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13. ABSTRACT During the period beginning on 1 September 1969 and continuing through 30 September 1971, the contractor conducted a program of basic research entitled, "Atomic and Molecular Lifetime Measurements". The research involved the investigation of phase shift measurements of selected metals, and metal oxides.			

Final Report
Atomic and Molecular Lifetime Measurements

The contract goal of measuring the radiative lifetimes for atomic and molecular species were fully realized for our electron beam phase-shift technique. During the initial contract period (1 September 1969 - 31 August 1970) substantial advances were made in instrumentation and analysis techniques which have improved the instrumental stability, lifetime range, resolution, and introduced the ability to obtain a wide range of refractory species in the vapor phase for lifetime determinations.

The contract was extended to 30 September 1971 to allow preparation and publication of papers discussing the work completed during the initial contract period. This report includes a copy of those published papers, which are in any case, the best evidence of a successful program of research.

Particular emphasis was placed upon problems related to metals and metal oxides. The use RKR routines for the computation of potential curves and Franck-Condon factors from molecular constants was initiated since it was found that in most cases needed vibrational transitional probabilities were not available for transitions of interest. Several publications resulted from these calculations. Silicon monoxide was the first and only metal oxide studied during the contract period when experimentation was proceeding. A paper describing these measurements is included.

Altogether eight papers have been published from work done during the first contract year. These are listed in the bibliography.

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USE OF ELECTRON BEAM PHASE-SHIFT TECHNIQUES IN RADIATIVE LIFETIME DETERMINATIONS†

Wm. H. SMITH*

Princeton University Observatory, Princeton, New Jersey, U.S.A.

A discussion is presented of theoretical and experimental aspects of radiative lifetime determinations using an electron beam phase-shift apparatus. Some new results for metals are reported.

1. Introduction

Radiative lifetime studies of atomic species have been carried out using a variety of excitation methods. Among them, photon, electron, and most recently foil excitation have played a prominent role. Each excitation method has significant advantages and shortcomings.

Photon excitation is highly selective, does not suffer from cascade problems in the levels excited, and has been used with a very wide variety of techniques for detection of upper state radiative lifetimes. To name a few methods, magnetic depolarization or Hanle effect, direct decay, and phase-shift type measurements have been widely applied. Usually photon excitation is restricted to neutral species, except where special arrangements, such as a pulsed discharge, are provided to produce a ionized species which may be studied during the period before recombination has too severely reduced the ionic concentration. The most serious limitation of photon excitation is the limited range of accessible upper states.

Electron excitation introduces the ability to excite a wide range of upper levels of neutral, singly, and doubly ionized species either from atomic vapor or by dissociative excitation. Since some levels thus populated may lie above, and connect with the upper state being studied, cascading can result from such non-threshold excitation. Delay-coincidence and phase-shift methods have often been applied using electron beams.

Foil excitation is by far the most severe excitation and has resulted in the observation of many previously unknown transitions, especially in higher ionized states, and may result in severe cascading and/or line identification problems. The purpose of this paper is to discuss our particular version of an electron beam

excitation technique which determines mean radiative lifetimes by measuring the phase delay in response of the system under influence of a sinusoidally modulated electron beam.

2. Theory of the experiment

The relation between excitation $e(t)$ and response $I(t)$ is assumed to be linear and expressible by the inhomogeneous linear differential equation $\dot{I}(t) = e(t)$. The excitation function $e(t)$ may be considered to be an impulse function $\delta(t)$ which evokes a system response $I(t) = e^{-t/\tau}$ for $t > 0$, where τ is the mean lifetime of the system. In the present case, $e(t)$ is represented by a sinusoid $e^{i\omega t}$, which has a steady state solution to the above differential equation in the form $I(t) = e^{i\omega t}G(\omega)$, where $G(\omega)$ is the Fourier transform of the system response to the impulse $\delta(t)$, i.e. $G(\omega) = (1 + i\omega\tau)^{-1}$. $G(\omega)$ then is the transfer function which introduces the phase delay $\tan \phi = \omega\tau$ between the input excitation and the output response, with amplitude proportional to $(1 + \omega^2\tau^2)^{-1/2}$. Since for $\omega\tau < 1$, the amplitude is nearly independent of frequency, but not source parameters, the phase shift is the preferred experimental quantity.

In the case where cascading occurs, as often happens when non-threshold excitation is used, the excitation function is considered to result in at least two upper states, one being the measured state and the other an optically connected state which populates the measured state either directly or through an intermediate state. Considering the case where the cascading may be represented by a single state, the excitation is $e^{i\omega t}$ into the measured state and $\beta e^{i\omega t}$ into the cascading state, where β is the ratio of excitation of the cascading state to that of the measured state. Proceeding as before, we find that the transfer function for the complete process is given by

$$G(\omega) = (1 + i\omega\tau)^{-1} [1 + \beta(1 + i\omega T)^{-1}],$$

where T is the mean lifetime of the assumed single cascading state. The measured phase shift ϕ is then given by

* Presented the paper.

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$\phi = \tan^{-1} \omega \tau + \tan^{-1} \omega T - \tan^{-1} [\omega T / (1 + \beta)]$,
with output lagging the input.

This equation has been transformed by Lawrence and Savage¹ into the form:

$$F(\phi, \omega T) = \frac{\omega T [1 + (\omega T) \tan \phi]}{\omega T - \tan \phi}$$

$$= (\omega T)^2 \left(\frac{bc}{b-c} \right) + \frac{1}{b-c},$$

where $b = 1/(1 + \beta)$ and $c = \tau/T$, and the other variables have their previous meanings. Here a linear relation exists between measured absolute phase shifts and assumed cascade lifetimes at each modulating frequency, and the quantity $(\omega T)^2$. From a least squares fit of the data using this relationship, the unknown radiative lifetime and cascade fraction β are obtained as a function of the slope and intercept of the least squares plot.

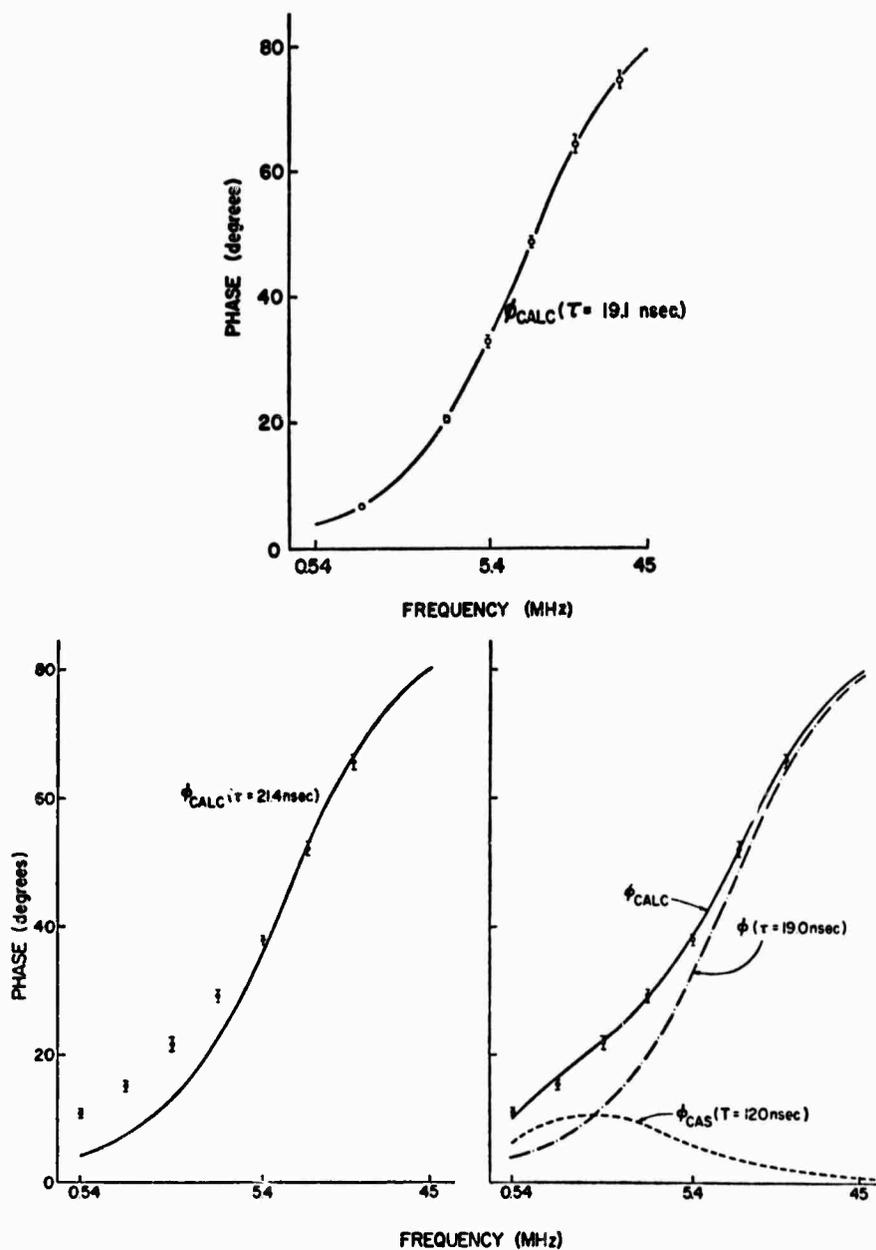


Fig. 1. Phase-frequency diagrams (taken from ref. 3). a) Cascade-free; b) cascade, $T > \tau$, $\beta \ll 1$.

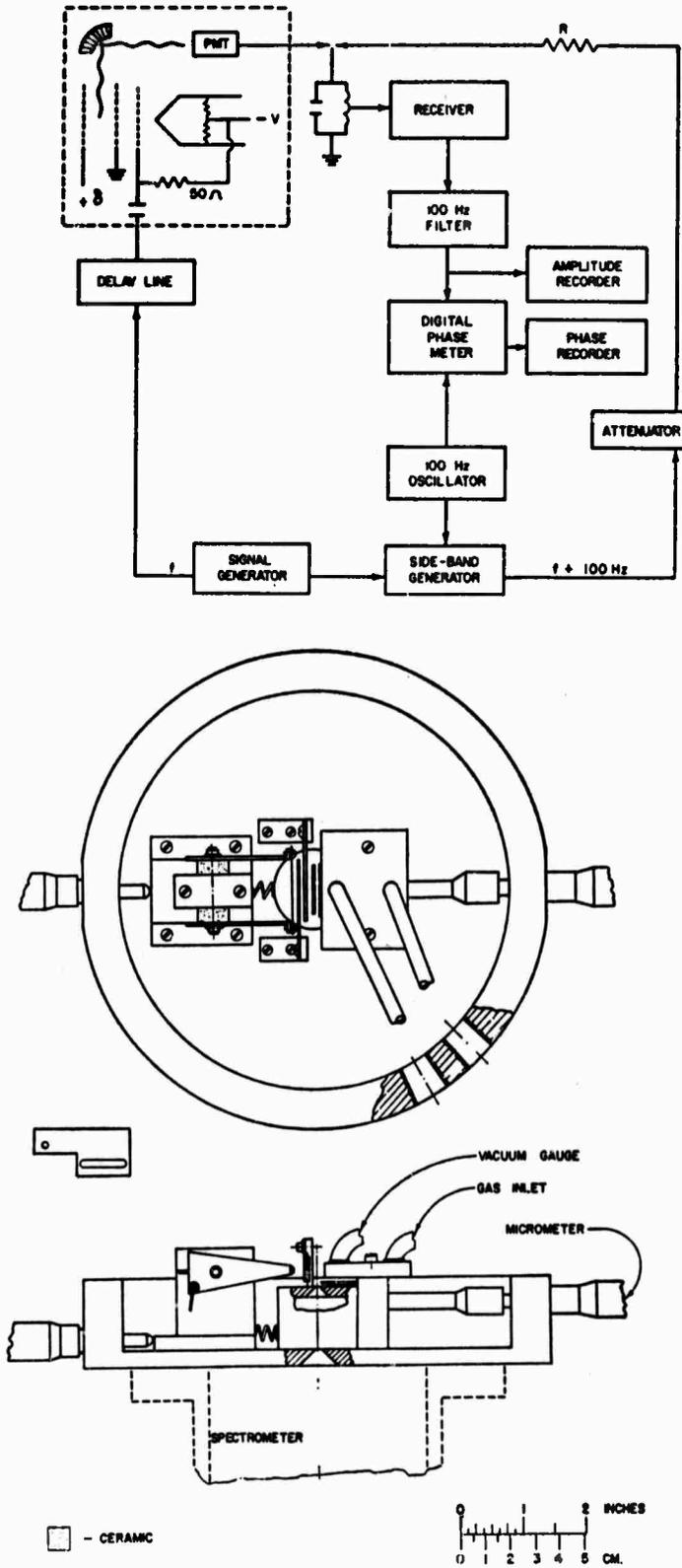


Fig. 2. Schematic of the present electron beam phase-shift apparatus (taken from ref. 3). a) Signal path; b) electron beam source layout.

II. LIFETIMES AND TRANSITION PROBABILITIES

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In fig. 1, we have plotted the two most common phase-frequency diagrams which are encountered in practice, that of the cascade-free case and that of cascading where the cascading state is longer-lived than the measured state. Certain pathological cases can also occur. For example, if $\tan^{-1}\omega\tau = \tan^{-1}[\omega T/(1+\beta)]$ an apparently cascade-free phase-frequency diagram yielding the cascade lifetime T is obtained. Also, if nearly all excitation occurs via a cascade channel, then a local maximum in the phase-frequency diagram occurs at $1/\sqrt{(T\tau)}$. In both cases, varying the parent gas or excitation conditions may suffice to give a different β which will allow understanding of the diagrams.

3. Experimental

The phase shift method described here is essentially that due to Lawrence²). Applications to numerous atomic and molecular systems may be found in papers by Hesser³), and Smith^{4,5}). In fig. 2, the schematic shows the signal paths which determine the measured phase shift. A signal generator followed by a 10 W broad-band amplifier drives the modulating grid in the typical triode-type source, which is self-biased to prevent drawing grid current during operation. Electron beam modulation is typically 90–95%. The operating frequency is varied from 0.54 MHz to 54 MHz, to allow measurement of lifetimes in the range from 10^{-10} to 5×10^{-7} sec, and also to allow the unfolding of cascade processes. The current modulated electron beam is typically from 50 to 200 V in energy. A single side-band generator is the only noncommercial component, aside from control logic which automates operation. The rf and audio signals are mixed in the phase-shift type side-band generator to produce an upper side band. Provision is made for mixing small amounts of carrier of the proper phase and amplitude into the receiver input to cancel such radio frequency interference as exists. The modulated, phase shifted photon signal is detected by an ITT F-4034 photomultiplier (rise time 0.8 nsec) at the exit slit of a McPherson 1-meter normal incidence vacuum grating monochromator. This signal is mixed with the upper side-band and passed into the receiver input where demodulation occurs. The receiver output, a 100 Hz audio signal, retains the phase information present in the radio frequency signals. The 100 Hz beat signal is then passed thru a 100 Hz active filter and clipper to remove harmonics and reduce the effect of amplitude variations. A 50 MHz counter then compares phases via zero-crossings in the reference 100 Hz oscillator and the 100 Hz beat signal. In a typical phase measure-

ment, 10^5 crossings are averaged, and corrected for system imbalance.

In order to understand the meaning of such a phase measurement, an absolute phase reference must be determined. With our apparatus this is done by comparing phase shifts, under identical (simultaneous) experimental conditions, of the system under investigation with that of a multiplet with a well-known mean life, preferably cascade-free and short. Originally, L_α was used for this purpose¹), and compared with N II $\lambda 1085$ which was known to be cascade-free. The data presented here was measured relative to Ne II $\lambda 1908$ ($\tau = 3.5$ nsec) and Ar II $\lambda 1575$, $\lambda 2943$ ($\tau = 4.7$ nsec), with consistent results in all cases.

Excitation is usually performed via electron impact on low pressure ($< 10 \mu\text{m Hg}$) gases of small molecules i.e. dissociative excitation. In some cases, readily volatile compounds which contain an atom of interest, or which produce no spectral or other interference are not available. In these instances, we resort to vaporization of metals, or metal halides for example. When using dissociative excitation, the assumption is made that no appreciable phase shift occurs due to the dissociation process which typically proceeds in times of 10^{-12} to 10^{-14} sec. Radiative entrapment can occasionally be important with resonance transitions exhibiting large f -values, such as Mg I $\lambda 2852$ or Ca I $\lambda 4227$, even when using dissociative excitation. Measurements then must be made over a range of densities. At the low pressures customarily utilized, collisional deactivation is seldom observed.

With regards to the present experiment, time resolution is customarily ± 0.2 nsec. Systematic errors are on the order of $\pm 10\%$. Accuracy degrades slightly when cascading is present. Two examples have been found which illustrate the limiting τ -values obtainable with the equipment, namely Ne II $\lambda 462$ with a $\tau = 0.0_{-0.0}^{+0.1}$ nsec. and N II $\lambda 776$ with $\tau = 0.0_{-0.0}^{+0.2}$ nsec, with both transitions being cascade-free.

The data listed in table 1 represent our most recent efforts in measuring radiative lifetimes for upper states of atomic species. All of the transitions, except for Mg I $\lambda 2026$, $\lambda 1828$ and Ca I $\lambda 2721$ have been studied using modern experimental methods. In general, we find excellent agreement with the published oscillator strengths, a fact which encourages the belief that the major experimental uncertainties in this and the other methods mentioned above have been solved. It may be expected that demands for reliable oscillator strengths for the low-lying levels of simpler atomic species soon will be adequately satisfied, although there remain a number of resonance multiplets for C I, N II and O I

TABLE I
Radiative lifetime data for some species presently under study.*

Species	λ (Å)	Transition	τ (10^{-9} sec)	Cascade parameters
Mg I	2853	$3s^2 1S-3p 1P^0$	1.90 ± 0.3	$T = 100, \beta = 0.63$
Mg I	2026	$3s^2 1S-4p 1P^0$	10.4 ± 2.0	$T = 100, \beta = 0.2$
Mg I	1828	$3s^2 1S-5p 1P^0$	28 ± 5	$T = 150, \beta = 0.2$
Mg II	2789-2803	$3s 2S-3p 2P^0$	3.50 ± 0.5	$T = 85, \beta = 0.25$
Al II	1671	$3s^2 1S-3p 1P^0$	0.70 ± 0.10	$T = 20, \beta = 0.3$
Ca I	4227	$4s^2 1S-4p 1P^0$	4.5 ± 0.5	$T = 90, \beta = 0.18$
Ca I	2722	$4s^2 1S-5p 1P^0$	16.6 ± 2.0	$T = 200, \beta = 0.65$
Ca II	3968-3934	$4s 2S-4p 2P^0$	6.5 ± 0.7	$T = 110, \beta = 0.28$
Al I	3944	$3p 2P^0-4s^2S$	6.9 ± 0.7	unanalyzed
Al I	3082	$3p 2P^0-3d^2D$	14.0 ± 1.4	unanalyzed
B I	2497	$2p 2P^0-3s^2S$	3.3 ± 0.4	unanalyzed
Fe I	2474	$A^6D-X^6F^0$	3.0 ± 0.6	unanalyzed

* Final results submitted to *Astrophys. J.*

below $\lambda 1050$ which have not been investigated as yet, or for which disagreements exist. The study of higher excited states, especially of highly ionized atoms, is rapidly expanding now, and it is particularly in that area where beam-foil studies must assume the burden, since these other methods are not directly applicable.

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⁵⁾ W. H. Smith, *J. Quant. Spectr. Radiative Transfer* **9** (1969) 1191.

Discussion

HADEISHI: What is the minimum light intensity you can observe?
SMITH: ~ 100 photoelectrons/sec.

WIESE: When correcting for cascading, did you assume several feeder states?

SMITH: This is difficult to compensate for, since it is not clear that cascading always relates to one obvious state. We assume one state in our analysis, or what amounts to an average over all cascading states.

WIESE: It may usually be a mixture of states.

II. LIFETIMES AND TRANSITION PROBABILITIES.

Radiative and Predissociation Probabilities for the OH $A^2\Sigma^+$ State*

WILLIAM HAYDEN SMITH

Princeton University Observatory, Princeton, New Jersey 08541

(Received 18 March 1970)

Phase-shift lifetime measurements over a range of modulation frequency have provided data on the effects of the weak predissociation of the $A^2\Sigma^+$ state. The $v'=0$ radiative lifetime (850 ± 130 nsec) corresponds to an $f(0-0)$ of $7.7 \pm 1.1 \times 10^{-4}$ in agreement with previous absorption measurements. The higher vibrational quanta show shortened radiative lifetimes due to predissociation.

I. INTRODUCTION

The oscillator strength of the OH $A^2\Sigma^+ - X^2\Pi$ violet system has been carefully measured in absorption by Golden *et al.*¹ An f value of $7.1 \pm 1.1 \times 10^{-4}$ was obtained by them. At the same time, they surveyed previous results for f -value determinations for this system by a variety of means, and found that, by use of vibration-rotation corrections for the different effective temperatures of the previous experiments, and by use of new thermodynamic data, most of the earlier data seemed to be converging of an f value of about 8×10^{-4} , within 10%.

More recently, Marshall *et al.*² and German and Zare³ have measured $g\tau$ values for some rotational sublevels of the OH $A^2\Sigma^+$ state, and German and Zare⁴ have made ORFDOR (optical radio-frequency double resonance) measurements to determine g . The level-crossing measurements were for $K'=2, 3, 4, 5$ while the ORFDOR was for $K'=2$ ($F'=1, 2$). The ORFDOR gave g values agreeing with Hund's case (b) coupling, allowing τ to be calculated⁴ to be 770 ± 80 nsec. Marshall *et al.*² gave $g\tau$ values which were interpreted by German and Zare⁴ to be in approximate agreement with their results (i.e., 680 vs 770 ± 80 nsec).

The derived quantity, the absorption f value for the (0-0) transition $f(0-0)$, may be obtained from the radiative lifetime τ from the equation

$$f(0-0) = 1.499 \times 10^{-8} g'/g'' (\tau_{v'})^{-1} \times (\nu_{00}^3 q_{00} / \sum_{v''} \nu_{v''}^3 q_{v''}), \quad (1)$$

where g' , g'' are the upper and lower state electronic degeneracies, $\nu_{v''}$ is the wavelength in cm^{-1} of the v'' transition, and $q_{v''}$ is the v'' Franck-Condon factor. This equation assumes the constancy of the electronic transition moment ($R_{e(v'v'')}$) for those v'' transitions which significantly contribute to the sum $\sum_{v''} \nu_{v''}^3 q_{v''}$.

German and Zare⁴ derived an $f(0-0)$ of $9.3 \pm 1.0 \times 10^{-4}$ from their τ which results from the combined ORFDOR and level-crossing experiments. This value is not in good agreement with the absorption f value of $7.1 \pm 1.1 \times 10^{-4}$ found by Golden *et al.*,¹ although it does overlap the value of 8×10^{-4} (within 10%) estimated by them from consideration of all the previous data.

This slight discrepancy may have its origin in Eq. (1) being invalid, an incorrect τ_{00} , incorrect q_{00} , neglect of other processes depopulating the $A^2\Sigma^+$ state of OH, such as a possible predissociation (see Carlone and Dalby,⁵ and Michels and Harris⁶) affecting the $v'=0$ level, or the effect of reactions downstream which reduce the OH concentration in the absorption measurements (as noted by Golden *et al.*¹).

Using our phase-shift method, we have measured a direct τ and determined if significant predissociation effects are present. We have also recalculated Franck-Condon factors to use in Eq. (1).

II. EXPERIMENTAL

The phase-shift method applied here has been discussed in detail elsewhere.^{7,8} The OH $A^2\Sigma^+$ state was excited by an rf-modulated beam of 200-V electrons directed into water vapor. The phase shift between the input excitation and the modulated emission is a measure of the various processes, both radiative and radiationless which depopulate the $A^2\Sigma^+$ state of OH. The Ne(II) 1908-Å multiplet was used as a phase reference, along with the $N_2^+ B^2\Sigma^+ - X^2\Sigma_g^+$ (0-0) transition.⁸ The modulating frequency was varied from 0.54 to 30.4 MHz. No phase dependence on pressure or electron voltage was found from 0.5-5 μ pressure, or 50-200 V, respectively. A 0.5-m Seya-Namioka with a band pass of 5 Å was used with a cooled 6256S photomultiplier as detector. Radiative cascading was studied by the variation of the modulating frequency and corrected for by assuming a single cascading state with lifetime T , providing a cascading fraction β equal to the ratio of the cascading excitation to direct excitation, according to the procedure given by Lawrence and Savage.⁹ The ratio of the amplitude of the signal-to-noise elements was at least 20:1 in these measurements and usually 50:1 or more. The absolute accuracy of the measurements is taken to $\pm 15\%$, primarily from uncertainty in the cascade correction, photomultiplier delays which are a function of wavelength, and slight electrical changes in the electron beam source which can affect day-to-day ϕ values slightly. The relative ϕ values measured day to day are stable to better than 5%, so that dependence of τ on v' can be measured relatively to that precision.

TABLE I. OH A ${}^2\Sigma^+$ state radiative lifetimes, transition probabilities, and predissociation probabilities.

Band	λ (Å)	τ (nsec)	$A_{T(v'v')}$ (10^6 sec^{-1})	$D_{v'}$ (10^6 sec^{-1}) ^a	Cascading parameters
(0-0)	3050-3120	850±130	1.18	0	$T=70, \beta=0.10$
(1-1)	3150-3200	750±115	1.33	0.15±0.06	$T=70, \beta=0.11$
(2-2)	3220	550±85	1.82	0.64±0.10	$T=80, \beta=0.25$

^a All $A_{v'}$ assumed equal to $A_{v'=0}=1.18 \times 10^6 \text{ sec}^{-1}$ (see text). τ is the measured lifetime of the v' state. $A_{T(v'v')}$ is the total absolute transition probability, including all processes depopulating the v' level, radiative and radiationless. $D_{v'}$ is the predissociation probability [including overlapping

transitions for (1-1), (2-2)]. T is the approximate cascading state lifetime. β is the ratio of excitation by cascading to direct excitation. f values (Franck-Condon factors taken from Ref. 5): $f(0, 0)_{\text{abs}}=7.7 \pm 1.1 \times 10^{-4}$, $f(0, 1)_{\text{abs}}=0.62 \pm 0.08 \times 10^{-4}$, $f(0, 2)_{\text{abs}}=0.046 \pm 0.006 \times 10^{-4}$.

III. RESULTS

Using the above techniques, we find $\tau(0, 0)=850$ nsec, in agreement with German and Zare.³ As noted in Table I, this value holds for λ between 3050 and 3120 Å. At longer wavelengths, we determine a decreasing τ value. Our bandpass of 5 Å prohibits our measurement of individual rotational lines, but the $\tau(0, 0)$ remains constant to our experimental accuracy for $N' \leq 20$. At longer wavelengths, overlapping rotational transitions for the (0-0), (1-1), and (2-2) levels preclude definitely identifying the shorter τ values with certain N' values, although the emission comes predominantly from the v' levels noted in Table I. For the $v'=1$ level the shortening is marginal, but for $v'=2$ it is clearly present.

IV. DISCUSSION

Felenbok¹⁰ has given Morse curve Franck-Condon factors for the OH A ${}^2\Sigma^+-X^2\Pi_1$ transition. We have recomputed Franck-Condon factors using the RKR method and find very close agreement with his results for $q_{v',v''}$ for $v'=0, v''=0, 1, 2$ which are the important terms in computing an absorption f value from Eq. (1). In particular, we find $q_{0,0}$ to be 0.91 yielding $f(0-0)$ of $7.7 \pm 1.1 \times 10^{-4}$ from our measured $\tau(0, 0)$. Since our lifetime is in agreement with German and Zare,³ the Franck-Condon factor must be responsible for the difference noted above with the absorption f value of Golden *et al.*¹ since radiationless depopulating processes of the A ${}^2\Sigma^+$ state apparently are unimportant under the discussed experimental conditions. Using the present Franck-Condon factor, German and Zare's τ value yields an $f(0-0)=8.5 \pm 0.9 \times 10^{-4}$. Since we are dealing with a favorable case (i.e., a large $q_{0,0}$) variations in R_e are unlikely to cause significant errors in the approximation embodied in the use of Eq. (1) in the above calculations.

The agreement of the f value, $f(0-0)$, calculated as above with the absorption f value demonstrates that predissociation is unimportant for $N' \leq 20$ for $v'=0$ of the A ${}^2\Sigma^+$ state of OH. At $v' \geq 1$, the effects of the known predissociation do make themselves felt in the enlarged total transition probability. The $D_{v'}$ listed in Table I may be taken as an approximation to the predissociation probability for $v'=0, 1$, and 2. Higher resolution studies are needed to establish this firmly as a function of N' within v' levels. In any case, we have shown that $f(0-0)=8.0 \times 10^{-4}$ to within 10%, as favored by Golden *et al.*,¹ is in excellent agreement with the values derived from radiative lifetimes when the Franck-Condon factors derived by us, and previously by Felenbok¹⁰ are used.

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The author wishes to acknowledge conversations on the present results with Dr. R. N. Zare and Dr. B. Lutz.

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Atomic Transition Probabilities: Ultraviolet Multiplets of Zn I,II and Cd I,II*

SCOTT R. BAUMANN AND WILLIAM HAYDEN SMITH
 Princeton University Observatory, Princeton, New Jersey 08540
 (Received 1 October 1969)

Radiative lifetimes for eleven transitions in Zn I,II and Cd I,II have been measured by use of a phase-shift method. Lifetimes ranging from 1.75 nsec for the Zn I ($4s^1S_0-4p^1P_0$) multiplet to 460 nsec for the Cd II ($5p^2P_{1/2}-4d^95s^2^3D_1^0$) level were found. These results are compared with previously available data.

INDEX HEADINGS: Spectra; Zinc; Cadmium.

This research represents the first results of a continuing program designed to obtain reliable radiative lifetimes for uv and visible transitions of metals and metal oxides. The often-studied resonance transitions¹ of Zn I and Cd I were selected for our initial measurements because reliable f values are available with which to compare them. At the same time, we have measured radiative lifetimes for other transitions in Zn II and in Cd I,II which have not been previously studied experimentally.

EXPERIMENTAL

The radiative lifetimes reported here were measured by use of a phase-shift technique described by Lawrence.² In brief, this consists of an electron-beam excitation source which is current modulated at a radio frequency f , and which serves as the monochromator entrance slit. The modulated emission from the source is dispersed by a 0.5-m Seya-Namioka monochromator and focused onto an EMI 6256B photomultiplier. The photomultiplier signal is mixed with the output of a sideband generator at $f+100$ Hz and detected by a conventional radio receiver. The 100-Hz beat at the receiver output is compared with a reference 100-Hz quartz-crystal oscillator by a zero-crossing phase meter. The relative phase shift measured is then compared with the phase shift under identical (simultaneous) conditions of a transition with a known radiative lifetime, e.g., Ne II 1908 Å.³

The measured absolute phase shift ϕ is related to the lifetime τ by

$$\phi_{\text{abs}} = \tan^{-1}\omega\tau + \tan^{-1}\omega T - \tan^{-1}[\omega T / (1 + \beta)],$$

where T is the mean lifetime of the cascading state and β is the ratio of the excitation of the measured state by cascading to that of direct excitation.⁴ In all cases we assume a single cascade process, although several upper states may be responsible.

Zinc and cadmium metals of standard chemical purity were placed in quartz boats which were heated by a tungsten filament and which directed a beam of the atomic vapor through the excitation region. Adequate intensity for accurate phase measurements was the only criterion in adjusting the temperature. Photon entrapment was unimportant at all temperatures, except for the Zn I and Cd I resonance lines for which the effect was negligible at the densities used during the measurements.

By following the spectral appearance of lines as a function of voltage, we were able to identify the neutral and ionized species. There was no effect on measured phase shifts as long as voltages were not too near threshold.

Because cascading was present in all lines, the cascade-correction procedure due to Lawrence and Savage⁴ was applied; it yielded satisfactory results in all cases. The results of the analysis are listed in Table I.

RESULTS

Cadmium

The cadmium resonance line at 2288 Å ($5s^2^1S_0-5p^1P_0$) has been studied by various methods, including theoretical calculations^{5,6}; the consensus is that the radiative lifetime is about 2.0 nsec. Our measurement, when made at pressures low enough so that photon entrapment was

TABLE I. Radiative lifetimes and transition probabilities of some Zn and Cd levels.

(Å)	Designation	$A_T (\times 10^8/\text{sec})^a$	τ (nsec)	Cascading constants
Zn I 2139	$4s^1S_0-4p^1P_0$	571	1.75 ± 0.2	$T = 25$ nsec, $\beta = 0.10$
Zn II 2026	$4s^2S_{1/2}-4p^2P_{1/2}^0$	323	3.1 ± 0.4	$T = 80$ nsec, $\beta = 0.10$
Zn II 2062	$4s^2S_{1/2}-4p^2P_{3/2}^0$	328	3.05 ± 0.4	$T = 90$ nsec, $\beta = 0.15$
Zn II 2100	$4p^2P_{1/2}^0-4d^2D_{3/2}$	260	3.85 ± 0.7	$T = 150$ nsec, $\beta = 0.12$
Zn II 2502	$4p^2P_{3/2}^0-5s^2S_{1/2}$	260	3.85 ± 0.7	$T = 85$ nsec, $\beta = 0.46$
Zn II 2558	$4p^2P_{1/2}^0-5s^2S_{1/2}$	260	3.85 ± 0.7	$T = 70$ nsec, $\beta = 0.23$
Cd I 2288	$5s^2^1S_0-5p^1P_0$	476	2.1 ± 0.3	$T = 35$ nsec, $\beta = 0.11$
Cd I 1669	$5s^2^1S_0-6p^1P_1^0$	99	10.1 ± 1.0	$T = 170$ nsec, $\beta = 0.40$
Cd II 2144	$5s^2^3S_1-5p^2P_{1/2}^0$	294	3.4 ± 0.7	$T = 550$, $\beta > 1$
Cd II 2265	$5s^2^3S_1-5p^2P_{3/2}^0$	208	4.8 ± 1.0	$T = 400$, $\beta > 1$
Cd II 3250	$5p^2P_{1/2}^0-4d^95s^2^3D_1^0$	2.17	460 ± 90	$T = 60$ nsec, $\beta = 0.2$

* A_T = total transition probability.

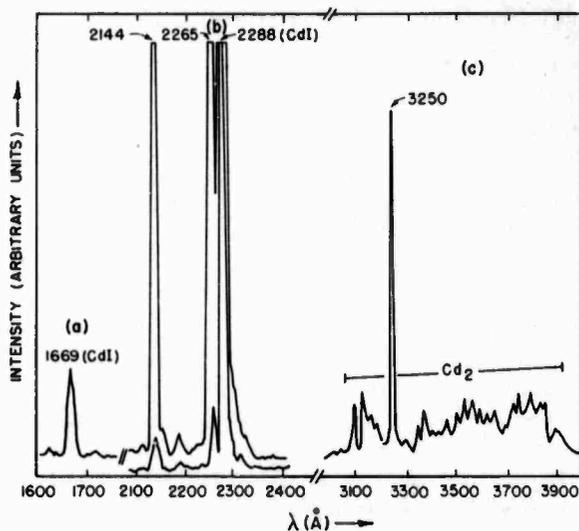


FIG. 1. Emission spectrum due to Cd as excited in our electron-beam source at 1.71-MHz modulation frequency.

not important, yielded a lifetime of 2.1 ± 0.3 nsec, in agreement with the previous results. There was only weak cascading. At high-enough pressures, emission from the Cd_2 molecule was also observed⁷ (see Fig. 1).

The cadmium 1669-Å ($5s^2\ ^1S-6p\ ^1P^0$) transition was also measured, with the result that $\tau = 10.1 \pm 1.1$ nsec; cascading was representable by a state with $T = 170$ nsec and $\beta = 0.40$. We have not located published values, either experimental or theoretical, for this transition. Qualitatively, the decrease of transition probability is, of course, expected.

The three Cd II transitions measured include the two levels of $5p^2P_{1,1}^0$ in their transition to the $5s^2S_{1/2}$ ground state. The $J = \frac{3}{2}$ level gave $\tau = 3.4 \pm 0.7$ nsec, whereas the τ for the $J = \frac{1}{2}$ level was found to be 4.8 ± 1.0 nsec. Although the values overlap slightly at

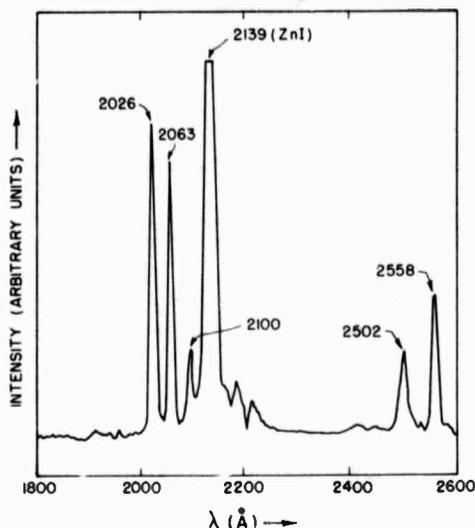


FIG. 2. Emission spectrum due to Zn as excited in our electron-beam source at 1.71-MHz modulation frequency.

the extremes of their error limits, the precision of experiment is such as to allow us to state that the $J = \frac{3}{2}$ level has a higher transition probability than the $J = \frac{1}{2}$ level. This result is believed to be a consequence of a breakdown of the pure-configuration approximation.

The mean cascading lifetime (~ 400 nsec) for these states populating the $5p^2P_{1,1}^0$ level of Cd II is close to the 460-nsec lifetime measured for the only observed Cd II transition ending in that level ($5p^2P_{1,1}^0-4d^95s^2\ ^2D_{3/2}$). This may be taken to imply that the cascading population is largely derived from the $4d^95s^2\ ^2D_{3/2}$ level. The 2144-Å Cd II transition ($5s^2S_{1/2}-5p^2P_{1,1}^0$) showed cascading due to a state with $T \approx 550$ nsec. Probably this is, in part, attributable to the $5p^2P_{1,1}^0-4d^95s^2\ ^2D_{3/2}$ Cd II transition, which we observed but did not measure owing to its low intensity under our experimental conditions. According to Geneux and Wanders-Vincenz,⁸ this state has a mean life of 830 ± 70 nsec. No published value was found for either the Cd II 2265- or 2144-Å radiative lifetimes or transition probabilities.

Zinc

The situation with respect to the value of the transition probability for the Zn I resonance transition at 2139 Å ($4s^2\ ^1S-4p\ ^1P^0$) shown in Fig. 2 is not so certain as for Cd I. Garstang⁵ has calculated that $\tau = 1.94$ nsec, in agreement with the other references noted in his paper, where Spitzer⁶ gave $\tau = 0.43$ nsec. The measurements of Lurio *et al.*⁹ by the level-crossing method gave $\tau = 1.41 \pm 0.04$ nsec. Our measurements yielded a radiative lifetime of 1.75 ± 0.2 nsec. The measurements over a wide range of frequencies (0.54–54 MHz) showed the transition to be nearly cascade free, so that little correction for cascading was necessary. Our result is therefore in disagreement with that of Spitzer⁶ and, less seriously, with those of Lurio *et al.*⁹ We overlap the calculated value of Garstang,⁵ but the lack of error limits on the theoretical calculation does not allow us to assess the meaning of such a coincidence of τ 's.

The remaining lines measured were all Zn II transitions, none of which to our knowledge have been previously studied. The transitions to the ground state ($4s^2S_{1/2}$) from the $4p^2P_{1,1}^0$ multiplet showed the same radiative lifetime of 3.1 ± 0.4 nsec, with a small amount of cascading present in both ($T \approx 85$ nsec, $\beta = 0.1$). The other three transitions measured were between excited states and populated the $4p^2P^0$ multiplet. All three showed radiative lifetimes of 3.85 ± 0.7 nsec. Because two of the transitions involved a change of the principal quantum number, a substantial decrease of transition probability usually results. It can be concluded that configuration interaction plays an important role in determining the transition probabilities observed for these levels.

DISCUSSION

It is of interest to note that, in a qualitative sense, the transition probabilities found in the heavier atom

Cd I and Cd II are regular, whereas the lighter atomic ion, Zn II, shows some anomalies. The large transition probabilities measured for the Zn II 2100-, 2502-, and 2558-Å lines could cause confusion in the measured radiative lifetimes for the lines originating in the multiplet they populate by cascading ($4p^2P^0$) because our cascade-correction procedure is not sensitive when the cascading state has nearly the same lifetime as the measured state. However, these cascading states were relatively much more weakly excited in our source, so it was likely that only a small fraction of the Zn II 2026-Å and 2062-Å emission resulted from cascades that originate in these states. The observed cascades come from other levels. Hence we believe that the measured lifetimes for the $4p^2P^0$ multiplet are essentially correct.

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FRANCK-CONDON FACTORS AND ABSOLUTE OSCILLATOR STRENGTHS FOR NH, SiH, S₂ AND SO*

W. H. SMITH and H. S. LISZT

Department of Astrophysical Sciences, Princeton University, Princeton, New Jersey 08540

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Abstract—RKR Franck-Condon factors and r -centroids have been calculated for transitions of NH, SiH(SiD), S₂, and SO. Radiative lifetime data from this laboratory are used to derive absolute transition probabilities for the prominent transitions. The derived absolute transition probabilities are compared with literature values.

INTRODUCTION

IN PREVIOUS reports,^(1,2) radiative lifetimes were measured for the SiH (and SiD) ($A^2\Delta-X^2\Pi$), NH ($d^1\Sigma-c^1\Pi$), ($c^1\Pi-a^1\Delta$), ($c^1\Pi-b^1\Sigma$), ($A^3\Pi-X^3\Sigma$), SO ($B^3\Sigma^- - X^3\Sigma^-$), and S₂ ($B^3\Sigma_u^- - X^3\Sigma_g^-$) upper states. At that time, RKR Franck-Condon factors for these transitions were not available in the literature. Accurate computations are difficult for molecules with a small reduced mass such as NH or SiH, and for cases where large equilibrium internuclear separation differences exist between states as in SO and S₂ for the B and X -states. In order to obtain absolute f -values from lifetime data, either experimental or computed vibrational transition probabilities are required. Experimental relative intensity data are missing for the transitions discussed here, and indeed would be difficult or impossible to obtain because of overlapping bands, predissociations, or other factors.

Using spectroscopic data, it is possible to compute vibrational transition probabilities. The RKR method has been shown to yield reliable relative vibrational transition probabilities when accurate spectroscopic data are available.⁽³⁾ We have employed computer routines due to ZARE,⁽⁴⁾ modified to be compatible with our 360/91 system and to perform calculations over a wider range of upper and lower state vibrational quanta as allowed by the larger capacity of the present computer system.

RESULTS

The calculated Franck-Condon factors, r -centroids, and $A_{v',v''}$ values for $v' = 0$ for the transitions studied (except for Table 10 where $q_{v',v''v',v''3}$ values are given) are listed in Tables 1-10. The radiative lifetimes from Refs. 1 and 2 are used to compute $A_{v',v''}$ values

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TABLE 1. FRANCK-CONDON FACTORS, r -CENTROIDS, AND SOME ABSOLUTE BAND TRANSITION PROBABILITIES FOR NH ($A^3\Pi-X^3\Sigma$)

v'	NH ($A^3\Pi-X^3\Sigma$)		
	0	1	2
$v'' = 0$	0.9998-0 1.078 0.220	0.204-3	0.202-4
1	0.198-3	0.997-0 1.148 0.220	0.258-2
2	0.284-4	0.250-2	0.987-0 1.218 0.220

Entries: Franck-Condon factor ($q_{v'v''}$),
 r -centroid ($\bar{r}_{v'v''}$ in Å),
 $A_{v'v''}$ ($\times 10^7 \text{ sec}^{-1}$).

from the equation:

$$A_{v'v''} = \frac{A_{v'} q_{v'v''} v_{v'v''}^3}{\sum_{v''} q_{v'v''} v_{v'v''}^3} \quad (1)$$

where $A_{v'}$, the total upper state transition probability, is the reciprocal of the measured upper state radiative lifetime, $q_{v'v''}$ is the calculated Franck-Condon factor, and $v_{v'v''}$ is the wavelength for the ($v'-v''$) transition in cm^{-1} . Only the $A_{v'0}$ transition probabilities have been calculated, that is, for absorption from the ground state. Other $A_{v'v''}$ values may be obtained from equation (1).

TABLE 2. FRANCK-CONDON FACTORS, r -CENTROIDS, AND SOME ABSOLUTE BAND TRANSITION PROBABILITIES FOR NH ($c^1\Pi-a^1\Delta$)

v'	NH ($c^1\Pi-a^1\Delta$)			
	0	1	2	3
$v'' = 0$	0.756-0 1.082 0.140	0.198-0 0.958 0.037	0.381-1 0.826 0.0074	0.700-2 0.672 0.001
1	0.199-0 1.265	0.296-0 1.111	0.304-0 1.023	0.133-0 0.931
2	0.390-1 1.367	0.312-0 1.300	0.190-1 1.038	0.185-0 1.076
3	0.500-2 1.513	0.150-0 1.387	0.209-0 1.354	0.420-1 1.375
4	0.100-2 1.495	0.360-1 1.536	0.267-0 1.427	0.280-1 1.471

Entries: $q_{v'v''}$,
 $\bar{r}_{v'v''}$ (Å),
 $A_{v'v''}$ ($\times 10^7 \text{ sec}^{-1}$).

TABLE 3. FRANCK-CONDON FACTORS, *r*-CENTROIDS, AND SOME ABSOLUTE BAND TRANSITION PROBABILITIES FOR NH (*c*¹Π-*b*¹Σ)

		NH (<i>c</i> ¹ Π- <i>b</i> ¹ Σ)			
<i>v</i> '		0	1	2	3
<i>v</i> " = 0		0.788-0	0.178-0	0.285-1	0.387-2
		1.087	0.957	0.810	0.612
		1.58	0.47	0.051	
1		0.178-0	0.377-0	0.293-0	0.105-0
		1.288	1.127	1.034	0.937
2		0.304-1	0.302-0	0.617-1	0.219-0
		1.375	1.333	1.126	1.107
3		0.238-2	0.119-0	0.262-0	0.172-1
		1.597	1.410	1.391	1.475

Entries: $q_{v'v''}$,
 $\bar{r}_{v'v''}$ (Å),
 $A_{v'v''}$ ($\times 10^5 \text{ sec}^{-1}$).

It is of particular interest to derive absolute oscillator strengths for the $\text{NH } A^3\Pi-X^3\Sigma$ transition. This line-like transition has essentially all intensity concentrated in the ($\Delta v = 0$) sequence as shown in Table 1. Using

$$f_{\text{abs.}}(v'-v'') = \frac{1.499 A_{v'v''}}{v_{v'v''}^2} \frac{(g')}{(g'')} \quad (2)$$

where $A_{v'v''} = A_{v'}$ in this particular case, $f_{\text{abs.}}(0-0) = 7.45 \pm 1.5 \times 10^{-3}$ is derived. This *f*-value must be considered as established to within 15 per cent by the close agreement of three radiative lifetime studies (see Ref. 1), and further, by the $f_{\text{abs.}}(0-0)$ value of $8.34 \pm 1.96 \times 10^{-3}$ obtained by HARRINGTON *et al.*⁽⁵⁾ from shock tube studies. We do find some difference with HARRINGTON *et al.*⁽⁵⁾ for $f_{\text{abs.}}(1-1)$ and $f_{\text{abs.}}(2-2)$ -values, in particular with the trend to higher values, respectively. Since $A_{v'}$ for $v' = 0, 1$, and 2 is constant within

 TABLE 4. FRANCK-CONDON FACTORS, *r*-CENTROIDS, AND SOME ABSOLUTE BAND TRANSITION PROBABILITIES FOR NH (*d*¹Σ-*c*¹Π)

		NH (<i>d</i> ¹ Σ- <i>c</i> ¹ Π)				
<i>v</i> '		0	1	2	3	4
<i>v</i> " = 0		0.995-0	0.339-3	0.404-2	0.241-3	0.144-3
		1.135		0.993		0.759
		5.54		0.021		
1		0.245-3	0.974-0	0.686-2	0.174-1	0.254-3
			1.191	2.884	1.210	0.600
2		0.367-2	0.111-1	0.862-0	0.616-1	0.578-1
		1.434	0.217	1.251	2.006	1.421
3		0.820-3	0.569-2	0.103-0	0.541-0	0.169-0
		1.087	1.817	0.949	1.300	1.849

Entries: $q_{v'v''}$,
 $\bar{r}_{v'v''}$ (Å),
 $A_{v'v''}$ ($\times 10^7 \text{ sec}^{-1}$).

TABLE 5. FRANCK-CONDON FACTORS, r -CENTROIDS, AND SOME ABSOLUTE BAND TRANSITION PROBABILITIES FOR SiH ($A^2\Delta-X^2\Pi$)

v'	SiH $A^2\Delta-X^2\Pi$			
	0	1	2	3
$v'' = 0$	0.994-0	0.529-2	0.828-3	0.293-3
	1.546	0.317		
	0.142	~0.001		
1	0.444-2	0.956-0	0.366-1	0.785-3
	3.054	1.597	0.992	
2	0.198-2	0.283-1	0.846-0	0.121-0
	1.601	2.489	1.650	1.285
3	0.174-5	0.985-2	0.868-1	0.686-0
		1.785	2.294	1.693

Entries: $q_{v'v''}$,
 $\bar{r}_{v'v''}$ (Å),
 $A_{v'v''} (\times 10^7 \text{ sec}^{-1})$.

experimental error, and $\bar{r}_{v'v''}$ increases slowly for the ($\Delta v = 0$) sequence, $f_{\text{abs.}}(v'-v'')$ will slowly decrease, primarily due to the wavelength increase for the higher members of the ($\Delta v = 0$) sequence. A similar result holds for the mean electronic transition moments $R_e(v')$.

For SiH $A^2\Delta-X^2\Pi$, an absorption f -value $f_{\text{abs.}}(0-0) = 3.7 \pm 0.7 \times 10^{-3}$ is derived from the lifetime data of Ref. 1 and the Franck-Condon factors of Table 5. This may be compared with an oscillator strength of $f_{\text{abs.}}(0-0) = 4.5 \times 10^{-3}$ derived by LAMBERT and MALLIA⁽⁶⁾ from measurements on SiH lines in the Fraunhofer spectrum. This may be considered excellent agreement in view of the theoretical considerations needed in converting such measurements into oscillator strengths. With the agreement of our independent

TABLE 6. FRANCK-CONDON FACTORS, r -CENTROIDS, AND SOME ABSOLUTE BAND TRANSITION PROBABILITIES FOR SiD ($A^2\Delta-X^2\Pi$)

v'	SiD $A^2\Delta-X^2\Pi$				
	0	1	2	3	4
$v'' = 0$	0.995-0	0.370-2	0.115-2	0.211-3	0.124-4
	1.538	0.276	2.069		
	0.146	~0.0006	~0.0004		
1	0.310-2	0.969-0	0.238-1	0.252-2	0.145-2
	3.057	1.571	0.908	2.342	1.552
2	0.194-2	0.182-1	0.890-0	0.759-1	0.289-2
	1.581	2.506	1.603	1.187	2.740
3	0.286-6	0.894-2	0.516-1	0.776-0	0.150-0
		1.702	2.314	1.628	1.315
4	0.211-4	0.219-4	0.263-1	0.941-1	0.688-0
			1.794	2.257	1.642

Entries: $q_{v'v''}$,
 $\bar{r}_{v'v''}$ (Å),
 $A_{v'v''} (\times 10^7 \text{ sec}^{-1})$.

TABLE 7. FRANCK-CONDON FACTORS, *r*-CENTROIDS, SOME ABSOLUTE BAND TRANSITION PROBABILITIES AND *f*-VALUES FOR S₂ (B³Σ_u⁻-X³Σ_g⁻)

S ₂ B ³ Σ _u ⁻ -X ³ Σ _g ⁻				
<i>v'</i>	0	1	2	3
<i>v''</i> = 0	0.115-4 2.020	0.988-4 2.010	0.442-3 2.001	0.138-2 1.992
1	0.159-3 2.036	0.114-2 0.026	0.426-2 2.016	0.110-1 2.007
2	0.106-2 2.052	0.622-2 2.042	0.187-1 2.032	0.381-1 2.023
<i>v'</i>	4	5	6	7
<i>v''</i> = 0	0.338-2 1.983	0.689-2 1.974	0.122-1 1.966 0.057 0.735	0.194-1 1.958 0.095 1.19
1	0.219-1 1.998	0.360-1 1.989	0.506-1 1.981	0.623-1 1.972
2	0.386-1 2.013	0.718-1 2.004	0.716-1 1.995	0.580-1 1.987
<i>v'</i>	8	9	10	11
<i>v''</i> = 0	0.280-1 1.950 0.142 1.75	0.374-1 1.942 0.195 2.44	0.468-1 1.935 0.252 2.96	0.552-1 1.927 0.306 3.60
1	0.682-1 1.964	0.669-1 1.956	0.588-1 1.948	0.462-1 1.941
2	0.369-1 1.978	0.164-1 1.969	0.326-2 1.959	0.174-3 1.973
<i>v'</i>	12	13	14	15
<i>v''</i> = 0	0.621-1 1.920 0.357 4.02	0.668-1 1.913 0.393 4.33	0.693-1 1.906 0.425 4.58	0.694-1 1.900 0.429 4.50
1	0.318-1 1.933	0.182-1 1.926	0.783-2 1.919	0.169-2 1.910
2	0.579-2 1.951	0.161-1 1.942	0.265-1 1.935	0.334-1 1.927

Table 7 continued on next page

0.013

TABLE 7—(continued)

v'	16	17	18	19
$v'' = 0$	0.675-1	0.638-1	0.591-1	0.335-1
	1.893	1.887	1.880	1.874
	0.432	0.420	0.411	0.233
	4.44	4.23	4.13	2.31
1	0.215-4	0.222-2	0.723-2	0.138-1
	1.930	1.902	1.895	1.888
2	0.352-4	0.302-1	0.253-1	0.172-1
	1.970	1.914	1.907	1.901
v'	20	21	22	23
$v'' = 0$	0.475-1	0.414-1	0.354-1	0.300-1
	1.868	1.862	1.856	1.850
	0.338	0.302	0.264	0.228
	3.27	2.88	2.48	2.08
1	0.208-1	0.273-1	0.326-1	0.362-1
	1.882	1.876	1.870	1.864
2	0.945-1	0.365-2	0.521-3	0.187-3
	1.895	1.888	1.882	1.878
v'	24	25	26	
$v'' = 0$	0.250-1	0.207-1	0.169-1	
	1.845	1.839	1.834	
	0.191	0.162	0.135	
	1.69	1.41	1.21	
1	0.382-1	0.389-1	0.384-1	
	1.858	1.852	1.847	
2	0.226-2	0.612-2	0.111-1	
	1.871	1.866	1.860	

Entries: $q_{v'v''}$. $\bar{r}_{v'v''}$. $A_{v'v''} (\times 10^7 \text{ sec}^{-1})$. $f(v'v'') (\times 10^{-3})$.

oscillator strength measurements, the reverse process can now be applied to derive other parameters of the model solar atmosphere.

Although neither NH nor SiH has yet been detected in the interstellar medium, this should be possible due to the high abundance of the constituent elements and the concentration of nearly all the intensity in the (0-0) transition in absorption in both cases.

The previously published Franck-Condon factors for the $B^3\Sigma^- - X^3\Sigma^-$ transition of SO,⁽⁶⁾ and analogous $B^3\Sigma_u^- - X^3\Sigma_g^-$ transition of S₂,⁽⁷⁾ were based on Morse potentials. The present RKR potentials are believed to be more accurate at high vibrational quantum numbers. Our knowledge of rotational constants limits the validity of the present calculation to states with $v \leq 26$. For both SO and S₂, this is beyond the maximum of the transition probability for the $v'' = 0$ progression, which occurred at $v' = 16$ for S₂ in absorption and at $v' = 20, 21$ for SO in absorption. Comparison with published spectra

TABLE 8. FURTHER FRANCK-CONDON FACTORS FOR S₂
(B³Σ_g⁻-X³Σ_g⁻)

v'	S ₂ B ³ Σ _g ⁻ -X ³ Σ _g ⁻		
	0	1	2
v'' = 0	0.115-4	0.988-4	0.442-3
1	0.159-3	0.114-2	0.426-2
2	0.106-2	0.622-2	0.187-1
3	0.451-2	0.211-1	0.488-1
4	0.140-1	0.494-1	0.823-1
5	0.332-1	0.841-1	0.893-1
6	0.635-1	0.105-0	0.555-1
7	0.100-0	0.933-1	0.109-1
8	0.133-0	0.526-1	0.329-2
9	0.151-0	0.115-1	0.387-1
10	0.147-0	0.129-2	0.713-1
11	0.126-0	0.293-1	0.611-1
12	0.341-1	0.750-1	0.218-1
13	0.623-1	0.109-0	0.100-4
14	0.366-1	0.116-0	0.206-1
15	0.192-1	0.980-1	0.658-1
16	0.896-2	0.688-1	0.101-0
17	0.376-2	0.412-1	0.106-0
18	0.141-2	0.213-1	0.865-1
19	0.480-3	0.965-2	0.573-1
20	0.145-3	0.384-2	0.319-1
21	0.395-4	0.135-2	0.151-1
22	0.961-5	0.416-3	0.620-3
23	0.209-5	0.114-3	0.220-2
24	0.404-6	0.275-4	0.679-3
25	0.693-7	0.585-5	0.183-3
26	0.105-7	0.109-5	0.428-4

TABLE 9. FRANCK-CONDON FACTORS, *r*-CENTROIDS, AND *qv*³-VALUES FOR THE SO (B³Σ⁻-X³Σ⁻) TRANSITION

v'	SO B ³ Σ ⁻ -X ³ Σ ⁻			
	0	1	2	3
v'' = 0	0.337-4	0.251-3	0.976-3	0.264-2
	1.620	1.612	1.605	1.598
1	0.120-3	0.807-3	0.287-2	0.713-2
	1.609	1.620	1.612	1.603
2	0.869-3	0.487-2	0.142-1	0.287-1
	1.645	1.636	1.627	1.618
v'	4	5	6	7
v'' = 0	0.556-2	0.978-2	0.149-1	0.203-1
	1.591	1.584	1.577	1.569
		0.728	1.160	1.790
1	0.140-1	0.229-1	0.327-1	0.419-1
	1.595	1.588	1.580	1.573
2	0.450-1	0.581-1	0.638-1	0.608-1
	1.610	1.602	1.594	1.586

Table 9 continued on next page

TABLE 9—(continued)

v'	8	9	10	11
$v'' = 0$	0.253-1	0.293-1	0.322-1	0.338-1
	1.562	1.554	1.547	1.539
	2.13	2.57	2.92	3.17
1	0.488-1	0.527-1	0.531-1	0.504-1
	1.566	1.560	1.553	1.547
2	0.505-1	0.364-1	0.222-1	0.107-1
	1.578	1.571	1.563	1.555
v'	12	13	14	15
$v'' = 0$	0.345-1	0.346-1	0.343-1	0.339-1
	1.532	1.524	1.518	1.512
	3.35	3.46	3.51	3.62
1	0.452-1	0.386-1	0.313-1	0.241-1
	1.541	1.535	1.530	1.524
2	0.326-2	0.184-3	0.652-3	0.348-2
	1.545	1.562	1.565	1.547
v'	16	17	18	19
$v'' = 0$	0.334-1	0.329-1	0.324-1	0.319-1
	1.507	1.503	1.500	1.497
	3.68	3.73	3.76	3.83
1	0.176-1	0.121-1	0.775-1	0.448-2
	1.519	1.513	1.507	1.501
2	0.743-2	0.115-1	0.150-1	0.175-1
	1.539	1.532	1.527	1.522
v'	20	21	22	23
$v'' = 0$	0.313-1	0.306-1	0.297-1	0.285-1
	1.495	1.493	1.491	1.489
	3.84	3.84	3.83	3.75
1	0.223-2	0.849-3	0.162-3	0.405-5
	1.494	1.482	1.454	1.778
2	0.190-1	0.194-1	0.189-1	0.178-1
	1.517	1.513	1.508	1.504
v'	24	25		
$v'' = 0$	0.272-1	0.261-1		
	1.487	1.485		
1	0.228-3	0.717-3		
	1.529	1.510		
2	0.163-1	0.147-1		
	1.501	1.497		

Entries: $q_{v'v''}$,
 $\bar{r}_{v'v''}$ (Å),
 $q_{v'v''}^3 v_{v'v''}^3 (\times 10^{12} \text{ cm}^{-3})$.

TABLE 10. FURTHER FRANCK-CONDON FACTORS FOR
 SO ($B^3\Sigma^- - X^3\Sigma^-$)

v''	SO $B^3 - X^3$		
	0	1	2
0	0.337-4	0.251-3	0.976-3
1	0.120-3	0.807-3	0.287-2
2	0.869-3	0.487-2	0.142-1
3	0.402-2	0.180-1	0.412-1
4	0.134-1	0.456-1	0.763-1
5	0.347-1	0.835-1	0.901-1
6	0.646-1	0.105-0	0.606-1
7	0.104-0	0.956-1	0.137-1
8	0.140-1	0.533-1	0.257-2
9	0.158-0	0.103-1	0.395-1
10	0.152-0	0.263-2	0.744-1
11	0.127-0	0.375-1	0.611-1
12	0.911-1	0.887-1	0.180-1
13	0.571-1	0.122-0	0.638-3
14	0.313-1	0.121-0	0.326-1
15	0.151-1	0.952-1	0.849-1
16	0.637-2	0.613-1	0.116-0
17	0.237-2	0.331-1	0.110-0
18	0.775-3	0.152-1	0.797-1
19	0.223-3	0.596-3	0.465-1
20	0.562-4	0.148-3	0.224-1
21			0.905-2
22			0.309-2

of S₂ in absorption⁽⁸⁾ shows that our maximum value of $q_{v',v''}$ is somewhat above the v' -value of the observed relative intensity maximum. This may be ascribable to the pre-dissociation which begins after $v' = 9$ and reduces the apparent intensity because of the competition between relaxation by molecular dissociation and radiation.

Both the RKR and Morse curve $q_{v',v''}$ values agree fairly well with each other particularly for the more probable transitions and have maxima near the positions of the Condon parabolae.^(7,8,10) Exceptions are found for the higher vibrational quantum numbers of both the upper and lower states, even when they lie on the Condon parabola, as for SO $B^3\Sigma^-(v' = 10) - X^3\Sigma^-(v'' = 0)$ where the RKR derived $q_{v',v''}$ is nine times larger than that derived from the Morse curves. This renders the transition more probable, in agreement with the observed position of the Condon parabola.⁽¹⁰⁾

Using equation (2), the $f_{v',v''}$ -values may be derived for individual v', v'' transitions. These are listed in Table 7. A $\Sigma f_{\text{abs.}}$ -value given by

$$\Sigma f_{\text{abs.}} \cong \sum_{v''=6}^{26} f(v' - 0)$$

is equal to 0.0617 for the S₂ $B^3\Sigma\bar{u} - X^3\Sigma\bar{g}$ transition.

Using the computed Franck-Condon factors, one may similarly derive an emission f -value, Σf_{emis} , given by

$$\Sigma f_{\text{emis}} \cong \sum_{v''=4}^{16} f(v' - 0) \quad (4)$$

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which is equal to 0.14, in excellent agreement with the f -value of 0.16 given by BOTT and JACOBS.⁽¹¹⁾ The agreement would be even closer if their f -value were recalculated with our Franck-Condon factors.

This difference between the calculated $\Sigma f_{\text{abs.}}$ and Σf_{emis} illustrates the ambiguity in publishing such f -numbers at all unless the derivation is very clearly stated. It is also of value to make the same f -value calculation using the simple formula

$$f = 1.499 A_{\nu'} (g'/g'') \bar{\lambda}^2, \quad (5)$$

where $\bar{\lambda}$ is now a mean transition wavelength (Å). This approximation is often used without regard to what accuracy may be obtained. As a concrete example, we find here that, using $\bar{\lambda} = 4200$ Å for emission and 2600 Å for absorption, f -values of 0.14 and 0.06 respectively are found. Since this transition is spread over a wide wavelength due to the large change in the internuclear equilibrium separation in the two states, a more pathological example would be difficult to describe. In situations (for example, polyatomics) where detailed branching ratios are unavailable, lifetime data can be converted with some confidence into f -values using the above equation, and within the restrictions described. The result is unlikely to differ by more than 20–30 per cent from a value derived from the more rigorous equation (2) if $\bar{\lambda}$ is chosen near the intensity maximum for the transition. In all cases, $f(v'-v'')$ values are to be preferred.

In the case of the SO $B^3\Sigma^- - X^3\Sigma^-$ transition, the Franck-Condon factors ($q_{v'v''}$) and the $q_{v'v''}^3$ values are still quite large, though decreasing in size, at $v' = 26$ for $v'' = 0$. The available spectroscopic data do not allow a calculation of the upper state potential beyond $v' = 26$. As a result, $A_{\nu'v''}$ -values cannot be given for absorption from the ground state for SO $B^3\Sigma^- - X^3\Sigma^-$, since the remaining Franck-Condon factors are significant.

Again, as for S_2 , the SO molecule undergoes an allowed predissociation which breaks off emission even for $v' = 1$ (at $K' = 66$). The slight decrease in measured lifetimes as a function of v' found earlier⁽²⁾ may be a result of this pre-dissociation in the levels observed ($v' = 0, 1, 2$).

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RKR FRANCK-CONDON FACTORS FOR BLUE AND ULTRAVIOLET TRANSITIONS OF SOME METAL OXIDES*

H. S. LISZT and WM. HAYDEN SMITH

Princeton University Observatory, Princeton, New Jersey 08540

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Abstract—RKR Franck-Condon factors and r -centroids are presented for eleven blue and ultraviolet systems in the oxides of B, Be, Ca, Sr, and Zr.

RKR FRANCK-CONDON factors for the major blue and ultraviolet systems in the oxides of B, Be, Ca, Sr, and Zr have been calculated using the program of ZARE.⁽¹⁾ This program has been discussed in the literature⁽²⁾ and will not be treated at length here. It was modified to be compatible with the 360/91 system at Princeton and enlarged to compute up to thirty levels in the upper and lower states.

The vibrational transition probabilities will be of use when lifetimes of these states are measured (work of this kind is now in progress at Princeton University Observatory). It is our desire that they be available in the literature in order that we may prevent duplication of our effort in their calculation. The computer program used is, we believe, in fairly wide circulation.

We have restricted our attention to transitions in the range 5000–2000 Å. The Franck-Condon factors in the following table cover fairly well the absorption and emission spectra of these systems. We have refrained from publishing vibrational transition probabilities smaller than 10^{-4} . In general, the relative smoothness of the calculated r -centroids provides a check on the accuracy of the smaller Franck-Condon factors. Irregularity in the behavior of the r -centroids does not, however, imply the converse, an error in the other quantity.

The RKR curves used in this work have been computed from molecular constants and these are reproduced in Table 1. This procedure ignores any local perturbations, of course. In any case, the accuracy with which rotational constants, and in particular γ_e are known for most of the states involved limits the accuracy of the potential curves at very high quantum number ($v \geq 20$). The error, δr , in the turning points calculated from constants is approximately (equally valid for both turning points of a level)

$$\delta r \sim -\delta B_e + \delta \alpha_e v - \delta \gamma_e v^2$$

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TABLE 1.

State	T_e	w_e	$w_e x_e$	B_e	α_e	r_e	References
Be⁹O¹⁶							
			$\mu_A = 5.76612$				
C (¹ Σ)	39120.1	1081.5	9.1	1.308	0.010	1.495	(4)
B (¹ Σ)	21253.94	1370.817	7.7455	1.5758	0.0154	1.3622	(4)
A (¹ Π)	9405.61	1144.238	7.4145	1.3661	0.01628	1.4630	(4)
X (¹ Σ)	0	1487.323	11.8297	1.6510	0.0190	1.3308	(4)
B¹¹O¹⁶							
			$\mu_A = 6.52305$				
B (² Σ)	43175.40	1280.30	10.66	1.5171	0.0210	1.3053	(4), (5)
A (² Π)	23836.40	1260.70	11.157	1.4132	0.0196	1.3524	(4), (5)
X (² Σ)	0	1885.44	11.769	1.7803	0.01648	1.2049	(4), (5)
Ca⁴⁰O¹⁶							
			$\mu_A = 11.4625$				
C (¹ Σ)	28770.0	560.9	4.0	0.3731	0.0032	1.989	(4), (7)
B (¹ Π)	25910.0	578.5	4.1	0.388	0.005	1.950	(4), (7)
X (¹ Σ)	0	650	6.6	0.4444	0.0033	1.864	(4), (6), (7)
SrO¹⁶							
			$\mu_A = 13.5302$				
C (¹ Σ)	28632.7	480.2	2.6	0.2742	0.0021	2.132	(4), (8)
B (¹ Π)	24702.8	519.1	3.50	0.2936	0.0013	2.060	(4), (8)
X (¹ Σ)	0	653.5	4.0	0.3378	0.0020	1.921	(4), (8)
Zr⁹⁰O¹⁶							
			$\mu_A = 13.5836$				
B (¹ Σ)	27217.9 + a	843.2	3.04	0.3951	0.0019	1.772	(4), (9)
A (¹ Σ)	a	977.6	3.82	0.4241	0.0023	1.711	(4), (9)
C (³ Π)	21698.1	820.6	3.31	0.4028	0.0023	1.755	(4), (10)
X (³ Π)	0	936.6	3.45	0.4155	0.0021	1.728	(4), (10)

TABLE 2. FRANCK-CONDON FACTORS AND r -CENTROIDS FOR BeO B-X

$v'' \backslash v'$	0	1	2	3	4	5	6	7
0	.8903 1.352	.1014 1.224	.7897-2 1.108	.4555-3 .967				
1	.1056 1.491	.7018 1.364	.1703 1.231	.2054-1 1.117	.1640-2 .982			
2	.4100-2 1.647	.1862 1.505	.5556 1.377	.2147 1.239	.3554-1 1.126	.3668-2 .996	.2444-3 .801	
3		.1062-1 1.666	.2478 1.519	.4426 1.391	.2407 1.245	.5114-1 1.134	.6529-2 1.008	.5382-3 .828
4			.1830-1 1.686	.2952 1.534	.3558 1.405	.2532 1.251	.6611-1 1.142	.1012-1 1.019
5			.1205-3 2.276	.2625-1 1.707	.3323 1.549	.2895 1.421	.2560 1.256	.7968-1 1.149
6				.1418-3 2.455	.3377-1 1.730	.3618 1.564	.2393 1.439	.2520 1.260
7					.1257-3 2.755	.4037-1 1.754	.3860 1.579	.2016 1.459
8							.4566-1 1.780	.4065 1.594
9								.4938-1 1.808

TABLE 3. FRANCK-CONDON FACTORS AND r -CENTROIDS FOR BeO C-X

$v'' \backslash v'$	0	1	2	3	4	5	6	7	8
0	.5784-1 1.411	.1508 1.586	.2130 1.382	.2061 1.339	.1645 1.515	.1044 1.292	.5817-1 1.268	.2859-1 1.245	.1163-1 1.216
1	.1879 1.446	.1962 1.419	.6360-1 1.595	(.2164-4) (1.334)	.4657-1 1.346	.1111 1.526	.1347 1.301	.1146 1.278	.7516-1 1.255
2	.2806 1.481	.4432-1 1.449	.2854-1 1.443	.1104 1.406	.7103-1 1.383	.5185-2 1.571	.1726-1 1.526	.7485-1 1.306	.1106 1.286
3	.2505 1.517	.1968-1 1.501	.1310 1.443	.2274-1 1.431	.2060-1 1.420	.6108-1 1.595	.5562-1 1.572	.4815-2 1.572	.1556-1 1.304
4	.1465 1.556	.1582 1.530	.3446-1 1.490	.4925-1 1.478	.8522-1 1.446	.5879-2 1.409	.2683-1 1.406	.6852-1 1.382	.5772-1 1.565
5	.5775-1 1.599	.2153 1.568	.2570-1 1.551	.1039 1.508	(.2920-4) (1.823)	.6827-1 1.459	.4761-1 1.430		.3600-1 1.595
6	.1565-1 1.648	.1427 1.810	.1642 1.581	.4930-2 1.507	.9033-1 1.520	.2758-1 1.480	.1976-1 1.476	.6555-1 1.442	.1714-1 1.612
7	.3012-2 1.701	.5626-1 1.857	.1927 1.625	.7294-1 1.598	.5131-1 1.546	.3649-1 1.538	.6508-1 1.497		.4571-1 1.455
8	.4585-5 1.750	.1398-1 1.712	.1062 1.670	.1937 1.638	.1248-1 1.851	.9051-1 1.562	.2675-2 1.592	.6969-1 1.510	.1456-1 1.470
9		.2213-2 1.775	.3347-1 1.725	.1372 1.683	.1500 1.830	.1205-2 1.487	.9173-1 1.577	.5579-2 1.504	.4657-1 1.528
10		.2197-5 1.651	.6402-2 1.787	.8287-1 1.738	.1859 1.698	.9556-1 1.667	.2348-1 1.592	.6409-1 1.592	.2902-1 1.540
11			.7118-3 1.867	.1398-1 1.804	.9495-1 1.751	.1983 1.710	.4465-1 1.690	.5455-1 1.615	.5525-1 1.615
12				.1758-2 1.885	.2489-1 1.818	.1288 1.766	.1876 1.725	.1535-1 1.728	.7915-1 1.651
13				.1117-3 2.001	.3422-2 1.904	.5913-1 1.834	.1591 1.780	.1645 1.741	.5261-5 1.982
14					.2258-3 2.033	.5990-2 1.921	.5518-1 1.850	.1817 1.796	.1555 1.758
15						.4141-3 2.054	.9330-2 1.941	.7402-1 1.866	.2006 1.611
16							.6843-3 2.075	.1553-1 1.960	.9572-1 1.884
17								.9797-3 2.108	.1817-1 1.981
18									.1576-2 2.152
19									
20									
21									
22									

where the coefficients of the various terms vary between 0.7 and 1.5 for all oxides examined here and in S_2 and SO .¹⁰ The contribution from δB_e is a change over and above the shift of the entire curve as determined from the reciprocal relationship between B_e and r_e^2 . These errors should not be serious here but neglect of a $\gamma_e \approx 10^{-6}$ can invalidate calculations of overlap integrals between states of quantum number $v \approx 20$. Errors in the vibrational constants are much less serious. The Morse approximation may or may not be a valid representation of these systems depending on the value D_e assigned to the quantity $w_e^2/4w_e x_e$. Thus for the X state of ZrO where D_e is almost $65,000 \text{ cm}^{-1}$ and the anharmonicity is quite

TABLE 3—continued

$v'' \backslash v'$	9	10	11	12	13	14	15
0	.4369-2 1.184	.1347-2 1.145	.3233-3 1.090				
1	.4137-1 1.227	.1899-1 1.198	.7107-2 1.163	.2131-2 1.115	.4332-3 1.033		
2	.1070 1.263	.7659-1 1.238	.4340-1 1.210	.2031-1 1.179	.7422-2 1.138	.1956-2 1.072	.2870-3 .920
3	.6494-1 1.292	.1010 1.271	.9813-1 1.248	.7152-1 1.222	.4000-1 1.192	.1746-1 1.154	.5763-2 1.101
4	.1168-2 1.416	.1841-1 1.286	.6636-1 1.273	.9751-1 1.256	.9111-1 1.232	.6243-1 1.203	.3311-1 1.170
5	.3629-1 1.375	.2119-1 1.366	.2466-3 1.052	.2953-1 1.272	.7492-1 1.260	.9470-1 1.240	.6203-1 1.213
6	.5724-2 1.416	.4283-1 1.386	.4007-1 1.371	.7109-2 1.392	.5548-2 1.230	.4466-1 1.259	.8469-1 1.246
7	.4342-1 1.426	.1613-2 1.371	.1814-1 1.403	.4233-1 1.382	.2238-1 1.380	.1620-3 1.874	.1922-1 1.243
8	.1619-1 1.471	.5078-1 1.438	.1697-1 1.406	.2011-2 1.448	.2872-1 1.397	.3168-1 1.387	.6815-2 1.431
9	.3901-1 1.488	.7417-3 1.532	.3873-1 1.450	.3449-1 1.420	.1721-2 1.345	.1218-1 1.422	.3067-1 1.401
10	.1849-1 1.546	.5206-1 1.502	.4134-2 1.455	.1936-1 1.463	.4133-1 1.432	.1238-1 1.392	.1669-2 1.502
11	.5183-1 1.557	.2218-2 1.605	.4860-1 1.516	.1815-1 1.480	.4689-2 1.482	.3655-1 1.443	.2545-1 1.409
12	.9342-2 1.647	.6251-1 1.572	.1428-2 1.457	.3423-1 1.532	.3185-1 1.495		.2482-1 1.452
13	.8804-1 1.647	.2014-3 1.944	.5920-1 1.587	.1160-1 1.526	.1775-1 1.552	.3690-1 1.510	.4170-2 1.477
14	.3376-2 1.549	.8447-1 1.662	.3750-2 1.546	.4646-1 1.602	.2541-1 1.548	.5411-2 1.589	.3775-1 1.525
15	.1023 1.777	.1345-1 1.654	.7121-1 1.679	.1485-1 1.598	.3086-1 1.619	.3724-1 1.564	.2126-3 1.829
16	.2096 1.827	.7444-1 1.799	.3226-1 1.684	.5370-1 1.697	.2834-1 1.621	.1630-1 1.642	.4370-1 1.376
17	.1123 1.901	.2145 1.843	.4989-1 1.825	.4823-1 1.705	.3711-1 1.718	.4073-1 1.640	.6193-2 1.677
18	.2314-1 2.003	.1302 1.919	.2137 1.862	.3067-1 1.858	.6210-1 1.723	.2230-1 1.746	.4914-1 1.636
19	.1733-2 2.164	.8833-1 2.024	.1481 1.938	.2113 1.961	.1796-1 1.900	.7299-1 1.740	.1130-1 1.784
20		.2096-2 2.201	.3373-1 2.048	.1631 1.957	.2073 1.900	.8843-2 1.967	.7930-1 1.736
21			.2437-2 2.234	.3840-1 2.073	.1774 1.977	.2026 1.920	.3336-2 2.084
22				.2663-2 2.276	.4270-1 2.096	.1911 1.998	.1963 1.941

small it is an excellent approximation to all but the uppermost levels. For the CaO X-state where $D_e \approx 17,000$ it fails completely.

In summary then, the RKR Franck-Condon factors presented here are probably quite accurate for the lower levels ($v', v'' \leq 10$) and generally less accurate but still quite reliable near the Condon parabola for the rest of the entries in the table (the emission spectra).

6 027

TABLE 4. FRANCK-CONDON FACTORS AND r -CENTROIDS FOR BeO C-A

$v'' \backslash v'$	0	1	2	3	4	5	6	7	8
0	.9158 1.485	.7847-1 1.315	.5530-2 1.189	.1749-3 .949					
1	.8253-1 1.663	.7758 1.498	.1303 1.316	.1092-1 1.163	.3967-3 .858				
2	.1648-2 1.924	.1407 1.687	.6794 1.511	.1597 1.316	.1780-1 1.162	.6493-3 .821			
3		.5078-2 1.901	.1771 1.713	.6120 1.525	.1830 1.316	.2181-1 1.147	.6841-3 .689		.1793-3 1.410
4			.7614-2 1.932	.2059 1.739	.5683 1.538	.1913 1.313	.2523-1 1.135	.7466-3 .608	.2297-3 1.832
5				.1123-1 1.938	.2167 1.772	.5432 1.552	.1996 1.312	.2713-1 1.120	.5044-3 .327
6				.1336-3 .754	.1351-1 1.954	.2266 1.804	.5293 1.564	.2014 1.308	.2619-1 1.093
7					.2438-3 .848	.1570-1 1.966	.2260 1.842	.5299 1.577	.1987 1.303
8						.5159-3 .990	.1795-1 1.966	.2200 1.884	.5368 1.591
9							.8568-3 1.051	.1878-1 1.971	.2141 1.929
10							.1468-3 .971	.1337-2 1.110	.2028-1 1.965
11								.3153-3 1.045	.2061-2 1.155
12								.1051-3 1.050	.5848-3 1.086
13									.1971-3 1.051
14									
15									
16									
17									
18									
19									

U 023

TABLE 4—continued

$v'' \backslash v'$	9	10	11	12	13	14	15
0							
1							
2							
3							
4	.3886-3 1.391	.1713-3 1.251					
5	.5362-3 1.714	.6670-3 1.372	.2665-3 1.224				
6	.2809-3	.9354-3 1.642	.1041-2 1.349	.4357-3 1.211			
7	.2529-1 1.068	(.7209-4)	.1661-2 1.574	.1650-2 1.334	.6368-3 1.199	.1177-3 1.024	
6	.1967 1.297	.2210-1 1.025	(.1897-4) (7.904)	.2708-2 1.525	.2288-2 1.314	.6259-3 1.174	.1451-3 .980
9	.5511 1.603	.1885 1.288	.1879-1 .964	.3131-3 3.022	.3967-2 1.484	.3068-2 1.295	.1094-2 1.159
10	.1997 1.963	.5734 1.617	.1787 1.279	.1381-1 .8822	.1152-2 2.233	.5762-2 1.448	.4079-2 1.261
11	.2134-1 1.950	.1656 2.041	.5961 1.631	.1680 1.267	.6910-2 .729	.2632-2 1.916	.7939-2 1.420
12	.2673-2 1.177	.2165-1 1.935	.1715 2.104	.5230 1.645	.1521 1.250	.4635-2 4.362	.5273-2 1.762
13	.9726-3 1.111	.3662-2 1.198	.2273-1 1.910	.1524 2.161	.6519 1.662	.1355 1.232	.1636-2
14		.1593-2 1.142	.5098-2 1.209	.2352-1 1.676	.1361 2.262	.6760 1.660	.1162 1.206
15		.6695-3 1.091	.2421-2 1.161	.6373-2 1.209	.2376-1 1.845	.1215 2.347	.6986 1.696
16		.3420-3 1.103	.1084-2 1.100	.3462-2 1.173	.7630-2 1.207	.2462-1 1.812	.1054 2.446
17		.1865-3 1.112	.5699-3 1.101	.1700-2 1.112	.4752-2 1.167	.8979-2 1.201	.2543-1 1.776
16		.1029-3 1.107	.3256-3 1.108	.9528-3 1.107	.2547-2 1.125	.6233-2 1.196	.1016-1 1.166
19			.1933-3 1.110	.5752-3 1.114	.1492-2 1.114	.3565-2 1.134	.7766-2 1.201

TABLE 5. FRANCK-CONDON FACTORS AND r -CENTROIDS FOR BO A-X

v' v''	0	1	2	3	4	5	6	7	8
0	.3631-1 1.276	.1012 1.258	.1546 1.241	.1724 1.225	.1576 1.205	.1258 1.194	.9108-1 1.180	.6149-1 1.166	.3945-1 1.153
1	.1329 1.302	.1867 1.284	.1109 1.265	.2429-1 1.246	.5717-3 1.260	.2688-1 1.222	.6327-1 1.206	.8501-1 1.191	.8773-1 1.177
2	.2283 1.330	.9851-1 1.310		.5376-1 1.277	.9437-1 1.259	.6463-1 1.241	.1812-1 1.223		.1200-1 1.206
3	.2452 1.359	.1625-2 1.325	.8506-1 1.321	.8632-1 1.301	.9671-2 1.279	.1284-1 1.273	.5681-1 1.254	.6643-1 1.237	.3966-1 1.220
4	.1851 1.387	.5508-1 1.369	.1037 1.347	.5472-3 1.302	.5359-1 1.313	.7227-1 1.293	.1950-1 1.273	.1358-2 1.281	.2946-1 1.250
5	.1045 1.416	.1580 1.397	.1284-1 1.371	.6738-1 1.358	.6348-1 1.337	.1155-3 1.259	.3872-1 1.306	.6108-1 1.287	.2601-1 1.268
6	.4584-1 1.446	.1793 1.426	.2686-1 1.409	.9022-1 1.394	.4379-3 1.399	.6559-1 1.349	.4333-1 1.328	(.2855-4) 1.184	.2893-1 1.300
7	.1602-1 1.477	.1255 1.456	.1260 1.436	.1029-1 1.407	.7292-1 1.395	.3743-1 1.372	.8185-2 1.364	.5878-1 1.340	.3228-1 1.320
8	.4530-2 1.509	.6215-1 1.486	.1649 1.465	.2827-1 1.448	.7272-1 1.422	.8802-2 1.411	.7034-1 1.384	.1210-1 1.360	.1556-1 1.354
9	.1048-2 1.542	.2322-1 1.518	.1223 1.496	.1231 1.475	.2654-2 1.436	.8259-1 1.433	.1184-1 1.406	.3361-1 1.397	.5160-1 1.375
10	.1998-3 1.576	.6774-2 1.551	.6168-1 1.527	.1550 1.505	.4314-1 1.487	.4890-1 1.459	.3051-1 1.445	.5576-1 1.420	.2217-3 1.460
11		.1575-2 1.585	.2290-1 1.560	.1104 1.537	.1321 1.515	.5196-3 1.534	.8309-1 1.471		.5818-1 1.432
12		.2954-3 1.621	.6519-2 1.594	.5313-1 1.569	.1450 1.546	.6856-1 1.526	.2190-1 1.495	.5903-1 1.482	.2563-1 1.455
13			.1456-2 1.630	.1867-1 1.603	.9350-1 1.579	.1422 1.556	.1254-1 1.542	.6606-1 1.509	.1307-1 1.498
14			.2588-3 1.667	.4988-2 1.639	.4116-1 1.613	.1303 1.588	.9974-1 1.567	.2539-2 1.520	.7749-1 1.520
15				.1035-2 1.676	.1324-1 1.648	.7355-1 1.622	.1454 1.598	.4196-1 1.579	.3477-1 1.546
16				.1689-3 1.716	.3219-2 1.686	.2877-1 1.658	.1094 1.632	.1279 1.609	.4114-2 1.603
17					.6028-3 1.725	.8238-2 1.695	.5289-1 1.667	.1367 1.642	.8335-1 1.620
18						.1774-2 1.735	.1796-1 1.705	.8376-1 1.677	.1432 1.652
19						.2913-3 1.777	.4464-2 1.744	.3410-1 1.415	.1154 1.688
20							.8286-3 1.787	.9826-2 1.754	.5717-1 1.725
21								.2066-2 1.797	.1924-1 1.765
22								.3213-3 1.843	.4599-2 1.808

030

TABLE 5—continued

v''	9	10	11	12	13
0	.2440-1 1.141	.1470-1 1.129	.8712-2 1.119	.5109-2 1.108	.2981-2 1.099
1	.7743-1 1.164	.6170-1 1.152	.4581-1 1.140	.3237-1 1.129	.2210-1 1.118
2	.3536-1 1.190	.5415-1 1.176	.6228-1 1.163	.6075-1 1.151	.5327-1 1.140
3	.104-1 1.201		.7756-2 1.194	.2336-1 1.177	.3748-1 1.163
4	.5296-1 1.233	.4748-1 1.217	.2522 1.201	.6193-2 1.182	
5	.3333-3 1.216	.1238-1 1.248	.3605 1.230	.4445-2 1.215	.3439-1 1.201
6	.5190-1 1.281	.3029-1 1.264	.3754-2 1.240	.3158-2 1.252	.2054-1 1.230
7	(.4907-4) 1.207	.2117-1 1.295	.4370-1 1.277	.3284-1 1.260	.9231-2 1.241
8	.5120-1 1.333	.2632-1 1.314	.2224-3 1.254	.1448-1 1.291	.3575-1 1.274
9	.2801-2 1.345	.1916-1 1.347	.4447-1 1.327	.2348-1 1.308	.7896-3 1.272
10	.4496-1 1.387	.3465-1 1.366	.3265-3 1.311	.1955-1 1.341	.3889-1 1.322
11	.2128-1 1.408	.8109-2 1.404	.4482-1 1.379	.2344-1 1.359	
12	.1900-1 1.447	.5053-1 1.422	.4471-2 1.393	.1661-1 1.394	.4017-1 1.373
13	.5843-1 1.469	.2989-3 1.395	.3808-1 1.435	.3279-1 1.413	.1294-3 1.324
14	.1970-2 1.475	.4954-1 1.481	.2377-1 1.456	.6521-2 1.454	.4170-1 1.426
15	.4556-1 1.533	.3101-1 1.504	.1427-1 1.497	.4784-1 1.470	.3784-2 1.437
16	.7021-1 1.559	.7840-2 1.552	.5964-1 1.518	.4816-3 1.448	.3662-1 1.483
17	.6215-2 1.577	.7301-1 1.571	.3000-2 1.526	.4693-1 1.531	.2157-1 1.503
18	.3321-1 1.633	.3824-1 1.598	.4228-1 1.584	.2991-1 1.554	.1535-1 1.547
19	.1230 1.663	.2925-2 1.664	.6931-1 1.611	.8487-2 1.605	.5443-1 1.568
20	.1386 1.698	.8207-1 1.675	.5612-2 1.627	.7307-1 1.624	.1475-2 1.563
21	.8545-1 1.736	.1444 1.709	.3670-1 1.690	.3359-1 1.650	.4779-1 1.638
22	.3390-1 1.776	.1144 1.747	.1285 1.721	.6002-2 1.715	.6415-1 1.665

TABLE 7. FRANK-CONDON FACTORS AND f -CENTROIDS FOR CaO B-X

ν	0	1	2	3	4	5	6	7	8	9	10	11
0	.1565 1.892	.2354 1.860	.2158 1.832	.1566 1.809	.9918-1 1.787	.5783-1 1.768	.3227-1 1.749	.1785-1 1.733	.1009-1 1.720	.5970-2 1.710	.3630-2 .704	.2451-2 1.701
1	.3396 1.931	.1038 1.885	.4166-3 1.790	.3280-1 1.850	.7858-1 1.819	.9551-1 1.797	.8942-1 1.778	.7095-1 1.762	.5248-1 1.747	.3716-1 1.734	.2568-1 1.722	.1808-1 1.712
2	.3226 1.975	.1657-1 1.978	.1353 1.902	.8375-1 1.860	.1330-1 1.812	.1700-2 1.896	.2165-1 1.816	.6200-1 1.790	.5174-1 1.771	.5177-1 1.756	.4624-1 1.743	.3871-1 1.731
3	.1400 2.025	.2322 1.986	.4657-3 1.916	.2235-1 1.977	.6824-1 1.874	.7357-1 1.838	.2807-1 1.803	.2897-2 1.738	.1583-2 1.865	.1113-1 1.796	.2127-1 1.772	.2375-1 1.756
4	.3527-1 2.092	.2694 2.031	.5689-1 2.012	.1260 1.937	.1119-1 1.860	.1781-1 1.902	.5986-1 1.852	.6111-1 1.820	.3652-1 1.792	.1343-1 1.761	.1929-2 1.699	.2317-3 1.962
5	.5391-2 2.165	.1154 2.093	.2614 2.041	.6839-3 1.692	.9362-1 1.952	.6915-1 1.897	.4680-2 1.811	.1030-1 1.887	.3809-1 1.837	.4771-1 1.808	.3869-1 1.784	.2350-1 1.761
6	.5519-3 2.227	.2415-1 2.174	.2094 2.097	.1608 2.056	.5281-1 1.961	.2064-1 1.984	.7971-1 1.912	.1864 1.864	.4968-1 1.789	.3411-2 1.899	.1996-1 1.829	.3179-1 1.800
7	.2826-2 2.261	.6447-1 2.175	.2672 2.104	.5113-1 2.085	.1077 2.085	.1077 1.982	.2180-2 1.613	.3475-1 1.932	.6225-1 1.800	.3676-2 1.839	.7852-2 1.784	.1018-3 2.227
8	.1658-3 2.360	.9168-2 2.276	.1249 2.176	.2643 2.112	.1016-2 2.409	.1012 1.996	.1012 1.966	.3902-1 1.924	.9779-3 2.007	.3299-1 1.899	.4868-1 1.856	.3360-1 1.821
9	.6044-3 2.596	.2316-1 2.280	.6044-3 2.280	.2316-1 2.180	.1946 2.112	.2037 2.125	.1968-1 1.963	.6942-1 2.016	.7167-1 1.943	.1408-1 1.871	.2614-2 1.901	.2512-1 1.877
10	.1711-2 2.623	.4813-1 2.281	.1711-2 2.623	.4813-1 2.184	.2559 2.184	.2559 2.184	.1156 2.145	.6809-1 2.010	.6177-2 2.088	.6143-1 1.958	.4551-1 1.902	.7429-2 1.828
11		.4172-2 2.438	.4172-2 2.438	.6636-1 2.281	.2912 2.190	.2912 2.190	.2912 2.190	.3948-1 2.194	.9864-1 2.027	.4918-2 1.880	.2429-1 1.982	.5325-1 1.917
12				.9002-2 2.444	.1373 2.282	.1373 2.282	.1373 2.282	.2882 2.199	.2359-2 2.528	.8852-1 2.041	.3474-1 1.958	.7270-3 2.186
13				.1022-3 3.055	.1768-1 2.445	.1022-3 3.055	.1768-1 2.445	.1977 2.283	.2476 2.211	.8116-2 1.864	.4958-1 2.059	.6037-1 1.978
14					.2120-3 3.106	.2120-3 3.106	.2120-3 3.106	.3200-1 2.443	.2598 2.285	.1811 2.232	.3912-1 1.996	.1227-1 2.104
15					.4088-3 3.149	.4088-3 3.149	.4088-3 3.149	.5389-1 2.248	.5389-1 2.248	.3142 2.268	.1077 2.268	.6863-1 2.029
16								.7583-3 3.169	.7583-3 3.169	.8496-1 2.833	.3525 2.294	.4727-1 2.549

TABLE 10. FRANCK-CONDON FACTORS AND ν -CENTROIDS FOR SiO C-X

ν	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	0.6446-2	2.682-1	3.986-1	9.334-1	1.217	1.324	1.276	1.123	0.9137-1	0.7031-1	0.5138-1	0.3606-1	0.2447-1	0.1613-1
	2.024	2.006	1.989	1.973	1.942	1.942	1.913	1.874	1.831	1.887	1.874	1.862	1.831	1.839
1	3.813-1	1.026	1.372	1.157	6.237-1	1.643-1	1.2815-4	1.043-1	0.821-1	0.6372-1	0.502-1	0.392-1	0.292-1	0.214-1
	2.048	2.025	2.011	1.994	1.977	1.958	1.933	1.908	1.882	1.856	1.833	1.806	1.770	1.734-1
2	1.057	1.513	0.849-1	0.989-2	8.121-2	0.764-1	0.7047-1	0.582-1	0.470-1	0.3718-2	0.287-2	0.212-2	0.152-2	0.108-1
	2.073	2.033	2.033	2.010	2.008	1.987	1.969	1.953	1.937	1.918	1.946	1.906	1.851	1.878
3	1.826	1.034	1.363-2	0.974-1	0.786-1	0.660-1	0.542-2	0.434-2	0.346-1	0.271-1	0.212-1	0.162-1	0.122-1	0.083-2
	2.098	2.077	2.037	2.044	2.024	2.003	1.981	1.963	1.943	1.927	1.932	1.917	1.900	1.832
4	2.200	1.632-1	0.502-1	0.839-1	1.698-1	0.620-2	0.473-1	0.337-1	0.223-1	0.140-1	0.088-2	0.054-1	0.034-1	0.024-1
	2.126	2.096	2.063	2.041	2.040	2.015	1.996	1.976	1.958	1.938	1.960	1.941	1.926	1.912
5	1.863	1.589-1	1.039	1.217-1	2.583-1	0.633-1	0.483-1	0.343-1	0.231-1	0.146-1	0.088-2	0.054-1	0.034-1	0.024-1
	2.133	2.161	2.111	2.082	2.077	2.054	2.032	2.008	2.007	1.980	1.971	1.951	1.936	1.936
6	1.199-1	1.024	0.4410-1	0.2652-1	0.7238-1	0.6833-2	0.471-1	0.3236-1	0.204-1	0.129-1	0.078-1	0.051-1	0.034-1	0.024-1
	2.184	2.164	2.135	2.124	2.097	2.067	2.044	2.022	2.002	1.978	2.001	1.981	1.964	1.947
7	3.061-1	1.664	0.808-3	0.9056-1	0.9306-2	0.3329-1	0.2473-1	0.1698-2	0.109-2	0.063-1	0.033-1	0.021-1	0.014-1	0.008-1
	2.213	2.192	2.163	2.143	2.111	2.100	2.083	2.053	2.037	2.011	2.033	2.013	1.998	1.974
8	1.029-1	1.331	0.6639-1	0.7129-3	0.2974-1	0.6039-1	0.3976-3	0.2647-1	0.1826-1	0.1049-1	0.067-1	0.042-1	0.028-1	0.018-1
	2.248	2.223	2.202	2.169	2.158	2.128	2.044	2.094	2.070	2.038	2.047	2.023	2.004	1.981
9	2.816-2	0.9580-1	1.463	0.6771-1	0.8492-1	0.1624-2	0.4958-1	0.3375-1	0.1122-2	0.067-1	0.0385-1	0.024-1	0.015-1	0.008-1
	2.283	2.233	2.231	2.266	2.106	2.117	2.139	2.111	2.135	2.081	2.058	2.024	2.008	2.013
10	0.6068-3	0.4376-1	1.493	1.1456	0.3024-1	0.6661-1	0.3970-1	0.2379-2	0.150-2	0.096-1	0.054-1	0.034-1	0.024-1	0.018-1
	2.320	2.290	2.263	2.242	2.202	2.191	2.158	2.160	2.131	2.094	2.101	2.069	2.047	2.011
11	1.029-3	1.506-1	0.946-1	1.404	0.6032-2	0.7582-1	0.2868-2	0.6028-1	0.7633-2	0.2133-1	0.172-1	0.093-2	0.0883-2	0.057-1
	2.361	2.328	2.298	2.272	2.269	2.213	2.228	2.170	2.133	2.133	2.107	2.073	2.084	2.057
12	0.3933-2	0.4260-1	0.8273-1	0.8914-1	0.033-1	0.6058-1	0.1290-1	0.1290-1	0.3196-1	0.3899-1	0.4331-4	0.3154-1	0.3023-1	0.202-2
	2.369	2.333	2.306	2.282	2.222	2.222	2.273	2.182	2.182	2.150	2.364	2.118	2.093	2.045
13	0.7910-3	1.185-1	0.3003-1	0.3003-1	0.1315	0.2624-1	0.3218-1	0.2354-1	0.4716-1	0.2131-2	0.161-1	0.134-1	0.3518-2	0.3413-1
	2.416	2.376	2.346	2.316	2.297	2.297	2.248	2.240	2.200	2.221	2.161	2.129	2.139	2.104
14	1.191-3	0.3229-2	0.9271-2	1.242	0.1213	0.4796-4	0.7486-1	0.2914-3	0.3562-1	0.8933-2	0.2087-1	0.2087-1	0.3740-1	0.2632-2
	2.466	2.422	2.384	2.331	2.321	2.321	2.260	2.260	2.271	2.211	2.168	2.173	2.163	2.098
3	0.3582-3	0.1838-2	0.2094-1	0.2094-1	0.1504	0.6818-1	1.1747-1	0.6138-1	0.1368-1	0.1369-1	0.3091-1	0.3446-1	0.8116-3	0.3406-1
	2.574	2.430	2.392	2.359	2.359	2.355	2.273	2.273	2.273	2.222	2.224	2.187	2.236	2.154
6	0.2319-3	0.2094-1	0.9803-1	0.9803-1	1.1502	0.2071-1	0.2071-1	0.2071-1	0.3273-1	0.2386-1	0.4262-1	0.4604-2	0.4300-1	0.7709-2
	2.483	2.439	2.401	2.369	2.369	2.333	2.293	2.293	2.286	2.286	2.240	2.254	2.199	2.158
7	0.4794-2	0.3949-1	1.318	1.227	0.4794-2	0.3949-1	1.318	1.227	0.3182-3	0.7463-1	0.2003-2	0.527-1	0.2491-2	0.3016-1
	2.692	2.447	2.409	2.379	2.379	2.332	2.303	2.303	2.332	2.361	2.332	2.332	2.182	2.212
8	0.7210-3	0.1028-1	0.6433-1	1.134	0.8226-1	0.6433-1	1.134	0.8226-1	0.9473-2	0.6892-1	0.4877-2	0.4877-2	0.4246-1	0.2103-1
	2.356	2.301	2.456	2.419	2.392	2.392	2.303	2.316	2.243	2.316	2.243	2.243	2.264	2.222

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TABLE 11. FRANCK-CONDON FACTORS AND r -CENTROIDS FOR ZrO SINGLET SYSTEM

$v'' \backslash v'$	0	1	2	3	4	5	6	7	8
0	.9020 1.744	.3366 1.702	.1223 1.661	.3154-1 1.620	.6353-2 1.576	.1037-2 1.528	.1373-3 1.472		
1	.3564 1.792	.4982-1 1.731	.2772 1.708	.2067 1.667	.8190-1 1.626	.2243-1 1.583	.4667-2 1.537	.7587-3 1.482	
2	.1162 1.840	.3203 1.799	.8270-2 1.754	.1404 1.714	.2222 1.674	.1304 1.633	.4703-1 1.590	.1217-1 1.545	.2380-2 1.491
3	.2242-1 1.891	.2169 1.847	.1864 1.807	.7672 1.763	.4159-1 1.719	.1868 1.679	.1826 1.639	.7592-1 1.597	.2399-1 1.532
4	.2794-2 1.945	.6421-1 1.898	.2631 1.854	.7314-1 1.817	.1361 1.770	.2100-2 1.713	.1291 1.665	.1728 1.643	.1038 1.604
5	.2321-3 2.008	.1078-1 1.932	.1143 1.905	.2375 1.862	.1294-1 1.834	.1331 1.777	.7406-2 1.743	.7229-1 1.689	.1625 1.631
6		.1120-2 2.013	.2493-1 1.965	.1617 1.912	.2176 1.870	.3702-5 1.737	.1389 1.784	.5502-1 1.746	.2973-1 1.691
7			.3154-2 1.960	.4482-1 1.967	.1987 1.919	.1622 1.878	.1864-1 1.813	.1035 1.792	.6633-1 1.752
8			.2422-3 2.021	.6774-2 2.029	.6902-1 1.974	.2213 1.927	.1062 1.887	.4965-1 1.827	.6416-1 1.801
9				.3978-3 2.101	.1229-1 2.057	.9563-1 1.982	.2295 1.934	.5915-1 1.898	.8037-1 1.856
10					.1231-2 2.109	.1903-1 2.044	.1226 1.989	.2256 1.942	.2555-1 1.915
11						.2234-2 2.118	.2942-1 2.032	.1482 1.997	.2075 1.950
12						.1386-3 2.209	.3691-2 2.126	.4083-1 2.060	.1709 2.005
13							.2484-3 2.219	.5670-2 2.135	.5380-1 2.068
14								.4112-3 2.230	.8222-2 2.144
15									.6586-3 2.224
16									
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TABLE 10. FRANCK-CONDON FACTORS AND r -CENTROIDS FOR $SiO-C-X$

v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	.6446-2	.3842-1	.5986-1	.9334-1	.1217	.1324	.1278	.1123	.9157-1	.7031-1	.5138-1	.3606-1	.2447-1	.1615-1
1	2.026	2.600	1.989	1.975	1.957	1.942	1.937	1.931	1.900	1.887	1.874	1.862	1.851	1.839
2	2.048	2.026	2.011	1.996	1.977	1.958	(.2812-4)	1.939	.5362-1	.5572-1	.6902-1	.7202-1	.6695-1	.5724-1
3	2.075	2.053	2.035	2.010	2.008	.6764-1	.7047-1	.5822-1	.2870-1	.918	.3666-5	.1022-1	.2472-1	1.858
4	2.099	2.077	2.037	2.004	2.026	.6660-1	.5423-2	.5546-2	.3264-1	.5127-1	.4647-1	1.906	1.891	.4186-1
5	2.126	2.096	2.068	2.065	2.041	2.040	.6796-1	.5387-1	.2283-1	.952	.1932	.917	1.900	.1180-5
6	2.155	2.141	2.111	2.082	2.077	2.054	2.032	2.008	1.978	1.968	1.960	1.941	1.926	1.912
7	2.184	2.164	2.135	2.126	2.097	2.083	2.067	2.043	2.022	1.988	1.971	.8427-2	.2564-5	.1181-1
8	2.215	2.192	2.165	2.145	2.111	2.108	2.083	2.053	2.027	.8487-3	.1210-1	.3531-1	1.994	1.938
9	2.248	2.223	2.202	2.169	2.158	2.128	2.104	2.076	2.048	.4311-1	.3001-1	.5288-2	.6993-2	.2500-1
10	2.283	2.255	2.231	2.202	2.177	2.147	2.123	2.094	2.067	.4156-2	.1049-1	.3624-1	.2935-3	.5935-2
11	2.320	2.290	2.265	2.242	2.209	2.180	2.152	2.125	2.098	.1122-2	.2047	.2882-2	2.004	1.981
12	2.361	2.328	2.298	2.272	2.239	2.215	2.188	2.162	2.135	2.081	2.058	2.024	2.008	2.004
13	2.406	2.370	2.340	2.313	2.280	2.255	2.228	2.202	2.175	2.135	2.107	2.075	2.069	2.061
14	2.454	2.415	2.384	2.357	2.324	2.299	2.272	2.246	2.220	2.175	2.147	2.118	2.093	2.085
15	2.505	2.464	2.432	2.405	2.372	2.347	2.320	2.294	2.268	2.223	2.195	2.166	2.141	2.133
16	2.560	2.517	2.484	2.456	2.423	2.397	2.370	2.344	2.318	2.273	2.245	2.216	2.191	2.183
17	2.619	2.574	2.540	2.512	2.479	2.453	2.427	2.401	2.375	2.330	2.302	2.273	2.248	2.240
18	2.681	2.635	2.600	2.572	2.539	2.513	2.487	2.461	2.435	2.390	2.362	2.333	2.308	2.300
19	2.747	2.699	2.663	2.635	2.602	2.576	2.550	2.524	2.498	2.453	2.425	2.396	2.371	2.363
20	2.817	2.768	2.731	2.703	2.670	2.644	2.618	2.592	2.566	2.521	2.493	2.464	2.439	2.431
21	2.891	2.841	2.803	2.775	2.742	2.716	2.690	2.664	2.638	2.593	2.565	2.536	2.511	2.503
22	2.969	2.918	2.879	2.851	2.818	2.792	2.766	2.740	2.714	2.669	2.641	2.612	2.587	2.579
23	3.051	2.999	2.960	2.932	2.899	2.873	2.847	2.821	2.795	2.750	2.722	2.693	2.668	2.660
24	3.137	3.084	3.045	3.017	2.984	2.958	2.932	2.906	2.880	2.835	2.807	2.778	2.753	2.745
25	3.227	3.173	3.134	3.106	3.073	3.047	3.021	2.995	2.969	2.924	2.896	2.867	2.842	2.834
26	3.320	3.265	3.226	3.198	3.165	3.139	3.113	3.087	3.061	3.016	2.988	2.959	2.934	2.926
27	3.417	3.361	3.322	3.294	3.261	3.235	3.209	3.183	3.157	3.112	3.084	3.055	3.030	3.022
28	3.517	3.460	3.421	3.393	3.360	3.334	3.308	3.282	3.256	3.211	3.183	3.154	3.129	3.121
29	3.620	3.562	3.523	3.495	3.462	3.436	3.410	3.384	3.358	3.313	3.285	3.256	3.231	3.223
30	3.727	3.668	3.629	3.601	3.568	3.542	3.516	3.490	3.464	3.419	3.391	3.362	3.337	3.329
31	3.837	3.777	3.738	3.710	3.677	3.651	3.625	3.599	3.573	3.528	3.500	3.471	3.446	3.438
32	3.950	3.889	3.850	3.822	3.789	3.763	3.737	3.711	3.685	3.640	3.612	3.583	3.558	3.550
33	4.066	4.005	3.966	3.938	3.905	3.879	3.853	3.827	3.801	3.756	3.728	3.699	3.674	3.666
34	4.185	4.124	4.085	4.057	4.024	3.998	3.972	3.946	3.920	3.875	3.847	3.818	3.793	3.785
35	4.307	4.246	4.207	4.179	4.146	4.120	4.094	4.068	4.042	4.007	3.979	3.950	3.925	3.917
36	4.432	4.371	4.332	4.304	4.271	4.245	4.219	4.193	4.167	4.122	4.094	4.065	4.040	4.032
37	4.560	4.499	4.460	4.432	4.399	4.373	4.347	4.321	4.295	4.250	4.222	4.193	4.168	4.160
38	4.691	4.630	4.591	4.563	4.530	4.504	4.478	4.452	4.426	4.381	4.353	4.324	4.299	4.291
39	4.825	4.764	4.725	4.697	4.664	4.638	4.612	4.586	4.560	4.515	4.487	4.458	4.433	4.425
40	4.963	4.902	4.863	4.835	4.802	4.776	4.750	4.724	4.698	4.653	4.625	4.596	4.571	4.563
41	5.105	5.044	5.005	4.977	4.944	4.918	4.892	4.866	4.840	4.795	4.767	4.738	4.713	4.705
42	5.251	5.190	5.151	5.123	5.090	5.064	5.038	5.012	4.986	4.941	4.913	4.884	4.859	4.851
43	5.401	5.340	5.301	5.273	5.240	5.214	5.188	5.162	5.136	5.091	5.063	5.034	5.009	5.001
44	5.554	5.493	5.454	5.426	5.393	5.367	5.341	5.315	5.289	5.244	5.216	5.187	5.162	5.154
45	5.711	5.650	5.611	5.583	5.550	5.524	5.498	5.472	5.446	5.401	5.373	5.344	5.319	5.311
46	5.871	5.810	5.771	5.743	5.710	5.684	5.658	5.632	5.606	5.561	5.533	5.504	5.479	5.471
47	6.034	5.973	5.934	5.906	5.873	5.847	5.821	5.795	5.769	5.724	5.696	5.667	5.642	5.634
48	6.201	6.140	6.101	6.073	6.040	6.014	5.988	5.962	5.936	5.891	5.863	5.834	5.809	5.801
49	6.371	6.310	6.271	6.243	6.210	6.184	6.158	6.132	6.106	6.061	6.033	6.004	5.979	5.971
50	6.544	6.483	6.444	6.416	6.383	6.357	6.331	6.305	6.279	6.234	6.206	6.177	6.152	6.144
51	6.721	6.660	6.621	6.593	6.560	6.534	6.508	6.482	6.456	6.411	6.383	6.354	6.329	6.321
52	6.902	6.841	6.802	6.774	6.741	6.715	6.689	6.663	6.637	6.592	6.564	6.535	6.510	6.502
53	7.087	7.026	7.000	6.972	6.939	6.913	6.887	6.861	6.835	6.790	6.762	6.733	6.708	6.700
54	7.275	7.214	7.190	7.162	7.129	7.103	7.077	7.051	7.025	6.980	6.952	6.923	6.898	6.890
55	7.467	7.406	7.390	7.362	7.329	7.303	7.277	7.251	7.225	7.180	7.152	7.123	7.098	7.090
56	7.662	7.601	7.590	7.562	7.529	7.503	7.477	7.451	7.425	7.380	7.352	7.323	7.298	7.290
57	7.861	7.800	7.800	7.772	7.739	7.713	7.687	7.661	7.635	7.590	7.562	7.533	7.508	7.500
58	8.063	8.002	8.000	7.972	7.939	7.913	7.887	7.861	7.835	7.790	7.762	7.733	7.708	7.700
59	8.269	8.208	8.210	8.182	8.149	8.123	8.097	8.071	8.045	8.000	7.972	7.943	7.918	7.910
60	8.479	8.418	8.430	8.402	8.369	8.343	8.317	8.291	8.265	8.220	8.192	8.163	8.138	8.130
61	8.692	8.631	8.650	8.622	8.589	8.563	8.537	8.511	8.485	8.440	8.412	8.383	8.358	8.350
62	8.909	8.848	8.880	8.852	8.819	8.793	8.767	8.741	8.715	8.670	8.642	8.613	8.588	8.580
63	9.129	9.068	9.110	9.082	9.049	9.023	8.997	8.971	8.945	8.900	8.872	8.843	8.818	8.810
64	9.352	9.291	9.350	9.322	9.289	9.263	9.237	9.211	9.185	9.140	9.112	9.083	9.058	9.050
65	9.579	9.518	9.590	9.562	9.529	9.503	9.477	9.451	9.425	9.380	9.352	9.323	9.298	9.290
66	9.809	9.748	9.840	9.812	9.779	9.753	9.727	9.701	9.675	9.630	9.602	9.573	9.548	9.540
67	10.042	9.981	10.090	10.062	10.029	10.003	9.977	9.951	9.925	9.880	9.852	9.823	9.798	9.790
68	10.279	10.218	10.350	10.322	10.289	10.263	10.237	10.211	10.185	10.140	10.112	10.083	10.058	10.050
69	10.519	10.458	10.610	10.582	10.549	10.523	10.497	10.471	10.445	10.400	10.372	10.343	10.318	10.310
70	10.762	10.701	10.870	10.842	10.809	10.783	10.757	10.731	10.705	10.660	10.632	10.603		

TABLE 11. FRANCK-CONDON FACTORS AND f -CENTROIDS FOR ZrO SINGLET SYSTEM

$v'' \backslash v'$	0	1	2	3	4	5	6	7	8
0	.5020 1.744	.5366 1.702	.1223 1.661	.3154-1 1.620	.6353-2 1.576	.1057-2 1.528	.1375-3 1.472		
1	.3564 1.792	.4982-1 1.751	.2772 1.708	.2067 1.667	.6190-1 1.626	.2245-1 1.583	.4667-2 1.537	.7587-5 1.482	
2	.1162 1.840	.3805 1.799	.8278-2 1.754	.1404 1.714	.2222 1.674	.1304 1.633	.4705-1 1.590	.1217-1 1.545	.2380-2 1.491
3	.2242-1 1.691	.2169 1.847	.1864 1.807	.7672 1.763	.4139-1 1.719	.1868 1.679	.1826 1.639	.7592-1 1.597	.2599-1 1.552
4	.2794-2 1.945	.6421-1 1.898	.2631 1.854	.7314-1 1.817	.1361 1.770	.2100-2 1.715	.1291 1.685	.1725 1.645	.1038 1.604
5	.2321-5 2.006	.1078-1 1.952	.1143 1.905	.2575 1.862	.1294-1 1.834	.1551 1.777	.7406-2 1.743	.7229-1 1.689	.1625 1.651
6		.1120-2 2.013	.2495-1 1.965	.1617 1.912	.2176 1.870	.5702-5 1.737	.1389 1.784	.5502-1 1.746	.2975-1 1.691
7			.5154-2 1.960	.4482-1 1.967	.1987 1.919	.1622 1.878	.1864-1 1.815	.1035 1.792	.6635-1 1.752
8			.2422-5 2.021	.6774-2 2.029	.6902-1 1.976	.2215 1.927	.1062 1.887	.4965-1 1.827	.6416-1 1.801
9				.5978-5 2.101	.1229-1 2.037	.9565-1 1.982	.2293 1.934	.5915-1 1.898	.8057-1 1.856
10					.1231-2 2.109	.1985-1 2.044	.1226 1.989	.2258 1.942	.2555-1 1.913
11						.2234-2 2.118	.2942-1 2.052	.1482 1.997	.2075 1.950
12						.1386-5 2.709	.5691-2 2.128	.4083-1 2.060	.1709 2.005
13							.2484-5 2.219	.5670-2 2.135	.5580-1 2.068
14								.4112-5 2.230	.8222-2 2.144
15									.6386-3 2.224
16									
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U 007

TABLE 11—continued

$v'' \backslash D'$	9	10	11	12	13	14	15	16	17
0									
1									
2	.3499-3 1.422								
3	.5567-2 1.501	.7580-3 1.435	.1135-5 1.332						
4	.3963-1 1.560	.1079-1 1.509	.2149-2 1.447	.2967-3 1.332					
5	.1260 1.610	.3773-1 1.567	.1828-1 1.516	.4179-2 1.458	.6548-3 1.570				
6	.1376 1.656	.1395 1.616	.7652-1 1.376	.2799-1 1.326	.7290-2 1.468	.1324-2 1.307	.1414-3 1.229		
7	.6103-2 1.683	.1052 1.661	.1433 1.622	.9400-1 1.581	.3937-1 1.334	.1167-1 1.478	.2402-2 1.402	.3003-3 1.262	
8	.8990-1 1.758	(.7328-4) (1.937)	.7192-1 1.664	.1376 1.628	.1083 1.587	.5238-1 1.542	.1741-1 1.468	.4033-2 1.416	.5833-3 1.291
9	.3119-1 1.812	.1009 1.763	.7092-2 1.747	.4265-1 1.666	.1243 1.633	.1186 1.393	.6563-1 1.549	.2450-1 1.497	.6350-2 1.429
10	.1037 1.843	.9468-2 1.831	.9949-1 1.772	.2161-1 1.743	.2044-1 1.664	.1058 1.637	.1237 1.599	.7843-1 1.556	.3277-1 1.506
11	.6225-2 1.943	.1158 1.832	.5365-3 1.923	.8828-1 1.779	.3849-1 1.746	.6473-2 1.648	.8467-1 1.641	.1236 1.605	.8993-1 1.563
12	.836 1.959	(.2349-4) (2.712)	.1169 1.860	.2092-2 1.760	.7114-1 1.787	.3383-1 1.751	.4492-3 1.511	.6326-1 1.643	.1187 1.610
13	.1897 2.012	.1558 1.967	.5918-2 1.847	.1090 1.868	.1132-1 1.799	.5188-1 1.796	.6509-1 1.737	.1098-2 1.836	.4354-1 1.644
14	.6797-1 2.076	.2040 2.020	.1263 1.977	.1483-1 1.885	.9476-1 1.876	.2491-1 1.814	.3360-1 1.807	.7113-1 1.764	.6623-2 1.769
15	.1137-1 2.153	.8296-1 2.084	.2156 2.028	.9817-1 1.987	.2980-1 1.901	.7706-1 1.904	.3984-1 1.824	.1847-1 1.820	.7183-1 1.771
16	.9408-3 2.231	.1512-1 2.162	.9837-1 2.093	.2187 2.036	.7253-1 1.999	.4616-1 1.913	.5836-1 1.893	.5375-1 1.833	.7699-2 1.842
17		.1326-2 2.262	.1945-1 2.171	.1138 2.101	.2193 2.045	.3011-1 2.012	.6192-1 1.923	.4103-1 1.904	.6503-1 1.840
18			.1801-2 2.273	.2433-1 2.180	.1290 2.109	.2166 2.033	.5202-1 2.028	.7569-1 1.932	.2603-1 1.916
19				.2367-2 2.285	.2970-1 2.190	.1436 2.118	.2108 2.062	.1822-1 2.051	.8659-1 1.940
20					.3024-2 2.297	.5551-1 2.199	.1575 2.127	.2021 2.071	.8586-2 2.086
21					.1252-5 2.440	.5769-2 2.309	.4168-2 2.209	.1703 2.133	.1917 2.080
22						.1569-5 2.479	.4594-2 2.521	.4814-1 2.219	.1824 2.144

0 003

TABLE 11—continued

$\frac{D''}{D'}$	18	19	20	21	22
0					
1					
2					
3					
4					
5					
6					
7					
8					
9	.1049-2 1.316				
10	.9461-2 1.441	.1770-2 1.338	.1498-3 1.070		
11	.4198-1 1.514	.1344-1 1.452	.2825-2 1.357	.2922-3 1.134	
12	.9939-1 1.569	.5174-1 1.522	.1831-1 1.463	.4295-2 1.375	.5291-3 1.184
13	.1097 1.614	.1063 1.576	.6165-1 1.530	.2405-1 1.473	.6258-2 1.391
14	.2693-1 1.641	.9764-1 1.619	.1102 1.581	.7124-1 1.537	.3056-1 1.483
15	.1508-1 1.759	.1421-1 1.631	.8361-1 1.622	.1111 1.587	.8010-1 1.544
16	.6794-1 1.778	.2468-1 1.758	.5663-2 1.603	.6876-1 1.624	.1090 1.592
17	.1637-2 1.899	.6051-1 1.786	.3392-1 1.761	.1103-2 1.491	.5412-1 1.625
18	.7283-1 1.848	(.2149-4) (.9850)	.5085-1 1.795	.4171-1 1.765	(.3633-4) (2.884)
19	.1433-1 1.931	.7683-1 1.855	.2169-2 1.735	.4022-1 1.805	.4738-1 1.711
20	.9423-1 1.949	.6173-2 1.956	.7722-1 1.862	.7166-2 1.778	.2976-1 1.816
21	.2743-2 2.164	.9859-1 1.957	.1511-2 2.017	.7448-1 1.869	.1402-1 1.797
22	.1800 2.089	.2096-3 2.597	.9988-1 1.965		.6932-1 1.877

U 000

TABLE 12—continued

$v'' \backslash v'$	9	10	11	12	13	14	15	16	17
0									
1									
2									
3									
4									
5	.1153-3 2.530	.1204-3 2.053							
6	.2172-1 1.443	.4072-3 .7159	.1490-3 2.176	.1157-3 1.706					
7	.1967 1.624	.3358-1 1.473	.1079-2 9.560	.1533-3 2.385	.1091-3 1.745				
8	.2845 1.718	.2283 1.837	.4832-1 1.499	.2392-2 1.105	.1252-3 2.703	.2825-3 1.788			
9	.4541-2 2.144	.2371 1.722	.2502 1.649	.6649-1 1.523	.4680-2 1.208	(.8341-4) (3.517)	.5879-5 1.837	.1484-3 1.589	
10	.1495 1.940	.1758-1 2.000	.1871 1.724	.2667 1.660	.8750-1 1.545	.8334-2 1.285	(.6679-5) (8.744)	.4901-3 1.895	.2398-3 1.623
11	.2295 1.986	.1083 1.952	.4061-1 1.965	.1384 1.722	.2745 1.670	.1106 1.564	.1376-1 1.345	(.2893-4) (2.435)	.5672-3 1.968
12	.9178-1 2.062	.2342 1.993	.7128-1 1.966	.8336-1 1.953	.9428-1 1.714	.2729 1.879	.1349 1.582	.2133-1 1.393	.2627-5 6.666
13	.1922-1 2.120	.1108 2.070	.2315 2.000	.4081-1 1.984	.8429-1 1.951	.5728-1 1.695	.2621 1.688	.1589 1.599	.3139-1 1.433
14	.2287-2 2.197	.2624-1 2.127	.1294 2.077	.2218 2.008	.1840-1 2.012	.1007 1.953	.2911-1 1.853	.2429 1.694	.1813 1.614
15	.1835-5 2.255	.3473-2 2.204	.3471 2.134	.1473 2.085	.2053 2.015	.4805-2 2.076	.1107 1.959	.1053-1 1.545	.2166 1.700
16		.3052-3 2.282	.5094-2 2.210	.4465-1 2.141	.1835 2.093	.1837 2.022	(.1977-4) (3.757)	.1138 1.966	.1357-2 1.031
17			.4891-3 2.269	.7248-2 2.217	.5599-1 2.149	.1772 2.100	.1583 2.029	.3326-2 1.840	.1094 1.974
18				.7584-3 2.277	.1004-1 2.224	.6863-1 2.156	.1878 2.108	.1303 2.036	.1341-1 1.918
19					.1142-2 2.284	.1357-1 2.231	.8233 2.163	.1944 2.116	.1022 2.042
20						.1677-2 2.291	.1794 2.238	.9682-1 2.171	.1968 2.142
21						.1261-3 2.383	.2404-2 2.299	.2323-1 2.245	.1117 2.178

TABLE 12—continued

$v'' \backslash v'$	18	19	20	21
0				
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
11	.3638-3 1.658			
12	.5946-3 2.065	.5196-3 1.695	.1427-3 1.490	
13	.9067-3 .678	.5509-3 2.206	.6999-3 1.734	.2339-3 1.528
14	.4406-1 1.467	.2228-2 9.585	.4290-3 2.436	.8892-3 1.778
15	.2005 1.628	.5932-1 1.497	.4552-2 1.122	.2483-3 2.904
16	.1852 1.703	.2152 1.641	.7689-1 1.523	.8241-2 1.231
17	.6337-3 3.052	.1509 1.703	.2260 1.653	.9622-1 1.547
18	.9903-1 1.985	.6732-2 2.232	.1161 1.699	.2263 1.663
19	.2853-1 1.948	.8386-1 1.997	.1757-1 2.100	.8321-1 1.689
20	.7496-1 2.048	.4663-1 1.966	.6585-1 2.012	.3086-1 2.053
21	.1947 2.132	.5041-1 2.053	.6557-1 1.980	.4712-1 2.031

0 010

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Radiative Lifetimes and Absolute Oscillator Strengths for the
SiO A¹Π - X¹Σ⁺ Transition*

by

William Hayden Smith and H.S. Liszt
Princeton University Observatory
Princeton, New Jersey 08540

ABSTRACT

Measurement of a radiative lifetime of 9.6 ± 1.0 nsec for the SiO A¹Π - state is reported. RKR Franck-Condon Factors have been computed and with these, absolute oscillator strengths are calculated. A band system at $\sim 3022\text{\AA}$ has been found that may be due to SiO⁺, but the band is not resolved at our experimental resolution, and identification remains uncertain. The upper state of the carrier of this spectrum has a radiative lifetime of 8.3 ± 0.8 nsec.

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INTRODUCTION

There have been few reliable measurements of absolute transition probabilities for species which can only be obtained at high temperatures. These include the refractory oxides in particular. Accurate values for these transition probabilities will find immediate application to problems of abundance determination in astrophysics and to many problems of radiative transfer in high temperature environments.

In our laboratory, we are now engaged in a broad study of the radiative lifetimes of such species, both atomic¹ and molecular. Our electron beam phase shift lifetime apparatus has been equipped with ovens to allow the evaporation of various species into the excitation area. This is necessary for those species which may not easily be derived from volatile molecules. There are, for example, very few volatile molecules which contain a SiO fragment and those that do can be quite large; in the process of excitation by dissociation the desired fragment may not even be excited. Evaporating smaller molecules at higher temperatures may avoid complications of overlapping emissions from other fragments which are more readily excited.

SiO is a species of the refractory type that has been studied previously in oscillator strength determinations^{2, 3} via density dependent methods which include shock tube and laser blow-off studies. The results differ among themselves by more than an order of magnitude. An independent check of these oscillator strengths is therefore of considerable value. In particular it would be preferable to use a method that is free from constraints imposed by the necessity of knowing thermodynamic properties, additional reaction processes, and the other complications that can enter the interpretation of density dependent experiments. We have computed the necessary

RKR Franck-Condon factors for the conversion of our lifetime data into oscillator strengths. These are listed in the table of oscillator strengths and will be fully reported elsewhere.⁴

EXPERIMENTAL

The lifetimes measured here were obtained with an electron beam phase-shift apparatus⁵ through the dissociative excitation of the SiO fragment from a parent molecule. The molecule $\text{SiO}(\text{Cl})_6$ has a sufficient vapor pressure at room temperature that it can be volatilized directly into our source. Samples of this molecule were obtained from Alpha Inorganics, and used without further purification. An alternate source of vapor phase SiO was the volatilization of silicates directly from the silicate-containing cement S-29 (Sauereisen Cement Co.). Both the $\text{SiO}(\text{Cl})_6$ and the silicate cement produced emission of the SiO $A^1\pi - X^1\Sigma^+$ transition and the Si I and II multiplets. They differed in that the cement produced much more intense Si II emissions and a very intense band system at about 3022\AA . The SiO emission and the other band had lifetimes that were independent of the pressure (temperature of SiO $A^1\pi - X^1\Sigma^+$ transition, of the frequency of modulation of the electron beam. In order to check and correct for non-exponential decays, logarithmically space frequencies from 0.54 to 17.1 MHz were used. The analysis of the cascading found for the A-state of SiO was carried out using the technique of Lawrence and Savage.⁶ All phase shifts were referenced to the Ne II 1908-1917 \AA transition,⁷ which was measured under simultaneous experimental conditions.

No other emissions were observed that could not be identified as background impurities (N_2 , primarily). In particular, there was no interference from the various possible silicon halides that could be formed from the dissociative excitation of $\text{SiO}(\text{Cl})_6$. The phase shifts found from both sources of SiO were in agreement within experimental error.

Results and Discussion

SiO

The spectrum of the SiO $A^1\tilde{\Gamma} - X^1\tilde{\Sigma}^+$ transition as it appears under our experimental resolution of $\sim 10\text{\AA}$ is shown in Figure 1. The spectrum has been observed under higher resolution to determine that in fact it is due to SiO. The measurements of the phase shifts were made in between the atomic lines present and showed little variation. Wavelengths corresponding to the $v' = 0, 1, 2,$ and 3 upper state vibrational quanta were measured. The results were consistent and resulted in phase-shift versus modulating frequency curves that were interpreted in terms of a main decay of 9.6 ± 1.0 ns, with a cascading transition having a lifetime of 70 ns and a cascading fraction of 1.35. This lifetime may be converted into $f_{v',v''}$ -values using our RKR Franck-Condon factors, and the equation:

$$f_{v',v''} = 1.499(g'/g'')A_{v',v''} \lambda_{v',v''}^2$$

where $g'/g'' = 2$, $\lambda_{v',v''}$ is given in cm^{-1} , and $A_{v',v''}$ is given by:

$$A_{v',v''} = 1/\gamma q_{v',v''} \lambda_{v',v''}^{-3} \left(\sum_{v''} q_{v',v''} \lambda_{v',v''}^{-3} \right)$$

where $1/\gamma = A_{v',0}$, $q_{v',v''}$ is the RKR Franck-Condon factor, and we assume that the variation of the dipole transition moment with internuclear distance is negligible.

In order to give an electronic oscillator strength, we use the approximation that $f_{el} = \sum_{v'} f_{v',0}$. An oscillator strength of 0.13 is indicated. This is comparable to the oscillator strength of 0.094 found by Hesser⁸, and the shock tube study of Rich⁹ (0.12) for the corresponding transition

of CO. If we compare with the results for the oscillator strength of the SiO $A^1\Pi-X^1\Sigma^+$ transition given in references 2 and 3, our value is nearly six times larger or more in all cases. We do not believe that we are in a position to specify the origin of the discrepancies in all cases. We can only point out that our measurement was obtained under experimental conditions that experience has taught us are likely to yield results of the quoted accuracy. While the preceding statement may seem presumptuous, it is based upon the use of the phase-shift apparatus in the measurement of the radiative lifetimes of several hundred levels in a wide variety of species over the last six years (see references 1 and 4-8 for many examples). Certainly an independent measurement of the type discussed here is needed to confirm our results. Although our result for the oscillator strength of the SiO A-X transition indicates a similar value to that found for the corresponding transition of CO, we see that it differs sharply from that found by Smith for the corresponding transition in CS¹⁰. Both these transitions are affected by perturbations^{11, 12} which evidence themselves strongly in the lifetimes measured for CS but not, apparently, in SiO. There was a slight effect of similar perturbations on the radiative lifetimes in the CO A-state as a function of vibrational quantum. The need to avoid the overlapping and much more intense atomic transitions of Si I and Si II rendered it impossible to detect small variations in upper state lifetimes for the vibrational quanta of the upper state of SiO, if they did exist. If our interpretation is correct, then the SiO transition is much more similar to the CO transition than to the CS transition.

The 3022Å Band

Along with the well known emissions due to Si I and II and the SiO $A^1\Pi - X^1\Sigma^+$ transition, the silicate cement also exhibited an emission that appeared continuous, even under 0.4Å resolution, although what may be band heads were observed, as shown in Figure 2. The transition was cascade free with a radiative lifetime of 8.3 ± 0.8 ns. Although the cement contains other atomic species, none of the possible transitions in the wavelength region studied were observed. The simultaneous appearance of the SiO and atomic Si transitions suggests strongly that the emission may be due to a species containing Si and O. In view of the strong emission from Si II for the cement compared with $\text{SiO}(\text{Cl})_6$, it is possible that the emission is due to an ion. This question is presently under investigation, and will be reported at a later date.

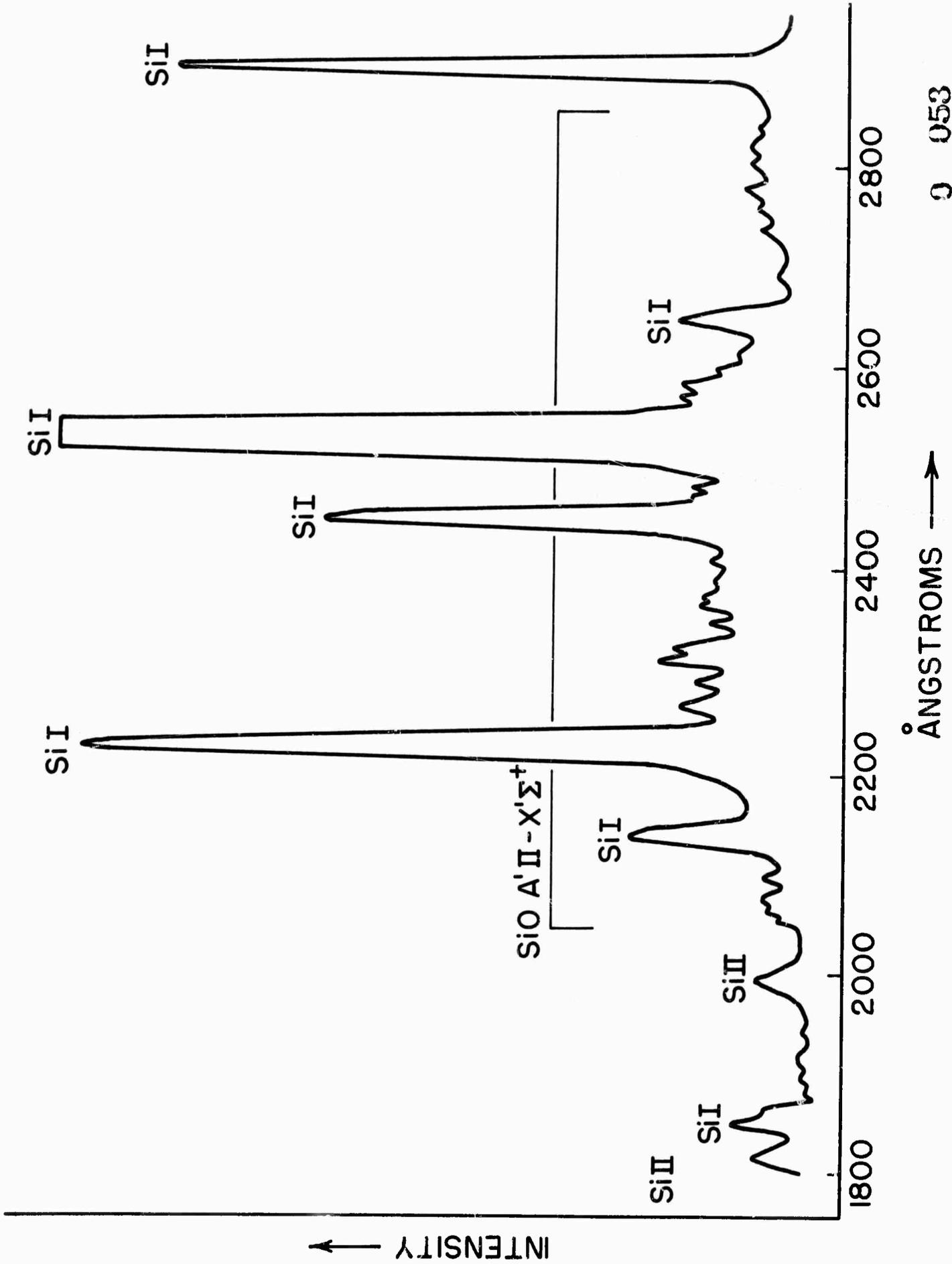
TABLE I
 Franck-Condon Factors and Absolute Oscillator Strengths
 for the Important (0, v') Transitions of SiO A' Π -X' Σ^+

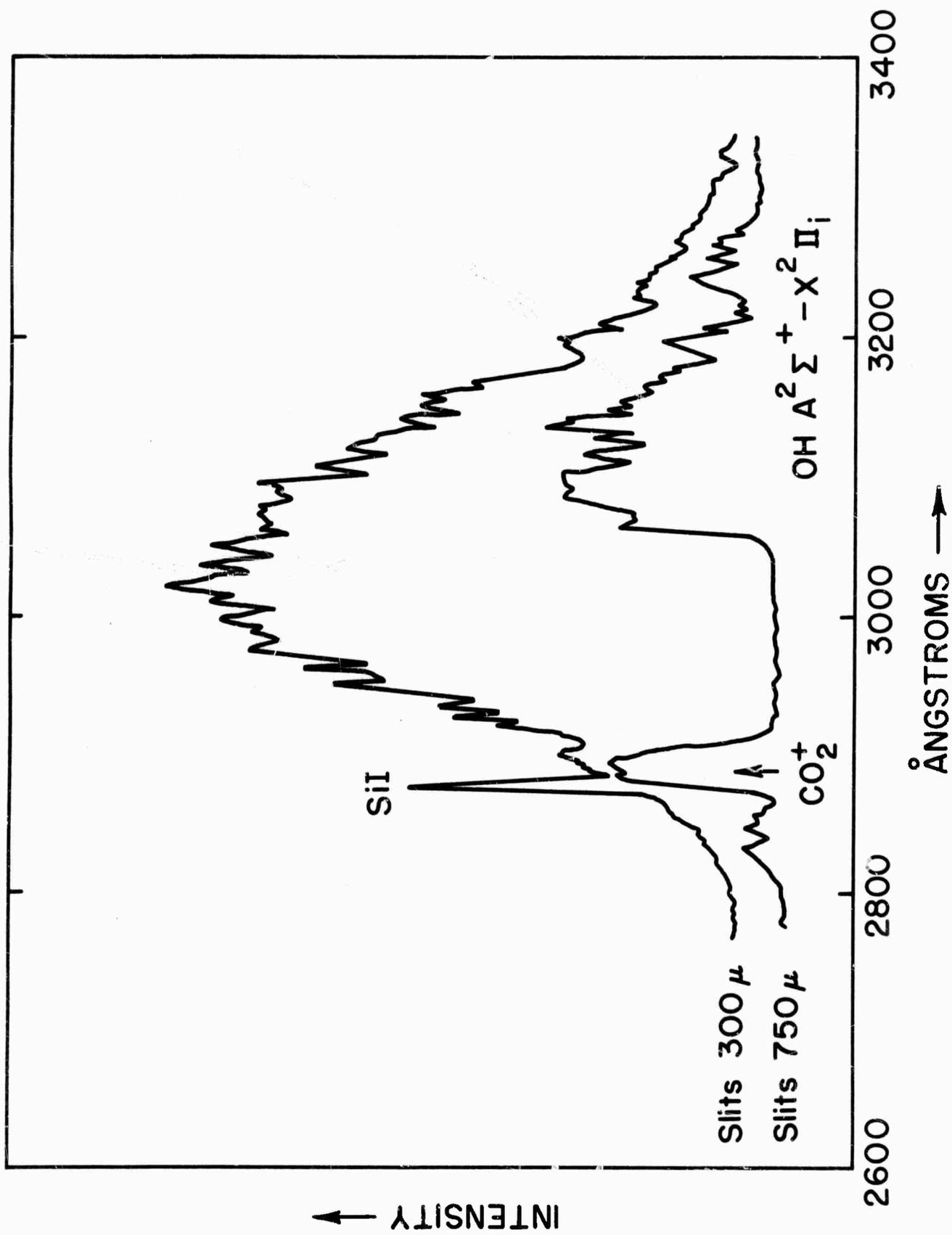
$q_{00} = 0.1405$	$f_{00} = 0.018$
$q_{01} = 0.2790$	$f_{01} = 0.036$
$q_{02} = 0.2741$	$f_{02} = 0.036$
$q_{03} = 0.1773$	$f_{03} = 0.025$
$q_{04} = 0.0863$	$f_{04} = 0.012$
$q_{05} = 0.0317$	$f_{05} = 0.0044$
$q_{06} = 0.0096$	$f_{06} = 0.0013$

$$\sum_{v'=0}^6 f_{v'0} = 0.133$$

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0 054

Absolute Oscillator Strengths for Some Resonance
Multiplets of Ca, Mg, B, and Al, and Their Singly Charged Ions *

by

William Hayden Smith and Harvey S. Liszt
Princeton University Observatory
Princeton, New Jersey

Abstract

Radiative lifetime studies of the more prominent resonance transitions of Ca, Mg, B, and Al between 1800 and 4250 Å are presented. The modulated electron beam phase-shift method has yielded lifetimes that may be considered accurate to $\pm 15\%$. The results for the lowest member of the resonance series are in good agreement with most previous literature values obtained with Hanle Effect or Beam-foil techniques. Results for the higher members of the resonance series for Mg I and Ca I differ with previous measurements. These data are discussed and oscillator strengths are given.

* This research was supported by Grant NGL-31-001-007 from the National Aeronautics and Space Administration and by the Advanced Research Project Agency of the Department of Defense, and was monitored by U. S. Army Office, Durham, Box CM, Duke Station, Durham, North Carolina, 27706, under Contract No. DAH C04 690081.

Introduction

This paper represents a portion of a continuing program at Princeton University Observatory for obtaining reliable oscillator strengths for ultraviolet and visible transitions for the astrophysically abundant metals. Among these species, neutral and once ionized calcium, magnesium, and aluminum are of great importance. Boron f -values find application in setting upper limits for the abundance of this element, (e.g., in stellar atmospheres).

Only recently have reliable methods become available for the accurate measurement of radiative lifetimes for excited states of the more refractory species and their ions. These methods include electron-beam phase-shift¹, beam-foil,²⁻⁴ Hanle Effect,⁵⁻⁸ and photon-resonance phase-shift techniques.⁹⁻¹⁰

The electron-beam phase-shift method is especially useful for the low charge states since dissociative excitation may be used in which the species of interest is excited by electron impact on a more volatile parent molecule containing the atom of interest. This method has the advantage of reducing the possibility of photon entrapment. It has in common with the other methods mentioned above that, in principle, no lifetime dependence on the vapor pressure exists for pressures sufficiently low that collisional deexcitation and/or photon entrapment do not occur. The lifetimes measured in all cases are the sum of all processes depopulating the upper states in question, both radiative and non-radiative. The transitions discussed here are not subject to autoionizations, so that the lifetimes are purely radiative in nature.

We also summarize all the recent data for these transitions and give averaged values for their oscillator strengths using all the values which may be considered of equal reliability.

Experimental

The radiative lifetimes reported here were measured using a phase shift technique described by Lawrence.¹¹ In brief, this consists of an electron beam excitation source which is current modulated at logarithmically spaced radio frequencies from 0.54 MHz to 54 MHz and serves as the monochromator entrance slit. The modulated emission output from the source is then dispersed by a 0.5 meter Seya-Namioka monochromator and focussed onto an EMI 6256B photomultiplier. The photomultiplier signal is mixed with the output of a side-band generator at frequency, $f+100$ Hz, and demodulated by a conventional radio receiver. The filtered 100 Hz beat at the receiver output is compared with a reference 100 Hz quartz crystal oscillator by a zero-crossing phase meter. The relative phase shift measured is then compared with the phase shift under identical (simultaneous) conditions of a cascade-free transition with a known radiative lifetime, e.g. NeII 1908 Å.¹²

The measured absolute phase shift (ϕ abs.) is related to the upper state radiative lifetime by

$$\phi_{abs.} = \tan^{-1} \omega \tau + \tan^{-1} \omega T - \tan^{-1} \left(\frac{\omega T}{1 + \beta} \right)$$

in the case where cascading exists.¹² In this equation, ω is the circular modulation frequency, $2\pi f$; τ is the upper state radiative lifetime, T is the lifetime of the cascading state (the cascading is assumed to be describable as arising from one state), and β is the ratio of the excitation cross-section for the cascading state to that of the measured state. This cascading correction was not applied in every case where cascading was found, due to the presence of radiative entrapment effects for the neutral atoms and the ions of magnesium and calcium.

No entrapment effects were found for the aluminum and boron transitions. The specific case is discussed in the text.

The magnesium, calcium, and aluminum neutrals and ions were obtained by dissociative excitation from their respective halides by evaporation from quartz boats via resistive heating. In each case, the vapor pressure was varied to test for radiative entrapment effects. Boron was obtained from a 10% mixture of diborane in He, obtained from Specialty Gases, Inc.

By following the appearance of the observed transitions as a function of the excitation electron voltage, identification of the transitions due to ions could be made, but there was no effect of voltage variation upon any of the measured lifetimes above threshold.

Discussion

The results of our measurements are listed in Table I and are compared to those previously published for corresponding transitions in Table II. We will discuss our measurements by species.

Mg I, II

Phase shifts for the first three resonance transitions in Mg I, the $3s^2 1S-3, 4, 5p 1P^o$ multiplets at 2853, 2026, and 1828 Å, were measured as a function of pressure and found to be slightly trapped i.e., the measured phase shifts were proportional to the pressure corresponding to delay in the escape of the photon from the gas. In such a case, extrapolation of the measured phase shift to zero pressure can be used to determine the existence of cascading effects. Furthermore the probable cascades for these states are generally much longer lived¹³ and can effectively be ignored at high enough modulation frequencies since the

percent modulation goes as $[1 + (\omega\tau)^2]^{-1/2}$, and detectivity goes to zero very rapidly for the cascading signal. Under the assumption that we were equally successful in extrapolating to zero pressure value of the measured phase shift at each frequency, we analyzed the phase-frequency curves for cascading and found a cascading lifetime in reasonable agreement with the values for the possible cascading transitions.¹³ These values are listed in Table I under "cascade parameters". Under these conditions, we found a $\tau = 1.9 \pm 0.3$ nsec for the 2853 Å $3s^2 1s-3p 1P^0$ Mg I upper level which is in very good agreement with the Hanle Effect study of Smith and Gallagher⁵, and the phase shift study of Hulpke et al.,¹⁰ with the beam foil studies of Berry et al.³ and Anderson et al.² Our result provides further proof that the measurements of Demtröder⁹ suffered from radiative entrapment as suggested by the previously listed authors.

The $4p 1P^0$ and $5p 1P^0$ levels had not been measured prior to our study. The lifetime of the $4p 1P^0$ has been calculated by Zare¹⁵ to be 8.3 nsec, in fair agreement with our result of 10.4 ± 2.0 nsec. The lifetime of the $5p 1P^0$ upper state was measured to be 28 ± 5 nsec.

The Mg II $3s 2S-3p 2P^0$ multiplet at 2796-2803 Å was also observed with adequate intensity for accurate measurements over a wide frequency range. Our measured lifetime of 3.7 ± 0.5 nsec is in close agreement with the Hanle Effect measurement of Smith and Gallagher,⁵ and less closely with those of Anderson et al.² and Berry et al.,³ which were beam foil studies. In these last two cases, appreciable cascading was found from the Mg II $3d-3p$ transition that feeds the upper state of the multiplet under study. This transition is expected to have a lifetime of about 2 nsec¹³ and overlaps the resonance transition at the experimental resolution used in our study. Anderson et al. have made their measurements at

sufficiently high resolution to reduce the spectral overlap between the transitions to the point where largely independent determinations of the radiative lifetimes could be made. The study of Berry et al. relied upon a cascade analysis with a growing-in (short-lived) cascade to derive their result. It is well known that beam foil excitation is very severe and results in many highly excited states of the particles passing through the foil. Since Smith and Gallagher⁵ measure only the Hanle Effect widths due the absorption from the ground state, their result cannot be affected by cascading. Similarly, although our excitation is non-threshold, our experience has been that the resonance transitions are much more strongly excited than transitions between higher states and the upper state of the resonance transition. Accordingly, we measured phase shifts across the observed contour and found little of the variation expected if the 3d level were excited with a cross-section comparable to that of the upper level of the resonance transition. This result is in agreement with relative mildness of the excitation in electron beams compared with that of the beam-foil method. Thus, we feel that the slight disagreement and larger than usual spread of values for the $3s^2S-3p^2P^0$ Mg II upper level lifetime is due to the difficulty of separating the similar lifetime of the excited state level which feeds the upper level of the resonance transition. This observation is supported by the trend to a longer mean life for the 3p level of Mg II from the Hanle Effect experiment and our experiment to Anderson et al.² where spectral separation of the cascading multiplet was possible to Barry et al.³, where it was not.

Ca I, II

The measurements for the Ca I resonance multiplet at 4227 \AA yielded a lifetime of 4.6 ± 0.5 nsec, while the "H and K lines" of the important Ca II multiplet

at 3934 and 3968 Å yielded identical lifetimes of 6.5 ± 0.7 nsec. These lifetimes are in very good agreement with earlier results from the "density independent" techniques quoted above.^{2,5,8,10} The agreement with the "density dependent" methods is not as good, but in most cases, within experimental error limits.^{2,14} The calcium ion multiplet (H and K lines) has a similar cascading scheme to that for the corresponding Mg II multiplet at 2796-2803 Å, but there is no spectral coincidence of the cascading and resonance transitions. Again, we find that the Hanle Effect measurement⁵ and our measurement indicate somewhat shorter lifetimes than are found in the beam-foil experiment. This may be due to the unusual difficulty of removing the effects of the growing-in cascade from the upper states feeding the level under study. All of these states have mean lives appreciably shorter than that of the H and K levels.² As noted above, the Hanle Effect does not suffer at all from cascading effects, and our experiment is less subject to them than the beam-foil experiment due to reduced excitation of the cascading levels.

The Ca I resonance multiplet at 2722 Å has been studied previously only by the density dependent methods of anomalous dispersion¹⁶ ($\tau = 3700$ nsec) and the arc method¹⁷ ($\tau = 135$ nsec). We find a much shorter lifetime of 16.6 ± 2.0 nsec. This value is more in line with what might be expected in view of the lifetime found by us for the analogous Mg I transition at 2026 Å ($\tau = 10.4$ nsec). Since the density dependent methods depend upon a calibration of some other transition and only measure relative values, all results are scaled by their reference. With the advent of many accurate reference lines, these methods will become much more useful, in particular since they are often able to excite many more transitions than the present methods by use of a variety of sources.

Al I and B I

The transitions in Al I at 3944 Å and 3082 Å and the B I transition at 2497 Å have been previously studied via beam-foil,^{22,23} and for the Al I multiplets, by phase-shift^{18,19} and level-crossing²⁰ techniques, using resonance photon excitation. We find complete agreement with these methods for the two transitions in Al I, but derive a somewhat shorter lifetime for the B I transition than the beam-foil measurements which do not agree with each other. Possibly the cascading scheme is responsible for these deviations in the beam-foil results. Our f -values for B I 2497 Å and Al I 3944 Å are similar as is the case for corresponding transitions in the Ca and Mg spectra studied here.

In Table II, we list f -values for the transitions that we have studied. The oscillator strengths are mean values of those measurements which we have discussed in the text, except that we have neither averaged in any of the measurements derived from the density-dependent type experiments, nor those experiments that may suffer from a probable systematic error. In this way, we present data taken under the most error-free conditions. Except for the higher resonance series members for Ca I and Mg I for which our results are the first obtained from density-independent techniques and the B I 2497 Å transition where disagreement still exists the oscillator strengths listed are reliable to within 10 percent.

Acknowledgement

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Table I

Mg I, II and Ca I, II Radiative Lifetimes and Absolute Transition Probabilities

Element	λ (Å)	Transition	J"-J'	A_T (10^8 sec^{-1})	f-value	τ (10^{-9} sec)*	Cascading Parameters
Mg I	2852.96	$3s^2 1s^0 - 3p 1p^0$	0-1	5.26	1.86	1.90 ± 0.3	T = 100, $\beta = 0.63$
Mg I	2026.54	"	0-1	0.96	0.18	10.4 ± 2.0	T = 100, $\beta = 0.27$
Mg I	1828.17	"	0-1	0.36	0.055	28 ± 5.0	T = 150, $\beta = 0.20$
Mg II	2803.52	$3s^2 s - 3p^2 p^0$	$\left. \begin{array}{l} 1/2-1/2 \\ 1/2-3/2 \end{array} \right\}$	2.70	0.31	3.7 ± 0.5	T = 85, $\beta = 0.25$
	2796.34			2.70	0.62		
Ca I	4226.73	$4s^2 1s^0 - 4p 1p^0$	0-1	2.18	1.75	4.6 ± 0.6	T = 90, $\beta = 0.18$
Ca I	2721.65	"	0-1	0.60	0.20	16.6 ± 2.0	T = 200, $\beta = 0.65$
Ca II	3968.47	$4s^2 s - 4p^2 p^0$	$\left. \begin{array}{l} 1/2-1/2 \\ 1/2-3/2 \end{array} \right\}$	1.41	0.34 [†]	7.1 ± 0.80	T = 110, $\beta = 0.28$
	3933.66			1.41	0.68 [†]		
Al I	3944.01	$3p^2 p^0 - 4s^2 s$	1/2-1/2	1.45	0.12	6.9 ± 0.7	-
Al I	3082.16	$3p^2 p^0 - 3d^2 d$	1/2-3/2	0.76	0.18	13.1 ± 2.0	T = 30, $\beta = 0.14$
B I	2496.77	$2p^2 p^0 - 3s^2 s$	1/2-1/2	4.0	0.12	2.5 ± 0.5	T = 30, $\beta = 1.2$

A_T = Total absolute transition probability to all lower states.

T = Cascading state lifetime in nsec, β = ratio of excitation by cascading to direct excitation

* Uncertainty limits apply to A_T , not f-values (see (a) below).

+ Assuming a branching ratio between the 2S and 2D lower levels of 17.5:1, see refs. 5,17.

a) f-value given is the average discussed in text.

Table II

Comparison with Previous Results

<u>Species</u>	<u>Wavelength</u>	<u>Lifetime*</u>	<u>Previous Results*</u>	<u>Reference</u>	<u>Technique</u>
Mg I	2852.96	1.90±0.3	1.99±0.08	10	phase shift
			2.03±0.06	5	Hanle Effect
			3.29±0.16	9	phase shift
			3.56±0.9	14	anomalous dispersion
Mg I	2026.54	10.4±2.0	8.3	15	theory
Mg I	1828.17	28±5	-	-	-
Mg II	2796.34, 2803.52	3.7±0.5	3.67±0.18	5	Hanle Effect
			3.84	18	theory
			3.97	19	theory
			4.2±0.4	2	beam-foil
			4.8±0.4	3	beam-foil
Ca I	4226.73	4.6±0.6	4.48±0.15	8	Hanle Effect
			4.62±0.15	5	Hanle Effect
			4.67±0.11	10	phase shift
			6.2±0.5	2	beam-foil
			5.4±0.14	14	Hook
Ca I	2721.65	16.6±2.0	3700	16	anomalous dispersion
			135	17	arc
Ca II	3933.68, 3968.47	7.1±0.8	6.72±0.20	5	Hanle Effect

continued

Table II

<u>Species</u>	<u>Wavelength</u>	<u>Lifetime*</u>	<u>Previous Results*</u>	<u>Reference</u>	<u>Technique</u>
Al I	3944-3961	6.9±0.7	6.4±0.4	4	beam-foil
			7.05±0.3	20	phase-shift
			6.43±0.12	9	phase-shift
Al I	3092	13.1±1.5	13.4±0.4	4	beam-foil
			13.7±0.4	20	phase-shift
			13.6±0.4	21	level-crossing
B I	2497	2.5±0.4	5.7±0.2	23	beam-foil
			3.8±0.2	22	beam-foil

Wavelengths in Å

* Lifetimes in nanoseconds

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RKR Franck-Condon Factors for Blue and Ultraviolet Transitions of some
Molecules of Astrophysical Interest and some Comments on the Interstellar
Abundance of CH, CH⁺, and SiH⁺.*

BY

H.S. Liszt and Wm. Hayden Smith
Princeton University Observatory
Princeton, New Jersey 08540

Abstract

RKR Franck-Condon factors for thirteen of the blue and ultraviolet transitions of AlF, AlO, BH, BD, CH, CD, CH⁺, SiO, and SiH⁺ have been calculated. The interstellar abundances of CH, CH⁺ and SiH⁺ are discussed with regard to recent laboratory measurements, our Franck-Condon factors, and observations of the sun and the interstellar medium.

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JQSR T (IN PRESS)

Introduction

This is the second paper in a series (see ref. 1) presenting Franck-Condon factors for blue and ultraviolet transitions in molecules of astrophysical interest, in this case metal oxides, hydrides, and one halide. In general the same comments apply here as to the earlier calculations. Briefly, the work was done using the program of Zare⁽²⁾ in double precision on the IBM 360/91 system at the Princeton University Computer Center. Potential curves were generated from the molecular constants listed in Table 1, with the exception of CH^+ for which it was necessary to use the observed vibrational and rotational intervals. The transitions fall in the range 2000-5000 \AA . Some of the Franck-Condon factors given here have important implications for astrophysical processes in the interstellar medium and these are discussed below.

Some idea of the internal accuracy of our Franck-Condon factors may be gained by comparing the A10 A-X calculation with the work of Sharma,⁽³⁾ who used the same program on this system earlier. Agreement for the range over which our and Sharma's tables overlap is generally better than 5% for the larger Franck-Condon factors and somewhat worse for the smaller ones. The very smallest ones are probably not reliable except in order of magnitude. Differences are due in part to computational errors but mostly to the method used to generate the potential functions employed. Slight differences in the molecular constants used could account for any differences, but Sharma does not state how he generated his curves.

SiH^+

The A state of SiH^+ is extremely shallow ($w_e = 534.16 \text{ cm}^{-1}$, $w_e x_e = 72.80 \text{ cm}^{-1}$) and has only two bound levels:⁽⁴⁾ In view of this and the fact that the difference in bond lengths for the A and X states (0.37\AA) is greater than the width of the potential well for the X state ground level (0.26\AA) it is not surprising that the sum $\sum_i q_{vi}$ is not nearly equal to unity. There must exist a large transition probability from the lowest level of the X state into the dissociation continuum of the A state. In interstellar space where recombination times are very long, most SiH^+ molecules formed will be photodissociated relatively soon and we should expect not to see SiH^+ in interstellar spectra.

Recently, Grevesse and Sauval⁽⁵⁾ reported an empirical determination of f-values for the (0-0) and (1-0) transitions of the A-X system of SiH^+ , based on fitting theoretical line profiles to features in the solar spectrum. If one desires to derive an electronic oscillator strength $f_{el} = \sum_i q_{vi}$ from their paper, it is not sufficient to set $f_{el} = f_{ic} = 0.0009$. The continuum contribution (as yet unmeasured) must be accounted for. This can be done approximately by setting $f_{el} = \frac{f_{00}}{q_{00}} = 7 \times 10^{-3}$ (q_{00} is the Franck-Condon factor) but this is correct only if the discrete and continuum transitions have the same dipole strength; however, we have reservations about using astrophysical objects as light sources for the determination of such molecular parameter since conditions under which molecular lines are formed are not always well

described by (equilibrium) models and the "experimental" situation must be considered highly complex.



A set of Franck-Condon factors, $q_{v'0}$ has been calculated by Nicholls (using Morse potentials) and quoted by Herbig.⁽⁶⁾ The value of 0.53 is given by Herbig for q_{00} , which differs substantially from our $q_{00} = 0.92$. This is an example of the extreme sensitivity of this type of calculation to using the correct potential. The A and X states of CH^+ are very poorly represented by Morse curves. Though the difference in bond lengths (0.1\AA) is significant, the anharmonicity of the upper state and the width of both the A and X states (about three times the difference in bond lengths) make for a large overlap between them. This has the immediate effect that the interstellar abundance derived by Herbig for the HI region in front of ζ Oph is high by a factor of order 1.8. It makes more difficult the problem of getting the predicted number densities of CH and CH^+ to agree with the observed equivalent widths.

The problem of predicting the number density $n(\text{CH}^+)$ and number density ratio $n(\text{CH}^+)/n(\text{CH})$ is a fairly old one. It has been thought, since the paper of Bates and Spitzer,⁽⁷⁾ that the process of two-body radiative recombination, for example, $\text{C}^+ + \text{H} \rightarrow \text{CH}^+(\text{A}^1\text{W}) \text{CH}^+(\text{X}^1\Sigma^+) + h\nu$ (and similar equations for the A, B, and C states of CH), is insufficient to account for the observed number densities. This process has been rehabilitated by Herbig who concluded that it works better near ζ Oph than in the general

interstellar field, owing to the high mass density in that region ($n(\text{H}) \approx 700$). He achieved fair success by assuming a high degree of diabaticity for the collisions involved in the production of CH^+ . The question of adiabaticity arises because interstellar C^+ should be mostly $\text{C}^+(^2\text{P}_{\frac{1}{2}}^0)$ and this does not correlate with the $\text{A}^1\Pi$ state, but with the $\text{X}^1\Sigma_1^+$ ground state and a $3\Sigma_1^+$ repulsive state. Only a level crossing will produce CH^+ by direct radiative two-body recombination from $\text{C}^+(^2\text{P}_{\frac{1}{2}}^0)$ and $\text{H}(^2\text{S})$. A level crossing may be achieved at either large or small internuclear separation, but we wish to argue that neither case is sufficiently diabatic to produce appreciable amounts of CH^+ .

Our RKR calculations show that the repulsive parts of the $\text{X}^1\Sigma_1^+$ and $\text{A}^1\Pi$ potential curves are not even close to intersecting at an energy corresponding to the dissociation limit. At the low temperatures of interstellar space ($T \leq 50$ K) the kinetic energy required to lift the $\text{C}^+ + \text{H}$ collision complex high enough on the repulsive part of the $\text{X}^1\Sigma_1^+$ potential curve to cross levels is simply not available.

For large internuclear distances it is possible to cross from the repulsive $3\Sigma_1^+$ state arising from $\text{C}^+(^2\text{P}_{\frac{1}{2}}^0)$ to the $\text{A}^1\Pi$ via a forbidden level-crossing of the sort which gives rise to one of the predissociations in the OH A state⁽⁸⁾ and which causes a maximum to occur in the potential curve of the $\text{A}^1\Pi$ state of BH around 2\AA internuclear separation.⁽⁹⁾ However, for CH^+ , the crossing would occur at very large ($\approx 12\text{\AA}$) separation and the slopes of

the potential curves involved will be extremely small. When this is combined with the very small relative kinetic energy of the separated atoms it seems highly unlikely that any appreciable level crossing will occur. In fact, assuming that the interaction energy of the states involved is of the order of the multiplet splitting in the ground state of C^+ , 64cm^{-1} , and using a relative velocity corresponding to 50°K , one can estimate (using the Landau-Zener formalism⁽¹⁰⁾) the difference in slopes the $3^1\Sigma^+$ and $X^1\Sigma^+$ states would have to have at 12\AA to achieve level crossing. This is of the order of $2000\text{cm}^{-1}/\text{\AA}^\circ$, and it is likely that neither curve has a slope which is as large as a few percent of this. The A state potential curve will in fact be more highly populated from the normal occupation of the $C^+(^2P_{3/2})$ state due to collisions of C^+ with ambient thermalized electrons. When one follows this line of reasoning, the agreement of theory and observation for the region of 10μ is no better than in previous investigations in the general field. This problem is one of considerable complexity and it will be treated at length in a future paper.

Recently, one of us (W.H.S. see ref.11) has published an experimental value for the oscillator strength of the CH^+ A-X (C-O) band of 0.06, the measurement having been performed with a phase-shift type lifetime apparatus. This may be considered large for a valence-type transition such as occurs in CH^+ . Though the CH^+ A-X transition f-value quoted by Smith could have been subject to systematic errors due to possible cascading effects as noted in the paper,⁽¹¹⁾ the corresponding transition measured in the isovalent molecule BH yielded an f-value, $f_{00}=0.035$. This measurement was not subject to the

possible errors noted above. Corresponding transitions in isovalent molecules should have similar oscillator strengths if, as in this case, they are similar vibrationally. Thus, the BH oscillator strength implies that the approximation necessary to analyze the CH^+ lifetime data, i.e., neglect of possible cascading effects, did not introduce order of magnitude errors.

Recently, Lutz⁽¹²⁾ has criticized the use of BH to support the CH^+ measurement. He preferred to compare with SiH^+ and used the f_{00} and f_{10} values of Grevesse and Sauval⁽⁵⁾ to derive an oscillator strength of 1.1×10^{-3} . As shown by our Franck-Condon factor calculations, this is in error due to neglect of transitions into the continuum. Of the three A-X transitions in BH, CH^+ , and SiH^+ , the vibrational structure of SiH^+ A-X is seen to be quite different from the other two and comparison should be made among the dipole strengths. However it is precisely this quantity which is unknown for SiH^+ . In any case, the remeasurement of the CH^+ oscillator strength with sufficiently high resolution to eliminate spectral overlap by CH emission has begun in our laboratory. Also highly desirable in this context are measurements or accurate calculations of all the cross-sections for photo-ionization, electron capture, etc. used in the detailed theory of radiative recombination. In spite of twenty years having passed since Bates and Spitzer first estimated them, there does not exist any better set of values for these critical parameters.

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TABLE CAPTIONS

- Table 1: Molecular Constants
- Table 2: Franck-Condon factors and r-centroids for the AlF A-X transition
- Table 3: Franck-Condon factors and r-centroids for the AlO A-X transition
- Table 4: Franck-Condon factors and r-centroids for the BH A-X transition
- Table 5: Franck-Condon factors and r-centroids for the BD A-X transition
- Table 6: Franck-Condon factors and r-centroids for the CH A-X transition
- Table 7: Franck-Condon factors and r-centroids for the CH B-X transition
- Table 8: Franck-Condon factors and r-centroids for the CH C-X transition
- Table 9: Franck-Condon factors and r-centroids for the CD A-X transition
- Table 10: Franck-Condon factors and r-centroids for the CD B-X transition
- Table 11: Franck-Condon factors and r-centroids for the CD C-X transition
- Table 12: Franck-Condon factors and r-centroids for the CH⁺ A-X transition
- Table 13: Franck-Condon factors and r-centroids for the SiH⁺ A-X transition
- Table 14: Franck-Condon factors and r-centroids for the SiO A-X transition

State	T _e	w _e	w _e x _e	B _e	α _e	r _e	References	Comments
Al ²⁷ _{F¹⁹} X ^{Σ⁺} A ^Π	0 43947.9	801.90 804.6	4.70 6.34	μ _a =11.1521 .5520 .5566	0.0040 0.0055	1.654 1.648	13, 14 13, 14	
Al ²⁷ _{O¹⁶} X ^{Σ⁺} A ^{Σ⁺}	0 20699.2	978.2 870	7.12 3.80	μ _a =10.0452 .64148 .60417	0.00575 0.00453	1.6176 1.6667	13, 15 13, 15	
B ¹¹ _{H¹} X ^{Σ⁺} A ^Π	0 23063.7	2367.5 2345.2	49 ^a 129	μ _a =0.923585 12.0164 12.205	0.408 0.5213	1.236 1.223	9, 13 9, 13	$a \omega_e x_e = 0.6 \omega_e \frac{x_e}{B_e}$
B ¹¹ _{H²} X ^{Σ⁺} A ^Π	0 23086.2	1759 1680	28 ^a 43	μ _a =1.703147 6.54 6.653	0.171 0.280	1.230 1.220	9, 13 9, 13	$a \omega_e x_e = 0.6 \omega_e \frac{x_e}{B_e}$
C ¹² _{I¹} X ^Π A ^{Σ⁺} B ^{Σ⁺} C ^{Σ⁺}	0 23150 25949 31821	2861.6 2921.0 2542.5 2824.1	64.3 90.4 373.8 105.8	μ _a =.930024 14.457 14.912 12.887 14.629	0.534 0.670 0.485 0.744	1.1198 1.1026 1.1861 1.1132	13 13 13 13	
C ¹² _{H²} X ^Π A ^{Σ⁺} B ^{Σ⁺} C ^{Σ⁺}	0 23183 25993 31828	2101.0 2144.5 1808.0 2075.4	34.7 48.7 201.5 57.0	μ _a =1.725173 7.808 8.032 7.171 7.880	0.212 0.260 0.528 0.282	1.118 1.103 1.167 1.113	13 13 13 13	
(C ¹² _{H¹}) ⁺ X ^{Σ⁺} A ^Π	0 24145	a a	a a	μ _a =.930021 14.177 11.898	a a	1.1309 1.2345	16 16	^a observed intervals used here
(S ³² _{I¹}) ⁺ X ^{Σ⁺} A ^Π	0 25725	2157.1 534.16	34.21 72.80	μ _a =.973077 12.0164 12.2050	.4080 .5213	1.5040 1.8782	4 4	
S ³² _{O¹⁶} X ^{Σ⁺} A ^Π	0 42835.3	1241.44 852.70	5.92 6.44	μ _a =10.18013 .7278 .6312	.0050 .0069	1.509 1.620	13, 17 13, 17	0 0.277

Table 1

v_i

	0	1	2	3
0	.9958 1.657	.42-2		
1	.41-2	.9908 1.670	.49-2	.2-3
2	.1-3	.47-2	.9912 1.686	.35-2
3			.33-2	.9941 1.702

Table entries: $q_{v',v''}$ (Franck-Condon factor followed by power of Ten)
 $r_{v',v''}$ (r-centroid in Angstroms)

Table 2

0 078

	0	1	2	3	4	5	6	7
0	.7228 1.647	.2270 1.575	.4313-1 1.509	.6223-2 1.443	.7341-3 1.370			
1	.2432 1.726	.3369 1.658	.3015 1.583	.9549-1 1.517	.1946-1 1.451	.3004-2 1.381	.3747-3 1.301	
2	.3209-1 1.812	.3528 1.737	.1331 1.672	.2955 1.519	.1401 1.525	.3783-1 1.460	.7325-2 1.392	.1115-2 1.315
3	.1859-2 1.924	.7723-1 1.824	.3850 1.748	.3759-1 1.699	.2526 1.598	.1704 1.532	.5856-1 1.468	.1381-1 1.401
4		.5980-2 1.939	.1249 1.836	.3755 1.760	.3570-2 1.777	.1979 1.606	.1854 1.538	.7898-1 1.475
5		.1284-3 2.163	.1205-1 1.955	.1698 1.848	.3457 1.772	.1967-2 1.524	.1446 1.613	.1872 1.545
6			.2705-3 2.206	.1948-1 1.971	.2097 1.860	.3084 1.785	.1539-1 1.629	.9909 1.620
7				.4305-3 2.258	.2760-1 1.988	.2441 1.872	.2708 1.799	.3385-1 1.646
8					.5650-3 2.324	.3579-1 2.006	.2734 1.885	.2366 1.814
9						.6313-3 2.412	.4348-1 2.024	.2985 1.897
10							.6006-3 2.538	.5023-1 2.044
11								.4696-3 2.744
12								

Table entries: $q_{v',v''}$ (Franck-Condon factor followed by power of Ten)

$r_{v',v''}$ (r-centroid in Angstroms)

Table 3

0 079

	8	9	10	11	12	13	14	15
0								
1								
2	.1400-3 1.226							
3	.2506-2 1.328	.3720-3 1.244						
4	.2219-1 1.410	.4716-2 1.340	.8140-3 1.261	.1212-3 1.173				
5	.9700-1 1.482	.3194-1 1.418	.7832-2 1.350	.1551-2 1.276	.2647-3 1.194			
6	.1789 1.551	.1113 1.489	.4238-1 1.426	.1185-1 1.360	.2661-2 1.289	.5150-3 1.213		
7	.6333-1 1.628	.1640 1.557	.1212 1.495	.2678-1 1.433	.1665-1 1.370	.4204-2 1.301	.9133-3 1.230	.1857-3 1.163
8	.5199-1 1.656	.3717-1 1.636	.1451 1.562	.1266 1.500	.6252-1 1.440	.2207-1 1.378	.6210-2 1.313	.1502-2 1.245
9	.2075 1.830	.6724-1 1.662	.1936-1 1.646	.1248 1.567	.1278 1.506	.7105-1 1.446	.2787-1 1.386	.8673-2 1.323
0	.3203 1.911	.1839 1.848	.7861-1 1.664	.8288-2 1.660	.1045 1.572	.1255 1.510	.7802-1 1.452	.3377-1 1.393
1	.5565-1 2.065	.3396 1.924	.1658 1.867	.8600-1 1.664	.2348-2 1.687	.8555-1 1.577	.1203 1.515	.8318-1 1.458
2		.5941-1 2.088	.3571 1.938	.1529 1.887	.8971-1 1.662	.1234-3 1.848	.6848-1 1.582	.1129 1.519

Table entries: $q_{v',v''}$ (Franck-Condon factor followed by power of ten)
 $r_{v''}$ (r-centroid in Angstroms)

Table 3 (cont.)

8	9	10	11	12	13	14	15
13		.6124-1 2.113	.3733 1.951	.1447 1.908	.9024-1 1.656	.4590-3 1.549	.5364-1 1.588
14			.6094-1 2.141	.3885 1.966	.1411 1.931	.8808-1 1.646	.2467-2 1.615
15				.5838-1 2.173	.4026 1.980	.1417 1.953	.8370-1 1.632
16					.5352-1 2.211	.4154 1.995	.1467 1.975
17						.4644-1 2.257	.4263 2.010
18							.3758-1 2.318
19							

Table entries: $q_{v',v''}$ (Franck-Condon factor followed by power of ten)
 $r_{v',v''}$ (r-centroid in Angstroms)

v'	0	1	2
0	.9986 1.245		
1		.9979 1.284	
2			.9967 1.311

Table entries: $q_{v'v''}$ (Franck-Condon factor followed by power of Ten)
 $r_{v'v''}$ (r-centroid in Angstroms)

Table 4

	0	1	2
0	.9992 1.257		
1		.9942 1.320	
2			.9819 1.365

Table entries: $q_{v'v''}$ (Franck-Condon factor followed by power of Ten)
 $r_{v'v''}$ (r-centroid in Angstroms)

Table 5

	0	1	2
0	.9930 1.136		
1		.9067 1.185	
2			.9894 1.214

Table entries: $q_{v',v''}$ (Franck-Condon factor followed by power of Ten)

$r_{v',v''}$ (r-centroid in Angstroms)

Table 6

0 084

v_i

	0	1
0	.8623 1.168	.1231 .9802
1	.1187 1.441	.5538 1.207
2	.1794-1 1.468	.2110 1.509
3		.9671-1 1.484

Table entries: $q_{v',v''}$ (Franck-Condon factor followed by power of Ten)

$r_{v',v''}$ (r-centroid in Angstroms)

Table 7

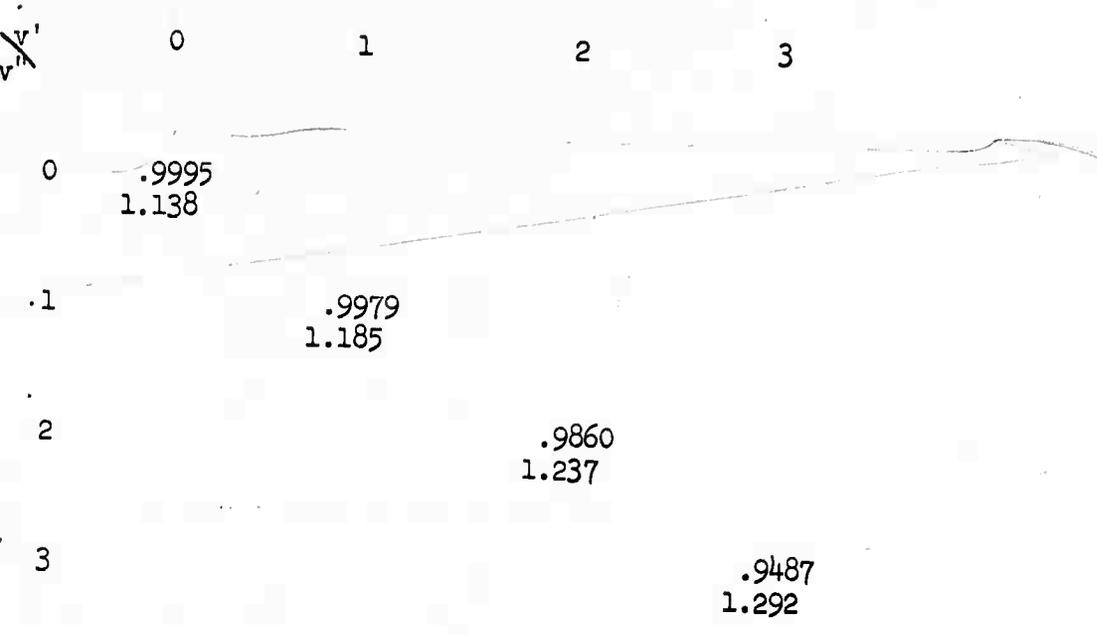


Table entries: $q_{v',v''}$ (Franck-Condon factor followed by power of Ten)

$r_{v',v''}$ (r-centroid in Angstroms)

Table 8

2/4

	0	1	2
0	.9899 1.127		
1		.9771 1.162	
2			.9767 1.198

Table entries: $q_{v'v''}$ (Franck-Condon factor followed by power of Ten)
 $r_{v'v''}$ (r-centroid in Angstroms)

Table 9

	0	1
0	.8513 1.160	.1389 1.002
1	.1324 1.370	.5834 1.189
2	.1530-1 1.449	.2288 1.406

Table entries: $q_{v',v''}$ (Franck-Condon factor followed by power of Ten)

$r_{v',v''}$ (r-centroid in Angstroms)

Table 10

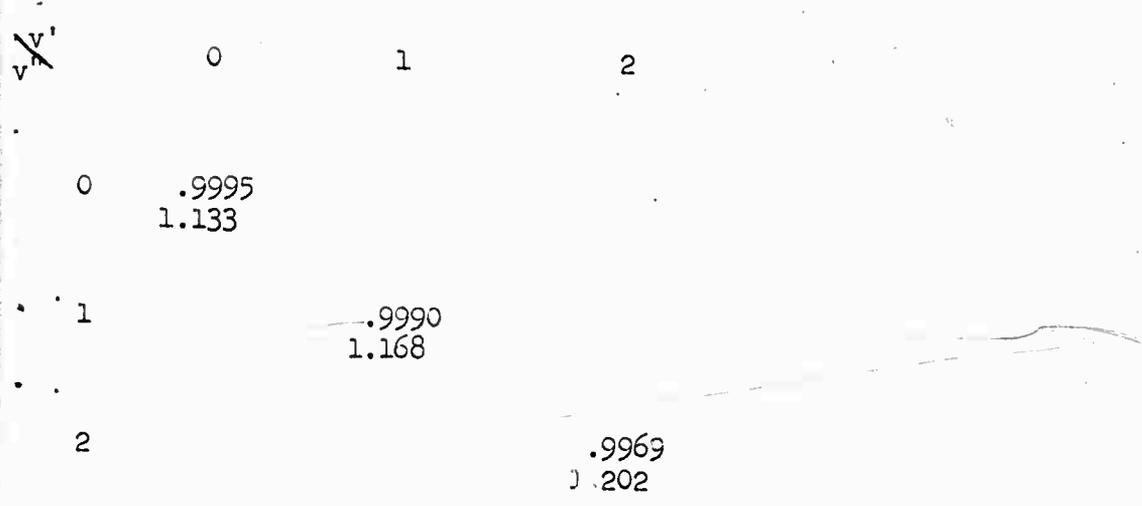


Table entries: $q_{v'v''}$ (Franck-Condon factor followed by power of Ten)
 $r_{v'v''}$ (r-centroid in Angstroms)

Table 11

	0	1	2	3	4
0	.9248 1.167	.6135-1 .870	.2835-2 1.775	.8213-2 1.103	.2263-2 .8285
1	.5350-1 1.594	.7868 1.194	.1016 .9270	.1212-1 1.637	.3450-1 1.124
2	.2040-1 1.343	.7139-1 1.770	.6416 1.222	.1540 1.029	.2185-1 1.572
3		.7277-1 1.344	.8160-1 1.918	.4440 1.244	.2087 1.134
4			.1480 1.378	.0934 2.016	.2874 1.252
5				.2332 1.433	.9400-1 2.111

Table entries: $q_{v',v''}$ (Franck-Condon factor followed by power of Ten)
 $r_{v',v''}$ (r-centroid in Angstroms)

Table 12

4/4

	0	1
0	.8566-1 1.616	.1505 1.585
1	.1146 1.777	.8560-1 1.790
2	.1651 1.857	.7050-1 1.794
3	.1611 1.941	.1368-1 1.981
4	.1478 2.009	
5	.1149 2.097	.1932-1 2.052

Table entries: $q_{v'v''}$ (Franck-Condon factor followed by power of Ten)
 $r_{v'v''}$ (r-centroid in Angstroms)

Table 13

	0	1	2	3	4	5	6	7
0	.1405 1.562	.2546 1.539	.2487 1.516	.1745 1.493	.9883-1 1.471	.4819-1 1.448	.2108-1 1.425	.8508-2 1.403
1	.2790 1.596	.1300 1.574	.6938-3 1.563	.5841-1 1.527	.1379 1.505	.1487 1.483	.1120 1.461	.6797-1 1.439
2	.2741 1.629		.1220 1.584	.1014 1.562	.7805-2 1.544	.2168-1 1.515	.8659-1 1.495	.1181 1.474
3	.1773 1.661	.9730-1 1.638	.9524-1 1.617	.4276-2 1.590	.9398-1 1.572	.7964-1 1.552	.9770-2 1.533	.1076-1 1.505
4	.8463-1 1.693	.1922 1.670	.1937-3 1.657	.1093 1.627	.3817-1 1.606	.1264-1 1.581	.8153-1 1.562	.6426-1 1.542
5	.3168-1 1.729	.1698 1.702	.7221-1 1.680	.6296-1 1.658	.2514-1 1.636	.8902-1 1.616	.1218-1 1.598	.2100-1 1.571
6	.9651-2 1.755	.9708-1 1.733	.1614 1.711	.7670-3 1.689	.1021 1.668	.4429-2 1.649	.5342-1 1.626	.6138-1 1.606
7	.2542-3 1.786	.4084-1 1.763	.1521 1.741	.7734-1 1.720	.3281-1 1.699	.5475-1 1.678	.5266-1 1.658	.4201-2 1.634
8	.5281-3 1.816	.1348-1 1.794	.9057-1 1.772	.1505 1.750	.8183-2 1.730	.8432-1 1.708	.3600-2 1.688	.7365-1 1.667
9		.3621-2 1.825	.3914-1 1.802	.1350 1.781	.9246-1 1.760	.9879-2 1.737	.7773-1 1.718	.1424-1 1.697

Table entries: $q_{v',v''}$ (Franck-Condon factor followed by power of Ten)

$r_{v',v''}$ (r-centroid in Angstroms)

Table 14

	8	9	10	11	12	13
0	.3238-2 1.380	.1182-2 1.359	.4195-3 1.337	.1466-3 1.317		
1	.3568-1 1.417	.1691-1 1.395	.7445-2 1.374	.3112-2 1.353	.1255-2 1.333	.4948-3 1.313
2	.1054 1.452	.7381-1 1.431	.4409-1 1.410	.2358-1 1.389	.1164-1 1.369	.5433-2 1.349
3	.6013-1 1.486	.9471-1 1.465	.9479-1 1.445	.7372-1 1.424	.4868-1 1.404	.2869-1 1.384
4	.9461-2 1.524	.6210-2 1.496	.4413-1 1.478	.7694-1 1.459	.8400-1 1.439	.7104-1 1.419
5	.7266-1 1.553	.5323-1 1.534	.8826-2 1.516	.3694-2 1.488	.3299-1 1.472	.6273-1 1.453
6	.2136-2 1.594	.2709-1 1.563	.6505-1 1.545	.4540-1 1.526	.8521-2 1.508	.2004-2 1.482
7	.6402-1 1.617	.3816-1 1.598		.3039-1 1.555	.5832-1 1.538	.4000-1 1.520
8	.1313-1 1.649	.2087-1 1.627	.5987-1 1.608	.2229-1 1.591	.9702-3 1.555	.3126-1 1.549
9	.3754-1 1.678	.5170-1 1.658	.2850-3 1.651	.3441-1 1.619	.5032-1 1.601	.1275-1 1.586

Table entries: $q_{v',v''}$ (Franck-Condon factor followed by power of Ten)

$r_{v',v''}$ (r-centroid in Angstroms)

Table 14 (cont.)

	0	1	2	3	4	5	6	7
10		.8108-3 1.855	.1314-1 1.833	.7816-1 1.811	.1447 1.790	.2542-1 1.770	.5580-1 1.747	.2816- 1.728
11		.1538-3 1.887	.3561-2 1.864	.3307-1 1.841	.1175 1.820	.1095 1.799		.8163- 1.757
12			.7993-3 1.895	.1089-1 1.872	.6387-1 1.850	.1371 1.828	.5070-1 1.808	.2524- 1.785
13			.1510-3 1.926	.2895-2 1.903	.2576-1 1.880	.9898-1 1.858	.1228 1.837	.6921- 1.820
14				.6359-3 1.934	.8139-2 1.911	.4962-1 1.888	.1252 1.867	.7878- 1.847
15				.1173-3 1.966	.2082-2 1.942	.1877-1 1.919	.7991-1 1.897	.1284 1.876
16					.4405-3 1.973	.5611-2 1.950	.3662-1 1.927	.1088 1.906
17						.1364-2 1.981	.1287-1 1.958	.6148- 1.936
18						.2745-3 2.013	.3605-2 1.989	.2565- 1.966
19							.8222-3 2.022	.8313- 1.998

Table entries: $q_{v'v''}$ (Franck-Condon factor followed by power of Ten)

$r_{v'v''}$ (r-centroid in Angstroms)

Table 14 (cont.)

	8	9	10	11	12	13
10	.5512-1 1.707	.1890-2 1.688	.5535-1 1.669	.2501-1 1.651	.2841-2 1.627	.4067-1 1.612
11		.6289-1 1.717	.1260-1 1.698	.2133-1 1.679	.5001-1 1.661	.8395-2 1.645
12	.5846-1 1.767	.2029-1 1.745	.2943-1 1.728	.4524-1 1.708		.3738-1 1.672
13	.6439-1 1.795	.1583-1 1.777	.5395-1 1.756	.1172 1.742	.5025-1 1.719	.1706-1 1.700
14	.4264-2 1.820	.7424-1 1.805	.4563-3 1.772	.5585-1 1.766	.1146-1 1.746	.2215-1 1.730
15	.2871-1 1.857	.3532-1 1.832	.4598-1 1.815	.2325-1 1.793	.2530-1 1.777	.4041-1 1.757
16	.1032 1.885	.1223-2 1.876	.6637-1 1.843	.9919-2 1.827	.5186-1 1.804	.9893-3 1.795
17	.1248 1.915	.5900-1 1.895	.9508-2 1.868	.6736-1 1.853	.1383-2 1.823	.5124-1 1.814
18	.8958-1 1.944	.1188 1.923	.1759-1 1.906	.4057-1 1.879	.3823-1 1.863	.2424-1 1.840
19	.4496-1 1.975	.1134 1.953	.9002-1 1.933		.6519-1 1.889	.7183-2 1.876

Table entries: $q_{v,v}$ (Franck-Condon factor followed by power of Ten)

$r_{v,v}$ (r-centroid in Angstroms)

Table 14 (cont.)