

Near-infrared bound-free emission from the NaK molecule

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We report the observation of bound-free emission corresponding to the lowest triplet transition $1^3\Pi \rightarrow 1^3\Sigma^+$ of the NaK molecule. In the experiment, specific levels of the upper triplet state were populated directly from the ground state by virtue of spin-orbit induced perturbations between the $1^3\Pi_0$ and $2^1\Sigma^+$ states. Oscillations in the fluorescence spectra between 1.1 and 1.6 μm reflect the probability distribution (wave function squared) in the bound upper state. We have also carried out quantum mechanical simulations of the fluorescence spectra, based on recent *ab initio* calculations of the relevant potential curves. These simulations verify the identification of this near-infrared emission and provide a critical test for the calculated potentials.

I. INTRODUCTION

Alkali diatomic molecules have been of interest both as a testing ground of electronic potential energy curve calculations, and as the active medium in many working and proposed laser designs. In particular, a large number of optically pumped laser (OPL) transitions have been observed in Li_2 , Na_2 , and K_2 .¹⁻¹⁰ Recently OPL transitions have also been observed in the heteronuclear molecule NaRb.¹¹ In the OPLs, molecules in low-lying thermally populated rovibrational levels of the ground ($1^1\Sigma^+$) state are pumped to levels of some electronically excited state (see Fig. 1). Lasing then takes place on transitions down to initially unpopulated high lying levels of the $1^1\Sigma^+$ state. Besides offering many new fixed-frequency laser transitions, these OPLs have yielded much useful information about the alkali molecules themselves. However, the OPLs are not continuously tunable due to the discrete nature of the bound-bound transitions.

The lowest triplet state $1^3\Sigma^+$, of all alkali molecules is unbound except for a shallow van der Waals minimum at large internuclear separation, R (see Fig. 1). Bound-free emission terminating on this repulsive triplet state should form true continua, and it was suggested in 1980 by Konowalow and Julienne that such emission could be used as a source of continuously tunable near-infrared lasers.¹² Since that time, much attention has been given to alkali triplet bands. These studies include observations of the sodium violet bands,¹³⁻²⁷ the potassium yellow bands,^{18-20,28-36} and analogous bands of Li_2 ,^{18,19,37-39} Rb_2 ,^{28,40-42} and Cs_2 .^{19,28,43-45} It is now known these bands involve transitions to the $1^3\Sigma^+$ state from a $3^3\Pi$ state which correlates at large R to one ground state atom plus one atom in the lowest D state. Near-infrared transitions to the $1^3\Sigma^+$ state from the lowest excited $3^3\Sigma$ state have also been studied.⁴⁶⁻⁵³ In recent years, Bahns and Stwalley have reported gain on the Na_2 violet bands,⁵⁴ while Wu *et al.* observed enhanced fluorescence

along the pump laser axis.²² Very recently, Wang *et al.* reported the observation of stimulated emission on these Na_2 violet bands.²⁷ Near-infrared stimulated emission on the Na_2 $1^3\Sigma_g^+ \rightarrow 1^3\Sigma_u^+$ band was reported by Dinev *et al.*,⁵⁵ but Wang *et al.*⁵⁶ have recently shown that this emission is actually atomic in nature and relates to various parametric processes.

Experimental observation of alkali triplet bands has, in general, been hindered by the dipole selection rule on spin, $\Delta S = 0$, and the fact that the molecular ground state is a singlet. Thus it is not easy to selectively excite the molecule to a specific triplet state. Many of the studies mentioned so far have relied on collisions to populate the upper triplet state. However, collisions are a nonselective population mechanism, so that much spectroscopic detail is lost. On the other hand, accurate spectroscopic constants have been obtained for a number of alkali triplet states in experiments

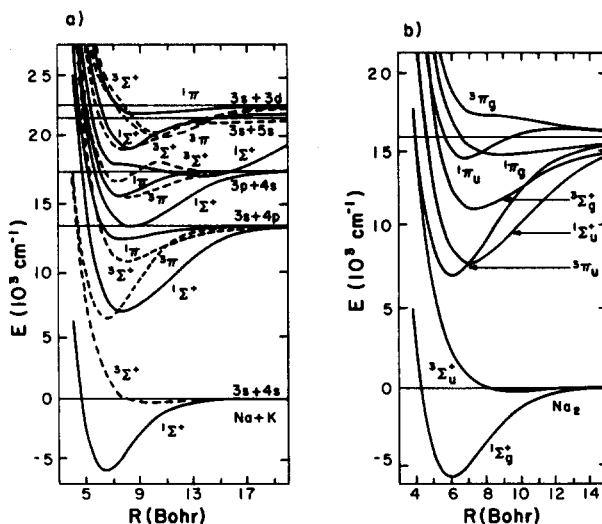


FIG. 1. (a) NaK and (b) Na_2 potential curves taken from Refs. 87 and 112, respectively (figures reproduced with permission from Dr. D. D. Konowalow). Note that throughout the text the notation $2^1\Sigma^+$ refers to the second lowest $1^1\Sigma^+$ state, etc.

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utilizing laser excitation of perturbed or mixed singlet-triplet levels. These mixed levels result from spin-orbit and other types of coupling between nearly degenerate singlet and triplet levels with the same rotational quantum number J . Laser-induced fluorescence experiments involving $2^1\Pi-2^3\Pi$ perturbations in the NaK molecule have yielded important information on the $1^3\Sigma^+$ state of that molecule.⁵⁷⁻⁶² $1^1\Sigma_u^+-1^3\Pi_u$ perturbations in Na_2 and Li_2 have also been studied extensively in recent years.⁶³⁻⁷² Of particular interest is the work of Field and co-workers, who have developed the technique of perturbation-facilitated optical-optical double resonance spectroscopy.^{23,73-79} Their work has yielded a wealth of information on many triplet levels of Li_2 and Na_2 . These various studies of $1^1\Sigma_u^+-1^3\Pi_u$ perturbations are not only important for the analysis of these states, but provide road maps for gaining access to the triplet manifolds of these molecules.

Ross, Effantin, d'Incan, and Barrow have also taken advantage of singlet-triplet perturbations to gain access to the triplet manifold.^{80,81} They and co-workers have obtained accurate spectroscopic constants for various triplet and singlet states by studying bound-bound emission using the techniques of Fourier transform spectroscopy.⁸⁰⁻⁸⁵ Of direct significance to the present work, they have accurately characterized the NaK $1^3\Pi$, $1^3\Sigma^+$, and $1^1\Sigma^+$ states.^{80,81}

In the present work we report bound-free emission corresponding to the NaK $1^3\Pi \rightarrow 1^3\Sigma^+$ transition (see Fig. 1). This transition was first observed in Ref. 86. However, in that work the upper state was populated through collisions so that most spectroscopic details were washed out. The emission appeared as a featureless continuum that decreased monotonically in intensity as the wavelength increased between 1.1 and 1.6 μm (see Fig. 4 of Ref. 86). Here, we directly populate specific perturbed $1^3\Pi-2^1\Sigma^+$ levels from the $1^1\Sigma^+$ ground state (see Fig. 2). We then observe the direct, near-infrared, bound-free emission to the $1^3\Sigma^+$

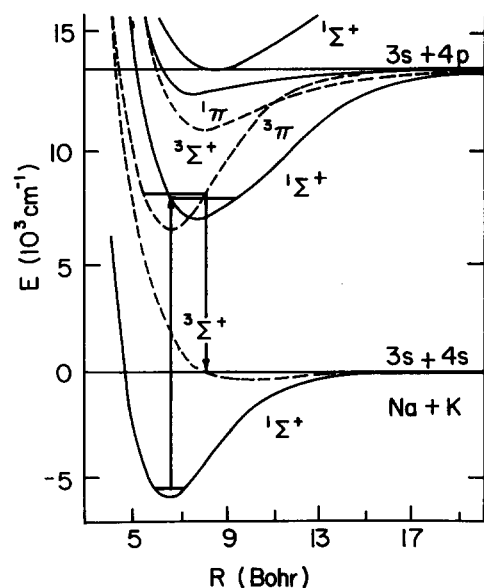


FIG. 2. Nearly degenerate levels of the $1^3\Pi_0$ and $2^1\Sigma^+$ states with the same rotational quantum number J are coupled by the spin-orbit interaction. The resulting mixed levels have both singlet and triplet character.

state. The observed spectra consist of a series of oscillations which reflect the probability distribution (wave function squared) in the upper bound state. In this preliminary study, we also present quantum calculations of theoretical spectra based upon recent *ab initio* NaK potential energy curves.^{87,88} These calculations verify the proposed explanation of the oscillatory spectra.

We are currently repeating the measurements using single-mode laser excitation. We are also calculating theoretical spectra using the accurate spectroscopic constants for the $1^1\Sigma^+$ and $1^3\Pi$ states which have been obtained from Fourier transform spectroscopy.^{80,81} The idea is to vary parameters of the lower $1^3\Sigma^+$ state until we obtain a good match to the observed spectra. Thus we hope to obtain an accurate mapping of the repulsive limb of the $1^3\Sigma^+$ state which will smoothly connect to the bound part of the curve obtained in Ref. 81. These results will be presented in a forthcoming publication.⁸⁹

II. THE EXPERIMENT

Figure 3 shows the experimental setup. The vapor containing the NaK molecules is produced in a crossed, stainless steel, heat-pipe oven⁹⁰ which was charged with a mixture of potassium and sodium in an approximately 2 to 1 ratio. This mixture was calculated to maximize the NaK concentration relative to other species.⁵⁸ The oven was operated at $\sim 360^\circ\text{C}$ with ~ 1.5 Torr of argon buffer gas. Thus the conditions were near to, but probably short of, those necessary for heat-pipe mode operation.

The laser is a multimode cw dye laser pumped by 4-5 W from an argon-ion laser. The dye laser output is typically 200-500 mW and is tunable from 680 to 775 nm using the dye LDS 722.

Fluorescence at right angles to the laser beam was dispersed by a 1/3-meter grating monochromator and detected by an intrinsic germanium detector. Longpass filters eliminated second order spectra. Fluorescence spectra were obtained by setting the laser wavelength to a value which yielded a relative maximum in the near-IR emission, and then scanning the monochromator wavelength.

In order to obtain the excitation spectra presented in

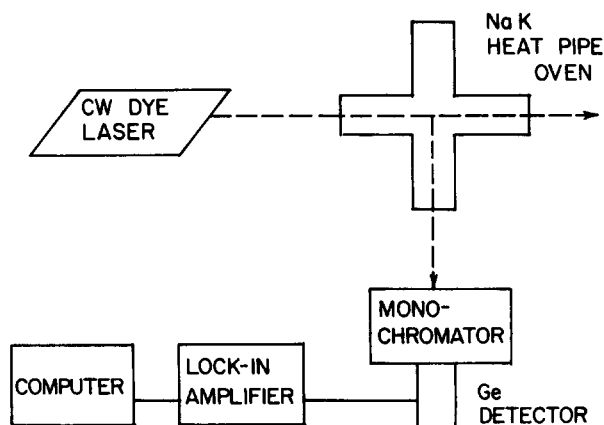


FIG. 3. Apparatus used in the fluorescence experiments.

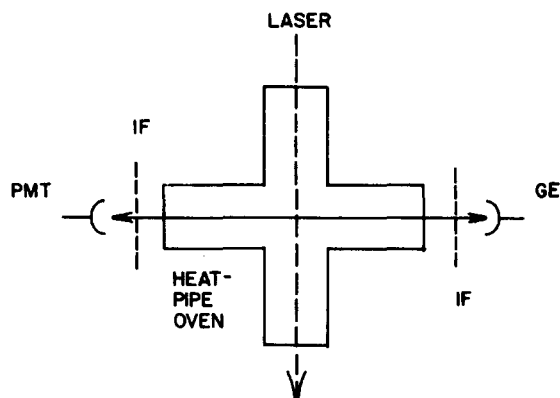


FIG. 4. Apparatus for measuring the $1^3\Pi$ excitation spectra. Ge represents the intrinsic germanium detector, while IF and PMT stand for interference filter and photomultiplier tube, respectively. The interference filters were such that, during scan of the laser wavelength, the photomultiplier recorded the total $2^1\Sigma^+ \rightarrow 1^1\Sigma^+$ emission, while the Ge detector simultaneously recorded the total $1^3\Pi \rightarrow 1^3\Sigma^+$ emission.

Sec. III C, the monochromator was replaced by an interference filter with a bandpass of 1.1 to 1.6 μm (see Fig. 4). A photomultiplier ($S-1$ response) was placed directly across from the Ge detector and an interference filter with a bandpass of 0.65 to 1.0 μm was placed between the oven and photomultiplier. Thus the germanium detector recorded the total triplet band ($1^3\Pi \rightarrow 1^3\Sigma^+$) emission, while the photomultiplier recorded the total singlet-band ($2^1\Sigma^+ \rightarrow 1^1\Sigma^+$) emission. In this experiment, the laser wavelength was scanned with a motorized drive connected to the dye laser birefringent filter. Dye laser wavelengths were measured with a monochromator-photomultiplier arrangement.

In either experiment (fluorescence or excitation spectra), the cw laser beam was chopped and the Ge detector output sent to a lock-in amplifier. The photomultiplier output was processed by an electrometer. Infrared fluorescence scans were recorded directly on a chart recorder, while for excitation spectra the lock-in and electrometer outputs were simultaneously digitized and recorded by a computer.

III. RESULTS

A. Fluorescence spectra

Figure 5 shows the fluorescence spectra obtained for various pump laser wavelengths. The spectra display the bound-free reflection structure first described theoretically by Condon in 1928,^{91,92} and later more rigorously by Coolidge *et al.*,⁹³ and Tellinghuisen and co-workers.^{94,95} Over the years, several specific cases of bound-free reflection structure have been studied both experimentally and theoretically (e.g. see Refs. 96–104 and references therein). However, a particularly graphic example of this type of emission has recently been observed in the spectrum of Hg_2 by Niefer and co-workers¹⁰⁵ (see Fig. 4 of Ref. 105).

The origin of the oscillatory structure in the present case can be crudely understood with reference to Fig. 6. The upper state ($1^3\Pi$) of the fluorescence forms roughly a harmonic well, so that the wave functions are similar to those of a harmonic oscillator. Of interest to this discussion is the prob-

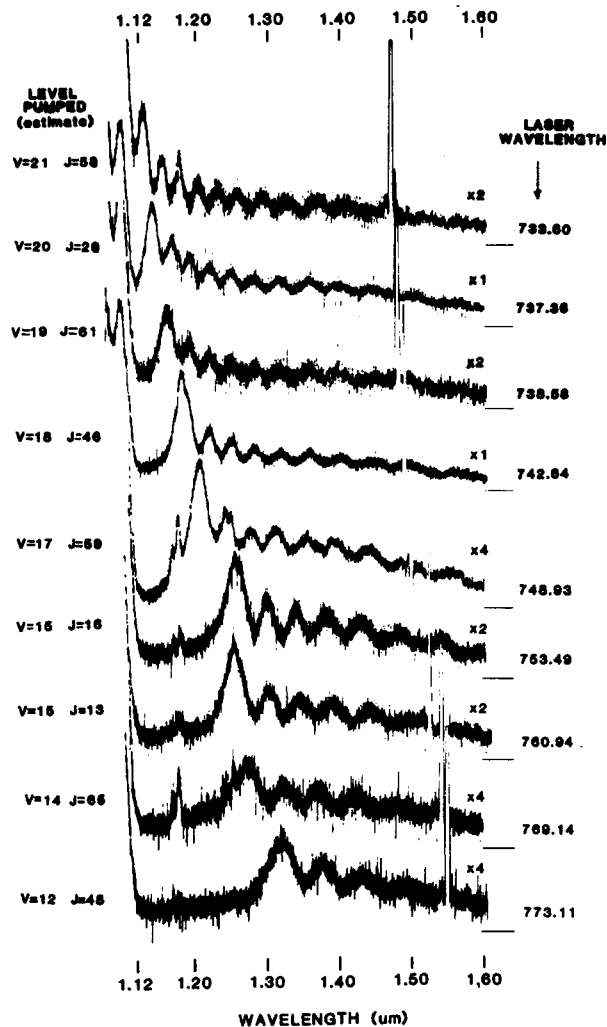


FIG. 5. NaK near-infrared $1^3\Pi \rightarrow 1^3\Sigma^+$ fluorescence spectra produced by pumping specific $1^3\Pi \leftarrow 1^1\Sigma^+$ transitions with selected frequencies from the tunable dye laser. The laser wavelength used for each spectrum is given on the right, while the v, J designation on the left is our best estimate of the pumped upper level.

ability distribution, or wave function squared, which is plotted in the figure. According to the classical Franck-Condon principle, neither the internuclear separation R nor the kinetic energy changes in an electronic transition. The first of these criteria requires that arrows representing transitions be vertical in this type of figure, while the second requires that the arrows terminate on the dashed line (the "Mulliken difference potential"^{94,95,106}) which represents the $1^3\Sigma^+$ potential energy plus the kinetic energy of the initial upper level. As can be seen in this simple classical picture, different R values yield different wavelengths in the fluorescence spectrum, and each wavelength is weighted by the probability $[\chi^*(R)\chi(R)]$ where χ is the nuclear wave function] that the atom pair is separated by that particular R . The largest peak in the fluorescence spectrum, which always occurs at the short wavelength end of the band, corresponds to the maximum in the wave function at the outer turning point. The analogous large peak corresponding to the inner turning

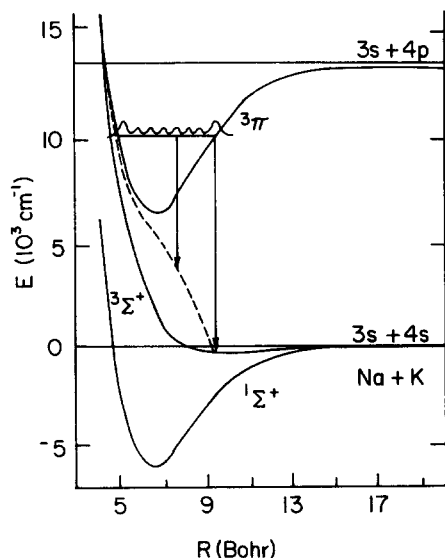


FIG. 6. A crude explanation of the oscillatory spectra can be obtained by applying the classical Franck-Condon principle (FCFP), in which the oscillations simply reflect the probability distribution (which is sketched here qualitatively) in the bound upper state. The dashed curve represents the lower state potential energy, plus the kinetic energy in the upper state (which is conserved according to the FCFP). Transitions at two R values are shown by arrows.

point cannot be observed in our case, because the difference potential becomes quite small at short R and the emission is past the long wavelength edge of our detector response. Since the difference potential is monotonic, there is no interference between contributions at one wavelength from two separate R values, nor do we expect to observe satellite features which commonly result from extrema in difference potentials. (Tellinghuisen and co-workers make a useful distinction between reflection structure, which occurs for a monotonic difference potential, and interference structure, which results when more than one R value can contribute to a single wavelength.^{94,95,107}) Also from Fig. 5 we see that the short wavelength edge of the emission moves to longer wavelengths as we increase the pump laser wavelength. This simply reflects the fact that photons of longer wavelength pump lower levels of the upper state, which then radiate at longer wavelengths.

Note that even though Na_2 and K_2 molecules also exist in the sodium-potassium mixture, the emission can unambiguously be assigned to NaK since the analogous ${}^3\Pi \rightarrow {}^3\Sigma$ transitions are forbidden by symmetry considerations ($u \leftrightarrow u$) in the homonuclear molecules. Since the signals are linear in laser power, the upper state of the emission must lie in the first excited manifold. Of all the possible transitions of NaK, Na_2 and K_2 involving these states, only the NaK $1\ {}^3\Pi \rightarrow 1\ {}^3\Sigma^+$ band lies in this wavelength range.

B. Calculations

Because of the complexity of the excitation spectra (see Sec. III C), it was difficult to determine which rovibrational levels of the $1\ {}^3\Pi$ state were populated for a given laser wavelength. New measurements, which are currently underway, will hopefully overcome this problem. For the present work,

we used the following argument to obtain a reasonable assignment of the pumped levels. As more accurate data becomes available, these assignments will most likely require modification.

Accurate spectroscopic constants exist for the $1\ {}^1\Sigma^+$ and $1\ {}^3\Pi_1$ states of NaK.^{80,81} By using the value for the ${}^3\Pi$ fine-structure splitting suggested in Ref. 80, we determined energies for the various levels of the $1\ {}^3\Pi_0$ state. This is the state which is most strongly perturbed by the spin-orbit interaction. Since the $1\ {}^3\Pi_0 \leftarrow 1\ {}^1\Sigma^+$ transitions are made possible by the admixture of $2\ {}^1\Sigma^+$ probability amplitude into the triplet state, the selection rules will be the same as for $2\ {}^1\Sigma^+ \leftarrow 1\ {}^1\Sigma^+$ transitions, namely $\Delta J = \pm 1$. We then matched the laser energy to a list of energies for $1\ {}^3\Pi_0(v', J' \pm 1) \leftarrow 1\ {}^1\Sigma^+(v'', J'')$ transitions. (The search was limited to the most heavily populated levels, i.e., $v'' \leq 5$, $J'' \leq 150$.) This yielded several possible transitions for each laser wavelength in Fig. 5. However, plausibility arguments could be used to further restrict the list. For instance, looking at Fig. 5 it seems likely from the regular progression of the short wavelength edge of the band that the upper state vibrational number must increase monotonically as we go from bottom to top. However, the close similarity of the 753.49 and 760.94 nm spectra argues that in those two cases we pumped the same upper vibrational state. Additionally we know that J levels near the most probable value [$(J_{\max} = (kT/2B)^{1/2} - 1/2 \approx 48)$]¹⁰⁸ are favored. Finally we used experimental $2\ {}^1\Sigma^+$ vibrational constants from Loomis and Arvin,¹⁰⁹ and calculated rotational constants from Stevens *et al.*⁸⁷ to predict perturbed level positions. Putting all of this information together allowed us to make an educated guess of the pumped upper level. We are confident that the vibrational numbering is correct at least to within ± 1 . The uncertainty in our rotational numbering is much greater and the values we present at this point are strictly for purposes of illustration.

In order to test this proposed explanation of the oscillatory fluorescence emission, we have carried out quantum mechanical simulations of the bound-free $1\ {}^3\Pi \rightarrow 1\ {}^3\Sigma^+$ emission. These calculations are based upon the Stevens *et al.*⁸⁷ potentials and the Ratcliff *et al.*⁸⁸ transition dipole functions. The calculations were carried out for the specific $1\ {}^3\Pi$ state levels that we estimated were pumped by the laser. Relative intensities were determined at 200 wavelengths covering the range of the observed spectra. Because we are simulating measurements of spontaneous emission power dispersed on a linear wavelength scale, a weighting factor of λ^{-6} was used. The calculated spectra are shown as solid lines in Fig. 7. The bound-free intensity drops abruptly to zero at short wavelengths due to the threshold for bound-free emission. We surmise that bound-bound emission beyond the bound-free threshold is experimentally indistinguishable from bound-free emission due to the resolution of the fluorescence detection (~ 5 nm) and the very close spacing of the $1\ {}^3\Sigma^+$ vibrational levels ($\sim 23\text{ cm}^{-1}$). Therefore, we have calculated intensities of the bound-bound transitions, weighted them by the density of states and plotted them as points in Fig. 7. All calculations were performed with the Iowa library of computer codes for diatomic spectroscopy¹¹⁰

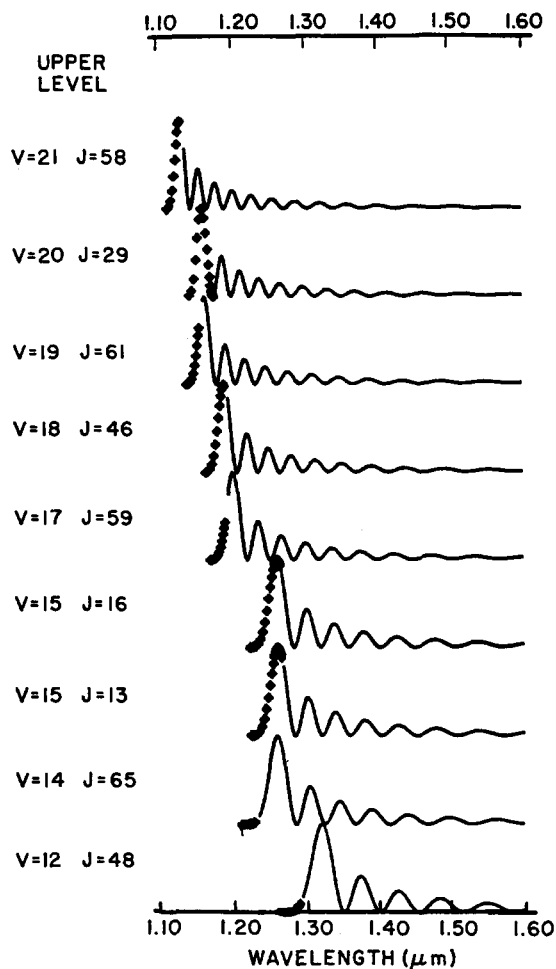


FIG. 7. Quantum mechanical calculations of the NaK bound-free $1^3\Pi \rightarrow 1^3\Sigma^+$ emission, based on the theoretical potentials of Ref. 87 and the transition dipole moments of Ref. 88. Solid lines represent bound-free emission while dotted lines represent bound-bound emission.

following methods outlined by Herman and Sando.¹¹¹ Only *Q*-branch transitions were included in these exploratory calculations. The addition of *P* and *R* branches would cause a slight broadening of the spectra and nonzero intensities at the “nodes”. The density of states was determined as $(dE_{v,J}/dv)^{-1}$ with the derivative determined by a spline interpolation of the vibrational energy vs vibrational quantum number. Intensities of transitions to the two highest bound states (usually quasibound) were discarded because the interpolation gave inaccurate derivatives near the end of its range. Note that this treatment of the bound-bound spectrum as an extension of the bound-free has previously been thoroughly tested (see, e.g., Ref. 103).

The trends in the emission threshold and frequency of oscillations can be seen in Fig. 7 while a detailed comparison to experiment in the case of 773.11 nm excitation is shown in Fig. 8. Figure 9 shows the effects of separately varying the upper state vibrational and rotational quantum numbers in the calculated spectra.

The good agreement between the calculated and observed spectra indicate that the proposed origin of the oscillatory fluorescence spectra is correct. More detailed com-

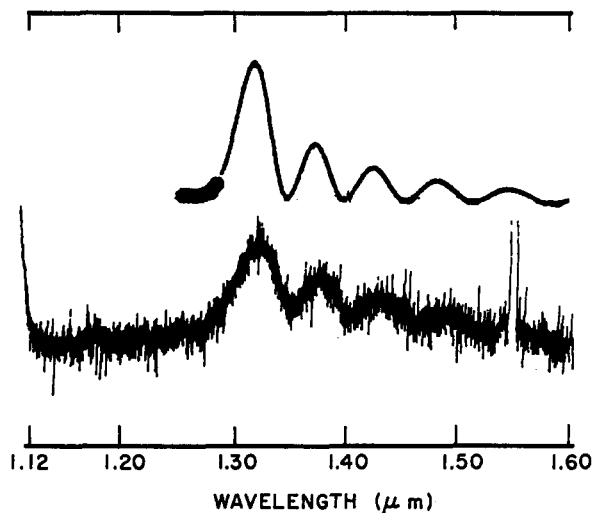


FIG. 8. Experimental and calculated spectra corresponding to excitation at 773.11 nm. We estimate that this laser wavelength populates the $v = 12$, $J = 48$ level of the $1^3\Pi$ state. In the calculated spectrum the thin solid line represents bound-free emission, while the thick line at the left represents bound-bound contributions.

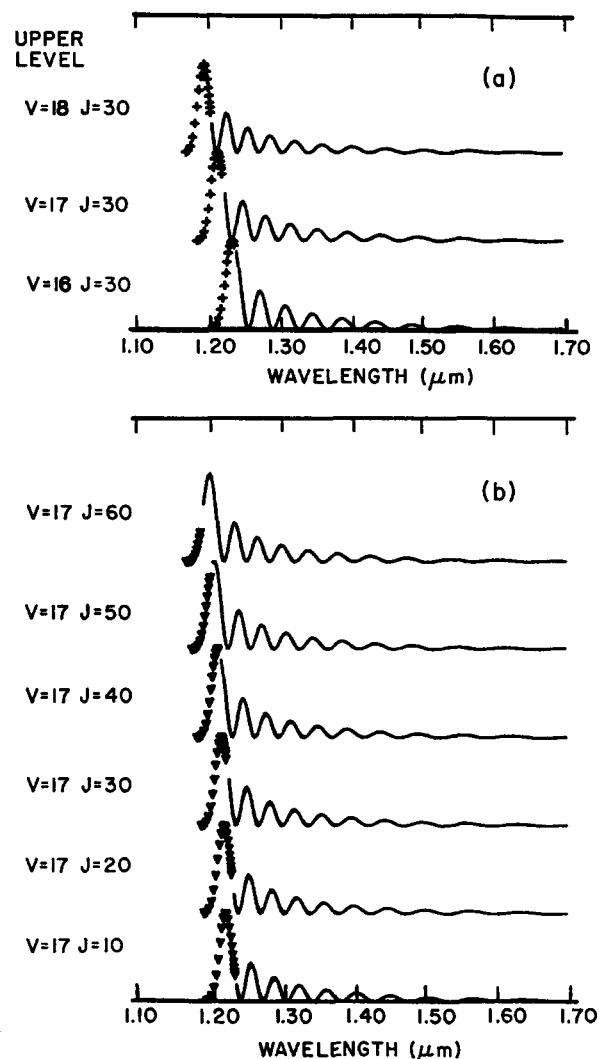


FIG. 9. Variation of the calculated spectrum due to (a) changes in the upper state vibrational quantum number and (b) changes in the upper state rotational quantum number. Solid lines represent bound-free emission and points represent bound-bound contributions.

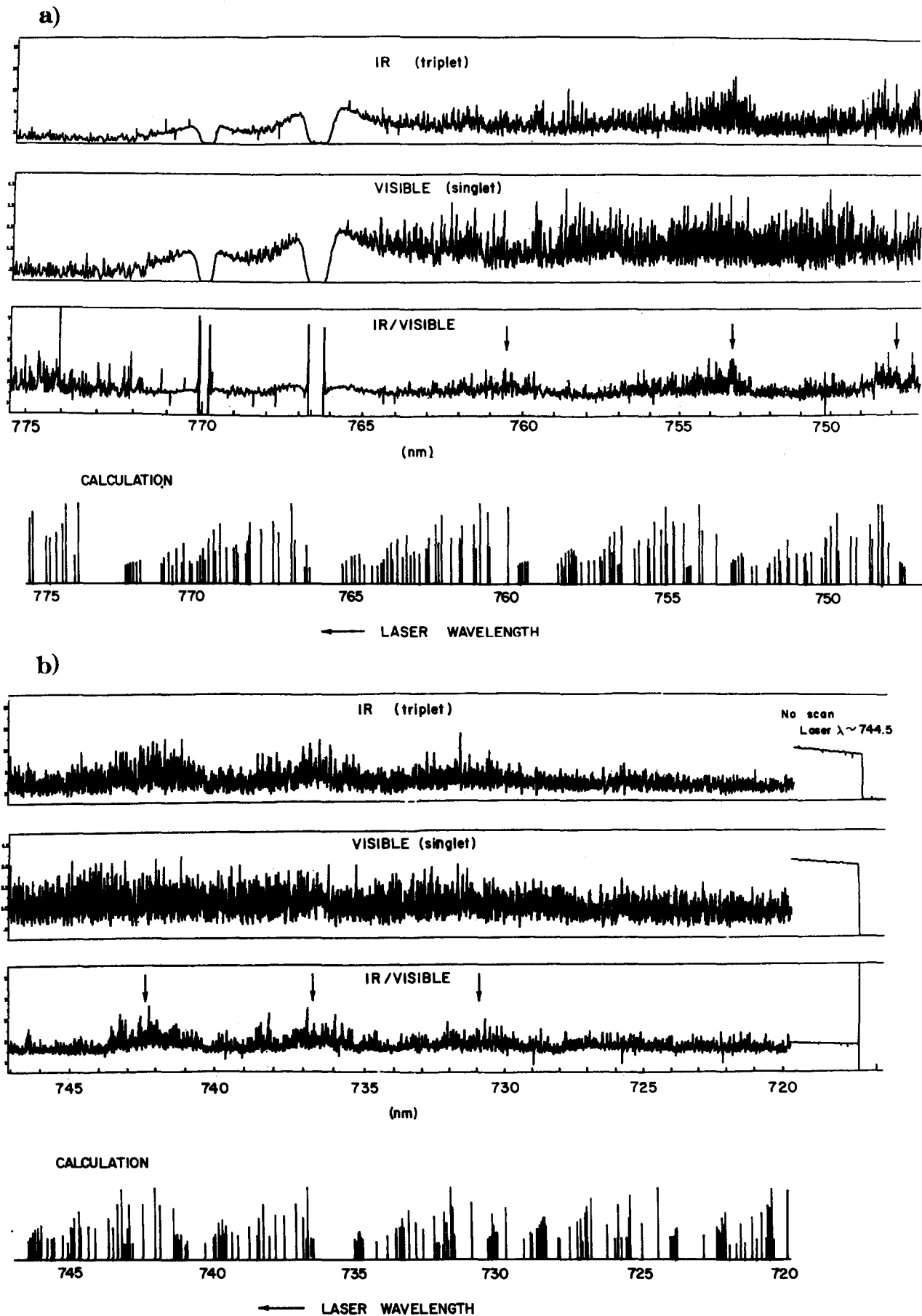


FIG. 10. NaK excitation spectra for laser wavelengths from (a) 775 to 747 nm and (b) 747 to 720 nm. First trace: $1^3\Pi \rightarrow 1^3\Sigma^+$ emission vs laser wavelength. Second trace: $2^1\Sigma^+ \rightarrow 1^1\Sigma^+$ emission vs laser wavelength (note Na_2 and K_2 singlet emission bands also contribute to this spectrum). Third trace: triplet spectrum divided by singlet spectrum (first trace divided by second). Bottom trace: calculated spectrum (see the text).

parisons of experiment and theory, which are now underway, should allow accurate mapping of the $1^3\Sigma^+$ state potential. This will be discussed further in Sec. IV.

C. Excitation spectra

An attempt was made to map out the perturbations that exist between the NaK $1^3\Pi$ and $2^1\Sigma^+$ states. The experimental setup is shown in Fig. 4 and described in Sec. II. In this experiment, the laser wavelength was scanned while the total $2^1\Sigma^+ \rightarrow 1^1\Sigma^+$ band fluorescence and the total $1^3\Pi \rightarrow 1^3\Sigma^+$ band fluorescence were simultaneously recorded using two separate detectors.

The singlet excitation spectrum was expected to be quite complicated since singlet fluorescence occurs whenever the laser wavelength matches that of an allowed rovibrational transition of the NaK $2^1\Sigma^+ \leftarrow 1^1\Sigma^+$ absorption band. Additionally, strong singlet bands of both Na_2 and K_2 absorb and radiate in this wavelength region and thereby contribute to the singlet excitation spectrum.

We expected the triplet excitation spectrum to be much simpler since Na_2 and K_2 cannot radiate in the 1.1 to 1.6 μm wavelength range (assuming absorption of only one laser photon), and the NaK triplet fluorescence requires pumping of one of the mixed $2^1\Sigma^+ - 1^3\Pi$ levels. Thus we hoped that the peaks in the excitation spectrum would map out the perturbations in a simple and direct way.

The singlet and triplet excitation spectra are displayed in Fig. 10. As can be seen, both the singlet and triplet spectra are quite complicated. That the many spikes are not noise is verified in the right-most part of Fig. 10(b), where the laser wavelength was fixed at ~ 744.5 nm. We also see reproducible regions of the triplet spectrum where the signal appears enhanced. These regions are more visible in the third trace of Fig. 10, where we have divided the triplet emission by the singlet emission. The enhanced triplet regions (marked by arrows in the third trace of Fig. 10) are roughly equally spaced, and we believe they represent pumping from the $v = 0$ level of the ground state (which is most heavily populated) into various levels of the upper $^3\Pi$ state. Thus the spacing between the enhanced regions simply reflects the vibrational spacing of the $1^3\Pi$ state.

As mentioned in Sec. III B, we used experimental vibrational constants from Ref. 109 and calculated rotational constants from Ref. 87 to obtain energies for the rovibrational levels of the $2^1\Sigma^+$ state. These were combined with the known $1^1\Sigma^+$ and $1^3\Pi$ level energies^{80,81} to obtain a "theoretical" list of levels which are most strongly perturbed. Laser wavelengths required to excite these levels were calculated, and a theoretical triplet spectrum was created (bottom trace of Fig. 10). The weighting of the lines is simply the Boltzmann population factor $(2J + 1)\exp(-E_{v,J}/kT)$ for the lower state.

Clearly we cannot expect a quantitative match between the observed spectrum and this simple calculation. However, we do see that perturbed levels are quite common, which explains the complexity of the triplet excitation spectrum. Strong perturbations are found almost every 15 rotational levels of each vibrational level of the $^3\Pi_0$ state. Nearby levels (not included in the calculated spectrum of Fig. 10)

are also somewhat perturbed, as are various levels of the $^3\Pi_1$ and $^3\Pi_2$ states. This results in perhaps 10% or 20% of all $2^1\Sigma^+$ levels having significant triplet admixtures. The calculated triplet excitation spectrum also verifies that the enhanced regions originate in the $v = 0$ levels of the ground state.

More accurate modeling of the excitation spectrum requires accurate experimental constants for the $2^1\Sigma^+$ state, which would permit calculation of perturbation positions and strengths, the inclusion of Franck-Condon factors, etc. Additionally, single-mode laser excitation spectra would also be useful. These experimental and theoretical studies are now underway in our laboratories and will be presented in a later publication.⁸⁹

IV. CONCLUSIONS

In summary, we have observed NaK $1^3\Pi \rightarrow 1^3\Sigma^+$ bound-free emission from specific vibrational levels of the upper state. We have also carried out quantum mechanical simulations of the emission spectra based upon recent *ab initio* NaK potentials.⁸⁷ These simulations verify that the emission is of the reflection type; i.e., that the oscillations in the spectra simply reflect the oscillations in the bound level probability distribution function.

At present, we are repeating the fluorescence experiment using a single-mode laser which hopefully will produce cleaner spectra. We are also redoing the calculations, but using the accurate $1^3\Pi$ and $1^1\Sigma^+$ potentials which are now available from Fourier transform spectroscopy.^{80,81} Parameters for the lower $1^3\Sigma^+$ state will be varied to maximize agreement between experimental and calculated spectra. This procedure should yield accurate information on the repulsive wall of the $1^3\Sigma^+$ potentials. Finally, we are in the process of using a single mode laser to obtain the triplet excitation spectra. It is hoped that the resulting simplification will allow an accurate mapping of the $1^3\Pi - 2^1\Sigma^+$ perturbations.

It is possible that this $1^3\Pi \rightarrow 1^3\Sigma^+$ band of NaK and analogous bands of other heteronuclear alkali molecules may be used to develop widely tunable cw or pulsed near-infrared lasers. In this context, the large number of $1^3\Pi - 2^1\Sigma^+$ perturbations is a distinct advantage. We are actively pursuing such possibilities for laser development in our laboratories.

Note added in proof: After submission of the manuscript, accurate experimental constants for the NaK $2^1\Sigma^+$ state became available from Fourier transform spectroscopy [A. J. Ross, R. M. Clements, and R. F. Barrow, *J. Mol. Spectrosc.* **127**, 546 (1988)]. In addition Le Roy, Keogh, and Child have recently developed a procedure for inverting bound-free spectra to yield potentials. They have used this procedure to map the NaK $1^3\Sigma^+$ state from Breford and Engelke's⁵⁷ data on bound-free $2^3\Pi \rightarrow 1^3\Sigma^+$ emission [R. J. Le Roy, W. J. Keogh, and M. S. Child, *J. Chem. Phys.* (submitted)].

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