.640	0	2	30	u	7892.296	— 1
1	60	а	79.601	2	2	14	u	7859.384	4	2	30	t	7903.012	4
1	60	b	69.261	1	2	14	v	7859.093	5	2	30	h	16.817	— 1
1	60	с	58.771	1	2	18	a	45.533	2	2	30	υ	7882.766	1
1	60	h	- 2.016	- 8	2	19	h	27.152	1					
1	60	u	7946.992	4	2	20	h	26.160	2					
1	60	t	7990.904	4	2	21	а	48.773	0					
1	60	р	8014.574	- 4	2	22	а	49.812	- 1					
1	60	q	8016.580	6	2	22	u	7874.221	- 6					

*See Table I and Fig. 1 for associated quantum number assignment.

As indicated by configuration (4), the unpaired electron is in an sp hybridized orbital thus allowing for bond formation between the 3d(Sc) and 2p orbitals. The 8σ orbital can be written as a linear combination of the 4s and 4p orbitals:

$$8\sigma \approx c_1 4s + c_2 4p,$$
 (5)

where c_1 and c_2 are the mixing coefficients. A comparison of

the experimentally determined Fermi contact value for ScO
$$(X^2\Sigma^+)$$
 ($b_F = 1.947$ GHz) with the calculated value for an unpaired electron in a 4s orbital of atomic Sc³⁶ ($b_F = 2.823$ GHz) establishes that $c_1 = 0.83$. This compares well to the Mulliken 4s population of 0.82 obtained by *ab initio* calculations.⁶

$$\gamma^{(2)} = 4 \sum_{n'v'} \frac{\left\langle X^2 \Sigma_{1/2}^+ | B(r) L^- | n'v' \right\rangle \left\langle n'v' | \Sigma_i (1_i^+ s_i^- + 1_i^- s_i^+) | X^2 \Sigma_{-1/2}^+ \right\rangle}{E(n',v') - E(X^2 \Sigma^+)}, \tag{6}$$

where the microscopic form of the spin-orbit operator has been used. In Eq. (6), the summation is over all the vibronic ${}^{2}\Pi_{1/2}$ states. Equation (6) simplifies greatly if it is assumed that the electronic wave function has a single unpaired electron in an essentially atomic orbital and there is only one interacting state. This simplified expression has been successfully used to predict $\gamma(X^2\Sigma)$ for the isoelectronic compound CaF,37 where the sole interacting state was assumed to be the $A^{2}\Pi$ state. When similar assumptions are made for ScO, the predicted value for $\gamma^{(2)}$ is greater than a factor of 10 larger than the observed value and shows little vibrational dependence.

The strong vibrational dependence of $\gamma(X^2\Sigma^+)$ of ScO suggests that there is more than one ${}^{2}\Pi_{1/2}$ state making substantial contributions to $\gamma^{(2)}$, or that a single interacting ${}^{2}\Pi_{1/2}$ state has a markedly different potential energy surface. Although there are a large number of plausible lowlying electronic configurations that would produce perturbing ${}^{2}\Pi_{1/2}$ states, the *ab initio* calculations⁶ give no indication of their existence. A possible configuration would be

core)
$$3\pi^3 7\sigma^2 8\sigma^1 1\delta^1 \rightarrow {}^2\Pi_i, {}^2\Pi_r {}^2\Phi_i {}^2\Phi_r {}^4\Pi^4\Phi$$
 (7)

which represent a promotion of a 3π electron of the $X^2\Sigma^+$ state into a $3d\delta$ molecular orbital centered on the scandium. The near degeneracy of the Sc⁺ (${}^{3}D_{1}$; 3d 4s) and Sc⁺ $({}^{3}F_{2}; 3d^{2})$ states $(\Delta E \sim 0.5 \text{ eV})^{38}$ and the known existence of low-lying states of ScF arising from Sc⁺ (4s3d) configurations¹² supports the suggestion that configuration (7) is important. As was demonstrated previously,²⁰ the two $^{2}\Pi$

TABLE III. Spectroscopic parameters for the v = 0, 1, and 2 levels of the $X^2 \Sigma^+$ state of ScO as determined by rf-optical double resonance.

Parameter	Parameter value (MHz)								
	v = 0	v = 1	v = 2						
 γ ₀	3.217 5(4)	4.434 4(2)	5.702 9(6)						
bo	1 922.534(1)	1 923.848(1)	1 925.124(7)						
C ₀	74.416(2)	74.656(2)	74.884(12)						
$(eqQ)_0$	72.240(5)	71.663(8)	71.177(59)						
$(C_I)_0$	0.021 81(1)	0.022 08(2)	0.022 38(10)						
γ1	2.323(4)×10 ⁻⁴	2.432(2)×10 ⁻⁴	(2.538×10 ⁻⁴)*						
b ₁	4.615(9)×10 ⁻⁴	$4.542(5) \times 10^{-4}$	$(4.49 \times 10^{-4})^{a}$						
c ₁	1.47(1)×10 ⁻⁴	1.49(1)×10 ⁻⁴	$(1.54 \times 10^{-4})^{a}$						
γ2	1.0(1)×10 ⁻⁹	0.79(3)×10 ⁻⁹	$(0.62 \times 10^{-9})^{a}$						

* Held fixed during fit.

(

The second order contribution $\gamma^{(2)}$ is given by

states of configuration (7) contribute with opposite sign to $\gamma^{(2)}$ and, therefore, could explain the strong vibrational dependence of $\gamma(X^2\Sigma^+)$.

CONCLUSIONS

The molecular-beam-optical and rf-optical techniques have provided precise spectroscopic information about gas phase scandium monoxide in its $X^{2}\Sigma^{+}$ and $A^{2}\Pi_{r}$ states. No localized perturbations for the $X^{2}\Sigma^{+}$ (v = 0-2) state were observed, but strong perturbations in the $A^{2}\Pi$ (v = 1) were detected. The optical spectrum could only be assigned by assuming a negative "d" ($A^{2}\Pi$) magnetic hyperfine parameter, which suggests that the current theoretical interpretation of this parameter must be modified. The magnetic hyperfine parameters of the $X^2\Sigma^+$ state can be interpreted in terms of the present theoretical model, while the fine structure parameter $\gamma(X^2\Sigma^+)$, cannot. The strong vibrational dependence of $\gamma(X^2\Sigma^+)$ suggest that the low-lying electronic state distribution is more complex than current spectroscopic data and ab initio calculations indicate. A manifold of low-lying states arising from a three-open-shell configuration can be responsible for this behavior.

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