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Experimental Studies of the NaCs 53Π0 and 1(a)3Σ+ States

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Experimental Studies of the NaCs $5^3\Pi_0$ and $1(a)^3\Sigma^+$ States

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Abstract

We present experimental studies of excited electronic states of the NaCs molecule that are currently underway in our laboratory. The optical-optical double resonance method is used to obtain Doppler-free excitation spectra for several excited states. The data that have been identified with the $5^3\Pi_0$ electronic state are used to obtain Rydberg-Klein-Rees (RKR) and Inverse Perturbation Approach (IPA) potential curves for this state. Bound-free spectra from single ro-vibrational levels of electronically excited states to the repulsive wall of the $1(a)^3\Sigma^+$ state also are recorded. Using the previously determined $5^3\Pi_0$ excited state potential, we fit the repulsive wall of the $1(a)^3\Sigma^+$ state to reproduce the experimental spectra using LeRoy's BCONT program. A slightly modified version of BCONT is also being used to fit the relative transition dipole moments, $\mu_e(R)$, as a function of internuclear separation, R, for the various bound-free electronic transitions.

Why Study NaCs?

Large permanent dipole moment

Permanent Dipole Moments of Heteronuclear Alkali Molecules in $X^1\Sigma^+$ State

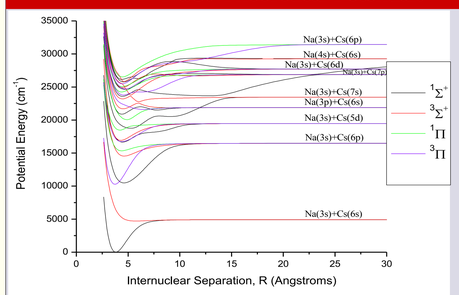
Molecule	*Expt. Dipole Moment (Debye)*
LiNa	0.47
LiK	3.45
LiRb	4.05
LiCs	6.3
NaK	2.73
NaRb	3.1
NaCs	*4.75*
KRb	0.2
KCs	2.58
RbCs	2.39

Large spin-orbit interactions:

Spin-Orbit Splitting of Alkali Atoms (E[P(J=3/2)] - E[P(J=1/2)])

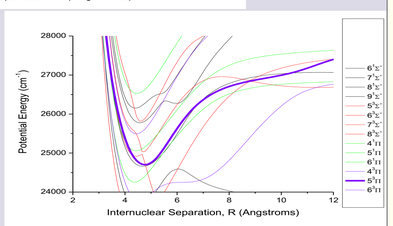
Atomic symbol	*Splitting (cm^{-1})*
Li	0.335
Na	17.196
K	57.71
Rb	273.595
Cs	554.0393
Fr	1686.589

NaCs Theoretical Potentials*



*M. Korek et al., JCP **126**, 124313 (2007)

*M. Korek et al., CJP **78**, 977 (2000)



Goals

- Map excited state potentials
- Determine $5^3\Pi_{\Omega=0}$ potential energy curve
- Map repulsive wall of the $a^3\Sigma^+$ state
- Determine transition dipole moment function, $\mu_e(R)$, for transitions between levels of the $5^3\Pi_{\Omega=0}$ and $a^3\Sigma^+$ states
- Study collisional energy transfer
- Study hyperfine structure

Transition Dipole Moment and Selection Rules

Transition Dipole Moment Functions

Emission intensity for bound-bound or bound-free transitions is proportional to the square of the dipole matrix element

$$I^{ab}_{emission} = N_J h\nu_{ab} A_{ab} \quad \text{with} \quad A_{ab} = \frac{8\pi^3\nu_{ab}^3}{3\varepsilon_0 c^3 h}|\mu_{ab}|^2.$$

Here, $\vec{\mu}_{ab} = \iint \Psi_a^* \vec{\mu}\, \Psi_b\, d\tau_R\, d\tau_E$ where

$$\vec{\mu} = -e\sum_i \vec{r}_i + Z_A\vec{R}_A + Z_B\vec{R}_B = \vec{\mu}_{el} + \vec{\mu}_N$$ is the dipole operator.

The total wave function can be separated into electronic and nuclear parts, and the nuclear part can be further separated into angular (rotational) and radial (vibrational) terms:

$$\Psi(\vec{r}_i, \vec{R}) = \phi^{el}(\vec{r}_i, \vec{R})\cdot\psi^{vr}(\vec{R}) = \phi^{el}(\vec{r}_i, \vec{R})\frac{\chi^{vib}(R)}{R}\varphi^{rot}(\theta,\varphi).$$

(Note that for bound-free transitions, the final state vibrational function must be replaced by a continuum function.)

Thus the dipole matrix element becomes: $\vec{\mu}_{ab} = \iint (\phi_f^{el})^*(\psi_f^{vr})^*(\vec{\mu}_{el} + \vec{\mu}_N)\phi_b^{el}\psi_b^{vr}\, d\tau_R\, d\tau_E$

For a transition between two electronic states, initial state *i* and final state *k*, the nuclear term is zero, the angular terms of the $\vec{\mu}_N$ integral lead to selection rules on *J*, and the radial term leads to

$$\mu_{ik} \propto \int \chi_i^{vib}(R)\mu_{el}(R)\chi_k^{vib}(R)dR \quad \text{with} \quad \mu_{el}(R) = \int(\phi_f^{el})^*(\vec{r}_i, R)\vec{\mu}_{el}\phi_i^{el}(\vec{r}_i, R)d\tau_R.$$

Therefore, $\mu_{el}(R)$ can be obtained by fitting the intensities of bound-bound emission lines or bound-free emission continua to experimental spectra.

Selection Rules for Electronic Transitions

$\Delta v = \text{anything}$

$\Delta J = 0, \pm 1$ with restriction that $\Delta J = 0$ forbidden for $\Sigma \leftrightarrow \Sigma$ transitions

Hund's case a)

$\Delta S = 0$

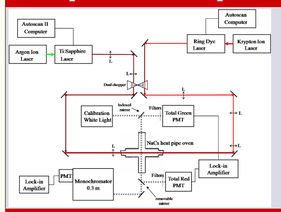
$\Delta\Lambda = 0, \pm 1$

$\Delta\Omega = 0, \pm 1$

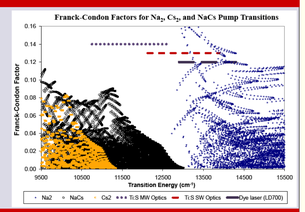
Hund's case c)

$\Delta\Omega = 0, \pm 1$

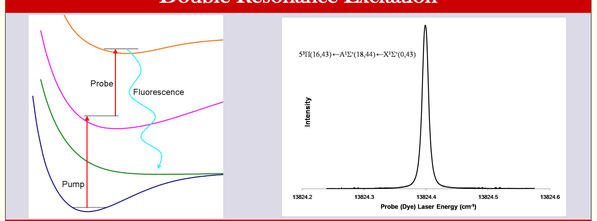
Experimental Setup



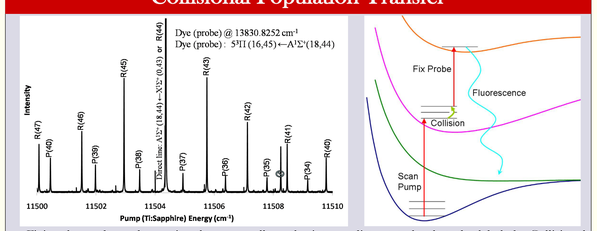
Franck-Condon Factors $A^1\Sigma^+ \leftarrow X^1\Sigma^+$



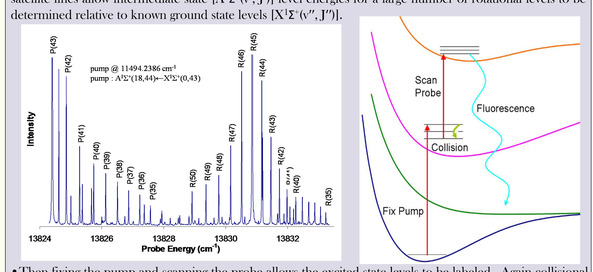
Double Resonance Excitation



Collisional Population Transfer

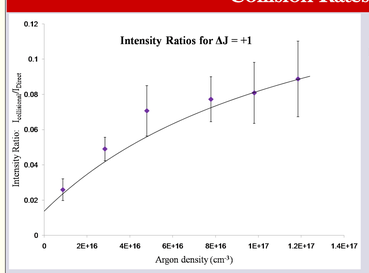


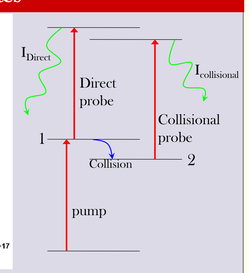
• Fixing the probe and scanning the pump allows the intermediate state levels to be labeled. Collisional satellite lines allow intermediate state $[A^1\Sigma^+(v', J')]$ level energies for a large number of rotational levels to be determined relative to known ground state levels $[X^1\Sigma^+(v'', J'')]$.



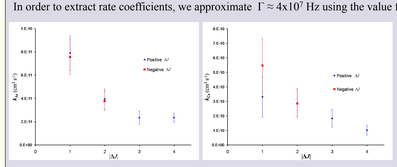
• Then fixing the pump and scanning the probe allows the excited state levels to be labeled. Again collisional satellite lines allow the upper state level energies for a large number of rotational levels to be accurately determined relative to $A^1\Sigma^+(v', J')$ levels.

Collision Rates





In order to extract rate coefficients, we approximate $\Gamma \approx 4\times10^7$ Hz using the value for NaK, and use a rate equation model:

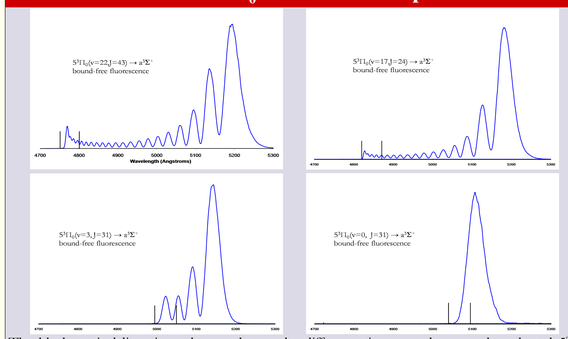


$$\frac{n_2}{n_1} = \frac{I_{collisional}}{I_{Direct}} = \frac{k_{Ar}^{\Delta J} n_{Ar} + k_{Cs}^{\Delta J} n_{Cs}}{\Gamma + k_{Ar}^{Q} n_{Ar} + k_{Cs}^{Q} n_{Cs}}$$

$$k_{Ar}^{Q} = (4.62 \pm 1.97)\times10^{-10}\, cm^3 s^{-1}$$

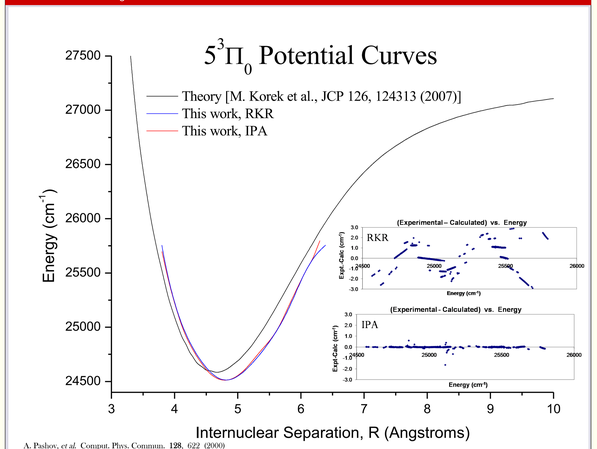
$$k_{Cs}^{Q} = (8.08 \pm 2.87)\times10^{-9}\, cm^3 s^{-1}$$

Resolved $5^3\Pi_0$ Fluorescence Spectra



The black vertical lines in each scan denote the difference in energy between the selected $5^3\Pi_0$ level to the $a^3\Sigma^+$ asymptotic limit or to the bottom of its shallow well. Thus the parts of the spectra between the vertical lines represents unresolved bound-bound transitions. A monotonic difference potential produces simple reflection spectra, which provide an easy method to determine the upper state vibrational quantum number at small values of v.

$5^3\Pi_0$ Theoretical, RKR, and IPA Potentials



A. Pashov, *et al.* Comput. Phys. Commun. **128**, 622 (2000)

M. Korek et al., JCP **126**, 124313 (2007)

R. J. LeRoy, RKR1 2.0: *A Computer Program Implementing the First-Order RKR Method for Determining Diatomic Molecule Potential Energy Curves*, University of Waterloo, Chemical Physics Research Report CP627R (2004).

Dunham Coefficients for $5^3\Pi_0$ State

Parameter	Energy* ± Error** (cm^{-1})	Theoretical values*** (cm^{-1})
Te	24511.79 ± 0.89	24880
Y(1,0)	64.24 ± 0.43	58.6
Y(2,0)	-1.750 ± 0.068	-
Y(3,0)	0.1060 ± 0.0041	-
Y(4,0)	- (2.211± 0.085) x 10^{-3}	-
Y(0,1)	0.03706 ± 0.00018	0.0394
Y(1,1)	- (4.0 ± 1.6) x 10^{-5}	-
Y(0,2)	-7.2 x 10^{-8} (fixed in fit)	-

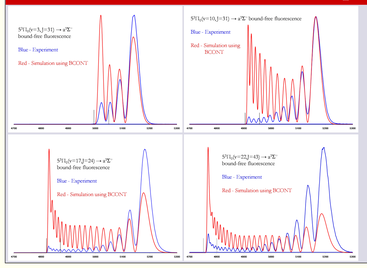
*Fit using DParFit program

R. J. LeRoy, DParFit 3.3: A Computer Program for Fitting Multi-Isotopologue Diatomic Molecule Spectra, University of Waterloo Chemical Physics Research Report CP-653 (2001)

**Statistical error only

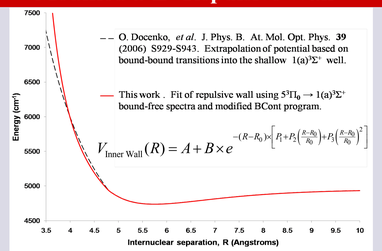
*** M. Korek et al., JCP **126**, 124313 (2007)

Spectra Simulation using BCont: Constant Transition Dipole Moment



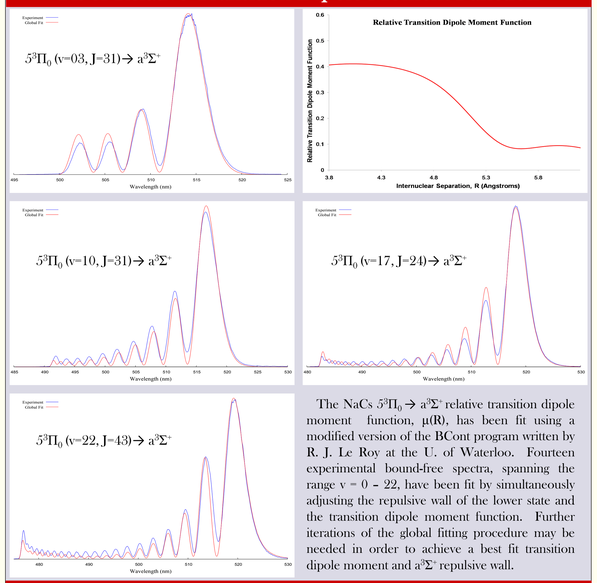
Using the $5^3\Pi_0$ IPA potential, the repulsive inner wall of the $a^3\Sigma^+$ potential was modified to align the maxima and minima of the simulated and experimental spectra. We also note that the increasing amplitude of the experimental bound-free intensity with increasing wavelength can be explained by a transition dipole moment function that generally decreases with increasing R. A global fit of the transition dipole moment using a larger, more complete data set will be carried out using accurate experimental potentials for the $5^3\Pi_0$ and $a^3\Sigma^+$ potentials. (Minor adjustments to the $a^3\Sigma^+$ potential repulsive wall and possibly of the upper state potential may still need to be made.) Positions of the peaks and nodes of the oscillating spectra depend on the upper and lower state potential energy curves while peak amplitudes depend primarily on the transition dipole moment function.

Modified $a^3\Sigma^+$ Repulsive Wall



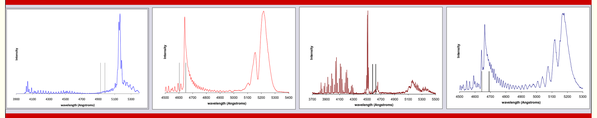
The inner repulsive wall of the $a^3\Sigma^+$ potential is adjusted as part of a global fit of multiple $5^3\Pi_0 \rightarrow a^3\Sigma^+$ bound-free spectra. The wall is described by the function shown on the above plot, where A and B are fixed in order to connect smoothly and continuously to the bound portion of the $a^3\Sigma^+$ potential. Using R_0=4.78, the best fit parameters are P_1=2.067523, P_2=3.800924, and P_3=12.02035.

Spectra Simulation using BCont: Fit of Relative Transition Dipole Moment Function

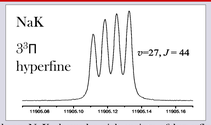


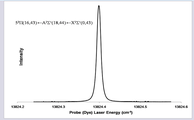
The NaCs $5^3\Pi_0 \rightarrow a^3\Sigma^+$ relative transition dipole moment function, $\mu(R)$, has been fit using a modified version of the BCont program written by R. J. Le Roy at the U. of Waterloo. Fourteen experimental bound-free spectra, spanning the range v = 0 – 22, have been fit by simultaneously adjusting the repulsive wall of the lower state and the transition dipole moment function. Further iterations of the global fitting procedure may be needed in order to achieve a best fit transition dipole moment and $a^3\Sigma^+$ repulsive wall.

Spectra of Other NaCs Excited States Under Investigation



Hyperfine Structure





Previous work on NaK showed a rich variety of hyperfine structure. Ongoing studies of NaCs have yet to reveal clear hyperfine structure.

Hyperfine interaction in NaCs should be described by:

$$\mathbf{E}_{hfs} = \mathbf{b_F\, I \cdot S}$$

b_F^{Na} = 886 MHz $\quad I_{Na} = 3/2$

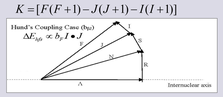
b_F^{Cs} = 2298 MHz $\quad I_{Cs} = 7/2$

From this we expect a larger hyperfine interaction for NaCs. However, states of NaK can often be described by Hunds case $b_{\beta J}$ or $b_{\beta c}$, while NaCs has a much stronger spin-orbit interaction and is likely described by Hunds case c.

Hunds case $b_{\beta J}$

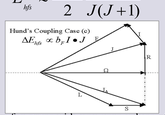
$$E^{b_{\beta J}}_{hfs} \approx \frac{b_F K}{4}\frac{J(J+1) - S(S+1) - N(N+1)}{J(J+1)}$$

$$K = [F(F+1) - J(J+1) - I(I+1)]$$



Hunds case c

$$E^{c}_{hfs} \approx \frac{b_F K}{2}\frac{\Sigma\Omega}{J(J+1)}$$



Therefore, the hyperfine structure might only be observable at lower J values for states with non-zero values of Σ and Ω.