Predictions of KRb and RbCs spectra under cold and thermal conditions

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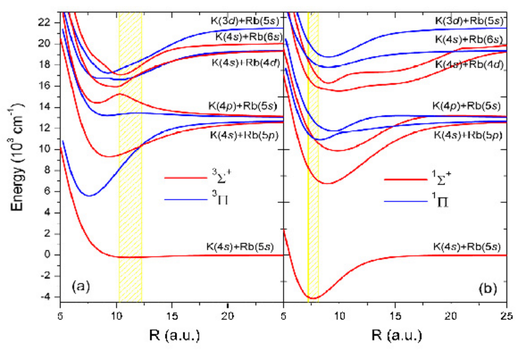
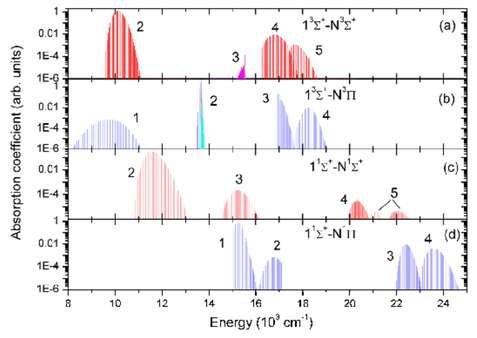
Quantum-mechanical simulations of the excitation spectra of KRb [1] and RbCs [2] from the lowest vibrational level of the lowest triplet and singlet electronic states have been performed using the manifold of potential curves for the Hund's coupling case *a* and the corresponding transition dipole moments (for KRb only, while for RbCs we assumed them to be constant.) Spin-orbit interaction was also neglected. The obtained spectra can be used for a comparison with experimental absorption spectra of KRb and RbCs molecules produced in their vibronic ground state or attached to cold helium droplets.

In addition, we compare the semiclassically simulated spectra with absorption measurements in dense K–Rb [1] and Rb–Cs [3] vapors at high temperatures, which helped us to identify three diffuse bands for KRb as $1\,^3\Sigma^+ \rightarrow 3\,^3\Pi$, $1\,^3\Sigma^+ \rightarrow 4\,^3\Pi$, and $1\,^1\Sigma^+ \rightarrow 4\,^1\Sigma^+$ transitions, while for RbCs the band at 717 nm is identified as the $1\,^1\Sigma^+ \rightarrow 1\,^1\Pi$ transition (*B-X* band) and the diffuse band at 563 nm as the $1\,^1\Sigma^+ \rightarrow 3\,^1\Pi$ transition.

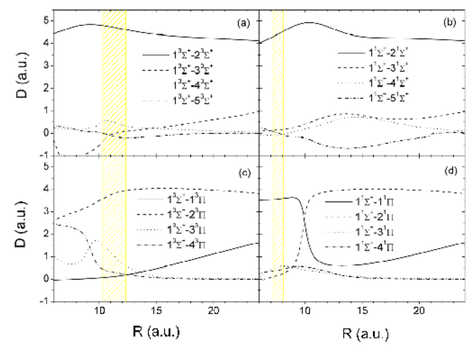
[1] R. Beuc, M. Movre, T. Ban, G. Pichler, M. Aymar, O. Dulieu, and W. E. Ernst, J. Phys. B: At. Mol. Opt. Phys. **39** (2006) S1191 – S1201
[2] R. Beuc, M. Movre, B. Horvatić, and G. Pichler, Chem. Phys. Lett. **435** (2007) 236 – 241
[3] R. Beuc, M. Movre, B. Horvatić, M. Čopor, S. Vdović, A. Nevsesyan, T. Varzhapetyan, D. Sarkisyan, and G. Pichler, Appl. Phys B **88** (2007) 111– 115



Potential energy curves from present *ab initio* calculations. (a) triplet and (b) singlet states. Narrow Franck-Condon windows around the equilibrium internuclear distance of the lowest singlet and triplet states are indicated by vertical bars.

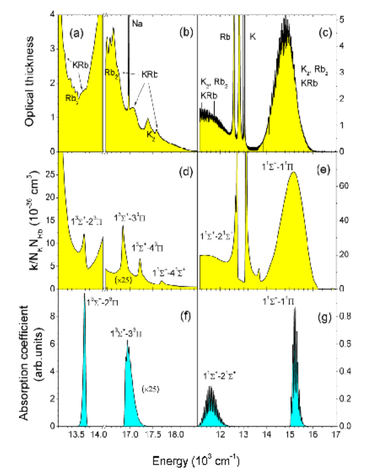


Calculated absorption band shapes for triplet and singlet transitions in KRb under cold conditions: (a) $1\,^3\Sigma^+ \rightarrow N\,^3\Sigma^+$ (N = 2, 3, 4, 5); (b) $1\,^3\Sigma^+ \rightarrow N\,^3\Pi$ (N = 1, 2, 3, 4); (c) $1\,^1\Sigma^+ \rightarrow N\,^1\Sigma^+$ (N = 2, 3, 4, 5); (d) $1\,^1\Sigma^+ \rightarrow N\,^1\Pi$ (N = 1, 2, 3, 4).



Electric dipole transition moments from present *ab initio* calculations: (a) $1\,^3\Sigma^+ - N\,^3\Sigma^+$ (N=2,3,4,5); (b) $1\,^1\Sigma^+ - N\,^1\Sigma^+$ (N=2,3,4,5); (c) $1\,^3\Sigma^+ - N\,^3\Pi$ (N=1,2,3,4); (d) $1\,^1\Sigma^+ - N\,^1\Pi$ (N=1,2,3,4). The states are labeled in the order of increasing energies.

KRb



Absorption spectrum of the K - Rb mixture in an all-sapphire cell obtained with a high resolution scanning monochromator at three different temperatures: (a) 613 K, (b) 713 K, (c) 575 K). (d) and (e): semiclassical simulation of the high-temperature reduced absorption coefficient at 650 K for the same spectral region as shown in (a), (b) and (c). (f) and (g) are predictions of absorption bands of the KRb molecule under low-temperature conditions (e.g. on cold helium droplets) for triplet (f) and singlet (g) transitions.

Theoretical simulations

The absorption coefficient from a single rovibrational level (v", J", Λ") of the lower electron state Λ" into all upper rovibrational levels (v', J, Λ') of the excited electron state Λ':

$$k(\nu) = N \sum_{v'J'} \sigma_{v''J''\Lambda''}^{v'J'\Lambda'}(\nu), \qquad (1)$$

where N is the concentration of molecules in the initial level and $\sigma_{v''J''\Lambda''}^{v'J'\Lambda'}(\nu)$ is the absorption cross section for the transition from (v", J", Λ") to (v', J, Λ'), given by

$$\sigma_{v''J''\Lambda''}^{v'J'\Lambda'}(\nu) = \frac{8\pi^3\nu}{3hc} \left| \left\langle \phi_{v''J''\Lambda''} \middle| D(R) \middle| \phi_{v'J'\Lambda'} \right\rangle \right|^2 g(\nu - \nu_{ij}) \frac{S_{J''\Lambda''}^{J'\Lambda'}}{2J''+1}, \qquad (2)$$

where $D(R)$ is the dipole transition moment, $S_{J''\Lambda''}^{J'\Lambda'}$ is the Hönl-London factor, ν_{ij} is the transition frequency ($h\nu_{ij} = E_{v'J'\Lambda'} - E_{v''J''\Lambda''}$), and $g(\nu - \nu_{ij})$ is the line-shape function of the molecular transition.

At the temperature of helium nanodroplets (T = 0.4 K) only a few rotational levels within the lowest vibrational level (v"=0) of a free RbCs molecule are populated. ➔ Neglect the J dependence of the matrix elements and put $J' = J'' = 0$

➔ $$k(\nu) = \frac{8\pi^3\nu}{3hc} N \sum_{v'} \left| \left\langle \phi_0 \middle| D(R) \middle| \phi_{v'} \right\rangle \right|^2 g(\nu - \nu_{ij}), \qquad (3)$$

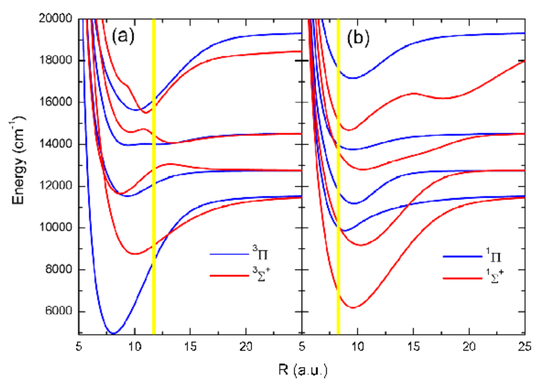
$\phi_{v''J''\Lambda''} \equiv \phi_0$ is the lowest rovibrational wave function (v" = 0, J" = 0, Λ" = 0).

➔ Energies and wave functions for vibrational levels determined by using the Fourier Grid Hamiltonian (FGH) method

To get a coarse-grained spectrum ➔ replace the summation over v' in (3) with an integral over (quasicontinuous) energy E. ➔ Turn the unity-normalized bound state wave function into an energy-normalized one, $\phi_E = \left|\partial E / \partial v\right|^{-1/2} \phi_{v'}$. ➔

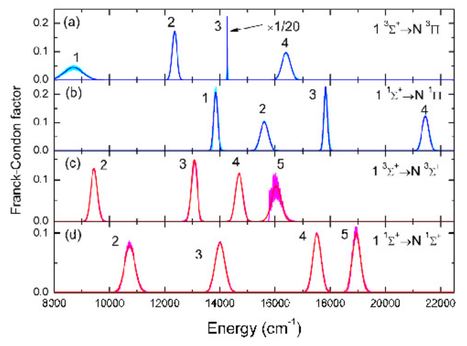
$$k(\nu) = \frac{8\pi^3\nu}{3c} N \left| \left\langle \phi_0 \middle| D(R) \middle| \phi_E \right\rangle \right|^2. \qquad (4)$$

To describe the lowest rovibrational level, it is sufficient to approximate the ground electron state by a harmonic potential around the minimum R_0,



Excited potential curves of the RbCs molecule: (a) $^3\Pi$, $^3\Sigma^+$, (b) $^1\Pi$, $^1\Sigma^+$.

RbCs



Absorption bands of RbCs on a cold He-cluster calculated in the Hund's case *a*. Franck-Condon factors calculated in the reflection approximation (blue and red full lines) compared with the quantum-mechanical band shapes (smeared tuquoiseand purple) obtained from equation (3) using a Gaussian line shape function of width w=30 cm^{-1} centered at the calculated transition frequency ν_{ij} for transitions shown in Fig. 2.

$V_g(R) = V_g + \frac{1}{2}V_g''(R - R_0)^2$, where $V_g \equiv V_g(R_0)$ and $V_g'' \equiv d^2V_g(R)/dR^2\,|_{R=R_0}$. The ground-state wave function is then simply a Gaussian with the maximum at R_0. The main contribution to the spectrum comes from the transitions around this minimum, say, from the classically allowed region of the width $\Delta R = 2\sqrt{\hbar/\mu\omega}$ around R_0, where $\omega = \sqrt{V_g''/\mu}$ and μ is the reduced mass.

Within the narrow region ΔR around R_0 all the excited-state potentials can be fairly well described by the linearized form

$$V_e(R) = V_e + V_e'(R - R_0), \; V_e \equiv V_e(R_0), \; V_e' \equiv dV_e(R)/dR\,|_{R=R_0}.$$

If the excited potential $V_e(R)$ is steep around R_0, the required matrix element [see equation (4)] is well described by

$$\left\langle \phi_0 \middle| D(R) \middle| \phi(E) \right\rangle = \frac{1}{\sqrt{|V_t'|}} D(R_t)\phi_0(R_t), \qquad (5)$$

where R_t is the turning point of the excited-state potential for a given energy E. Writing the ground-state wave function, the energy of the lowest vibrational level, and the transition energy as

$$\phi_0(R) = \frac{1}{\pi^{1/4}\sigma^{1/2}} e^{\frac{(R-R_0)^2}{2\sigma^2}}, \qquad (6)$$

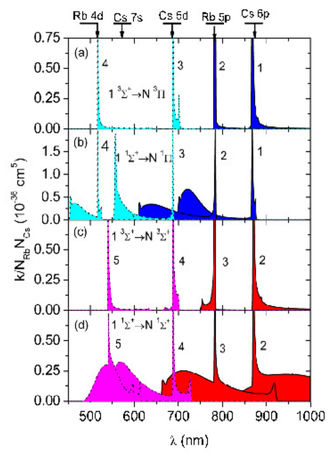
$$E_g = V_g + \tfrac{1}{2}\hbar\omega, \qquad (7)$$

$$h\nu = V_e - E_g + V_e'(R_t - R_0), \qquad (8)$$

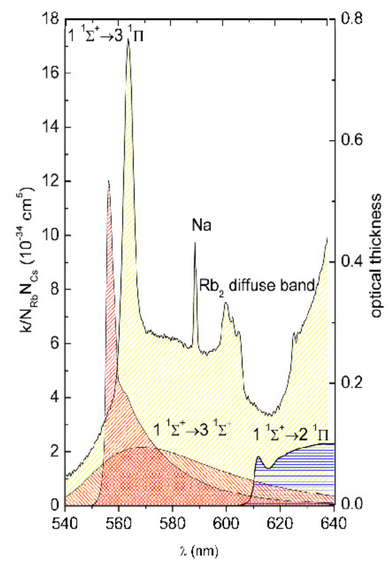
where $\sigma = \sqrt{\hbar/\mu\omega} = \Delta R/2$, one gets the expression (4) for the absorption coefficient in the form

$$k(\nu) = \frac{8\pi^3\nu}{3c} N[D(R_0)]^2 \frac{1}{w}\sqrt{\frac{2}{\pi}} e^{-\frac{2}{w^2}(E_0 - h\nu)^2}, \qquad (9)$$

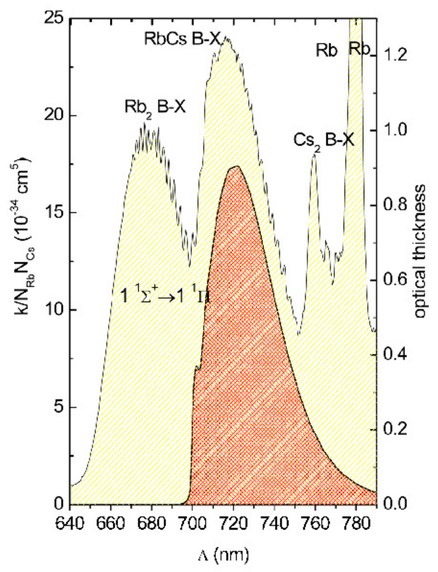
where $E_0 = V_e - E_g \equiv h\nu_0$ and $w = |2V_e'\sigma|$. Here we also assumed D to be a slowly varying function of R, replacing it with $D(R_0)$.



Particular contributions to the reduced absorption coefficient from hot (T = 720 K) RbCs vapor calculated applying the semiclassical approach: (a) $1\,^3\Sigma^+ \rightarrow N\,^3\Pi$ (N = 1, 2, 3, 4), (b) $1\,^1\Sigma^+ \rightarrow N\,^1\Pi$ (N = 1, 2, 3, 4), (c) $1\,^3\Sigma^+ \rightarrow N\,^3\Sigma^+$ (N = 2, 3, 4, 5), (d) $1\,^1\Sigma^+ \rightarrow N\,^1\Sigma^+$ (N = 2, 3, 4, 5). Solid-line curves denote asymptotically-allowed transitions and dotted-line curves denote asymptotically-forbidden ones, respectively. All sharp bands that lie on the forbidden asymptotes are artifacts of the assumed constant dipole moments and will not be observable. The arrows along the upper edge indicate the positions of the atomic asymptotes.



The portion of the thermal spectrum between 540 and 630 nm comprising the diffuse RbCs band at 563 nm. Semiclassical simulation of the reduced absorption coefficient due to the RbCs $1\,^1\Sigma^+ \rightarrow 3\,^1\Pi$ transition is compared to the experimental spectrum for the same temperature T = 757 K.



The portion of the thermal spectrum between 640 and 790 nm comprising the RbCs *B-X* band at 717 nm, both measured and calculated for the same temperature T = 641 K. Semiclassical simulation of the reduced absorption coefficient is compared to the experimental spectrum.