The \(^{39}\text{K}_2\) 2 \(^3\Sigma^+_g\) state: Observation and analysis

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(Received 8 January 2007; accepted 22 March 2007; published online 21 May 2007)

The \(^{39}\text{K}_2\) 2 \(^3\Sigma^+_g\) state has been observed by perturbation-facilitated infrared-infrared double resonance spectroscopy and two-photon excitation. Resolved fluorescence spectra into the \(^a\ ^3\Sigma^+_u\) state have been recorded. The observed vibrational levels have been assigned as the \(v = 23–25, 27, 28, 31–33, 38–45, 47,\) and 53 levels by comparing the observed and calculated spectra of the \(2\ ^3\Sigma^+_g \rightarrow a\ ^3\Sigma^+_u\) transitions. Molecular constants have been obtained using a global fitting procedure with a comprehensive set of experimental data. Fine and hyperfine splittings have been resolved in the excitation spectra. Perturbations between the \(2\ ^3\Sigma^+_g\) and \(2\ ^3\Pi^+_g\) states were observed. The hyperfine patterns of the \(2\ ^3\Sigma^+_g\) levels are strongly affected by the perturbation. The perturbation-free and weakly perturbed levels follow the case \(b_g\) coupling scheme, while the perturbed levels follow case \(b_u\) coupling. A Fermi contact constant, \(b_F = 65\pm 10\) MHz, has been obtained. Intensity anomalies of rotational lines appeared both in the \(2\ ^3\Sigma^+_g \rightarrow 2\ ^3\Pi^+_g \rightarrow b\ ^3\Pi^+_u\) excitation spectra and in the \(2\ ^3\Sigma^+_g \rightarrow 2\ ^3\Pi^+_g \rightarrow a\ ^3\Sigma^+_u\) resolved fluorescence spectra. These intensity anomalies can be explained in terms of a quantum-mechanical interference effect. © 2007 American Institute of Physics. [DOI: 10.1063/1.2730804]

I. INTRODUCTION

Triplet state spectra provide a wealth of information concerning hyperfine structure and spin-orbit, spin-spin, and spin-rotation interactions that is not available from singlet state spectra. However, the ground state of all alkali dimers is a singlet state, \(X^1\Sigma^+_g\), and experimental observation of triplet states is much more difficult than the observation of singlet states. Perturbation-facilitated optical-optical double resonance (PFOODR) spectroscopy uses a two-step excitation scheme through singlet-triplet mixed intermediate levels: a pump laser excites from the singlet ground state, \(X^1\Sigma^+_g\), to an \(A^1\Sigma^+_u \rightarrow b\ ^3\Pi^+_g\) mixed level, then a probe laser further excites into high-lying triplet states. Resolved fluorescence from high-lying triplet states provides information on both the high-lying states and the low-lying \(^a\ ^3\Sigma^+_u\) and \(^b\ ^3\Pi^+_u\) states.\(^{1–3}\) This PFOODR spectroscopic technique has been used to study triplet states of the \(\text{Li}_2\), \(\text{Na}_2\), \(\text{K}_2\), and \(\text{NaK}\) molecules.\(^{3,4}\) Recently, the \(^2\ ^3\Pi^+_g\) state of \(\text{K}_2\) has been studied by perturbation-facilitated infrared-infrared (IR-IR) double resonance with two tunable diode lasers.\(^{5–7}\) The present work reports our study of the \(\text{K}_2\) 2 \(^3\Sigma^+_g\) state.

II. EXPERIMENT

The IR-IR double resonance and two-photon excitation experimental setups have been described in Refs. 5 and 7. Briefly, potassium vapor was generated in a heat pipe oven, and 1 Torr of Ar was used as a buffer gas. In the IR-IR double resonance experiment, two single mode tunable diode lasers were used as the pump and probe lasers. The pump laser selectively excited an \(A^1\Sigma^+_u \rightarrow b\ ^3\Pi^+_g\) mixed intermediate rotational level from the singlet ground state; the probe laser frequency was scanned and transitions into the \(2\ ^3\Sigma^+_g\) state were monitored by detecting visible \(2\ ^3\Sigma^+_g \rightarrow a\ ^3\Sigma^+_u\) fluorescence. When the pump and probe lasers excited an upper \(2\ ^3\Sigma^+_g\) level, the \(2\ ^3\Sigma^+_g \rightarrow a\ ^3\Sigma^+_u\) fluorescence was collected and dispersed by a Spex 1404 monochromator. In the two-photon excitation case, one laser (either a diode laser or a CR 899-29 Ti:sapphire laser) was used.

For purposes of assigning the two-photon fluorescence spectrum, a second heat pipe oven containing a sodium-potassium mixture was also used in a similar setup. In this
case, the oven temperature was ~380 °C, and the argon pressure ~1.25 Torr. We estimated the ratio of K₂/NaK/Na₂ vapor pressures to be 5.1/2.8/1.0 in this oven. A few hundred milliwatts of Ti:sapphire laser power was used and resolved fluorescence was recorded with a 0.3 m McPherson monochromator and photomultiplier tube combination used in a photon counting mode.

III. RESULTS

A. The 2 3Σ⁺ → a 3Σ⁺ fluorescence: electronic and vibrational assignments

Theoretical potentials have been calculated for 98 electronic states of K₂ below the K(4s)+K(5d) atomic limit.⁸ In our probe region (21 100–24 000 cm⁻¹ above the potential minimum of the ground state), five electronic states could have been excited from the A 1Σ⁺ → b 1Πₗg, mixed intermediate levels: the 2 1Πₗg, 1 3Δₗ, 2 3Σ⁺ₗ, 3 3Σ⁺ₗ, and 4 3Σ⁺ₗ states. Among these five states, only the 2 1Πₗg and 2 3Σ⁺ₗ can radiate to the a 3Σ⁺ state. Previously, the 2 3Πₗg v=0–42 levels of K₂ have been observed and the 2 3Πₗg → a 3Σ⁺ fluorescence has been resolved.⁵⁻⁷ The K₂ 2 3Πₗg → a 3Σ⁺ fluorescence has a very similar pattern to the 2 1Πₗg → a 3Σ⁺ fluorescence of Li₂ and Na₂.⁹⁻¹¹ The Mulliken difference potentials¹²,¹³ of the 2 1Πₗg and a 3Σ⁺ states of Li₂, Na₂, and K₂ are not monotonic; hence, quantum interference structure appears in the fluorescence spectra from higher vibrational levels. The 2 3Σ⁺ₗ → a 3Σ⁺ fluorescence pattern of K₂, however, is quite different from the pattern of the 2 3Πₗg → a 3Σ⁺ fluorescence. Figure 1 shows the resolved fluorescence from the 2 3Σ⁺ₗ v=23, N=43 level. Spectrum A was recorded when the pump laser (11 548.035 cm⁻¹) and probe laser (9633.499 cm⁻¹) excited the 2 3Σ⁺ₗ v=23, N=43 ← b 1Πₗg v=19, J=42→ X 1Σ⁺ₗ v=0, J=43 transition; spectrum B corresponds to excitation with the pump laser only; and spectrum C is spectrum A−spectrum B, corresponding to the net fluorescence from the upper 2 3Σ⁺ₗ v=23, N=43 level to the a 3Σ⁺ state. The Mulliken difference potential curve of the K₂ 2 3Σ⁺ₗ and a 3Σ⁺ states calculated from ab initio potential curves¹⁴ shows no extrema, and the vibrational quantum number of the upper state can be determined simply by node counting. In the case of Fig. 1, the vibrational quantum number of the upper level is 23.

In Fig. 1, spectrum B was recorded with the pump laser alone. In this spectrum, we observe a diffuse band which has a maximum at 574 nm. This kind of diffuse band has been observed under various excitation conditions in Li₂ (peaking at 458.5 nm),¹⁴ Na₂ (peaking at 436.5 nm)¹¹ and K₂ (peaking at ~574 nm),¹⁵ and in each case the origin was the 2 1Πₗg → a 3Σ⁺ transitions.¹⁶ The 2 3Πₗg → a 3Σ⁺ 436 nm diffuse band of Na₂ has been observed whenever an A 1Σ⁺ₗ (or b 1Πₗg) → X 1Σ⁺ₗ transition was excited.¹⁶ The 2 3Πₗg state was populated by collisions of two excited Na₂ molecules in the A 1Σ⁺ₗ (or b 1Πₗg) state (energy pooling). The 574 nm diffuse band of K₂ seen in spectrum B could be produced by the same collision mechanism as in Na₂. The residual of this 574 nm peak in spectrum C might be due to collisions of the b 1Πₗg molecules populated by 2 3Σ⁺ₗ → b 1Πₗg radiation. The 2 3Σ⁺ₗ v=23 level is ~300 cm⁻¹ below the 2 3Πₗg v=0 level and the contribution from 2 3Σ⁺ₗ → 2 1Πₗg collisions to this 574 nm peak is therefore expected to be small.

B. Perturbation and quantum interference

We have also observed perturbations between the K₂ 2 3Σ⁺ₗ and 2 3Πₗg states. Figure 2 shows the resolved fluorescence spectra from the mutually perturbed 2 3Πₗg v=16, J=71 and 2 3Σ⁺ₗ v=40, N=71, J=71 levels to the a 3Σ⁺ₗ state. As seen in Fig. 2(a), in the 545–585 nm region, both spectra look similar to the spectrum from the unperturbed (or only weakly perturbed) 2 3Πₗg v=15 levels [Fig. 3(a)]. However, from the mixed levels, an additional oscillating continuum at wavelengths longer than 580 nm appears in both spectra [Fig. 2(b)]. While the 574 nm peak and emission at shorter wavelengths [see Fig. 2(a)] is stronger in the 2 3Πₗg → a 3Σ⁺ₗ spectrum (lower) than in the 2 3Σ⁺ₗ → a 3Σ⁺ₗ spectrum (up-
the intensity of the \( \lambda > 580 \) nm oscillating continuum [Fig. 2(b)] in the \( 2^3 \Sigma_g^+ \rightarrow a^3 \Sigma_u^+ \) spectrum (upper) is stronger than that in the \( 2^3 \Pi \rightarrow a^3 \Sigma_u^+ \) spectrum (lower), indicating that the origin of the 574 nm peak and associated continuum is the \( 2^3 \Pi \) state and the fluorescence at \( \lambda > 580 \) nm is due to the \( 2^3 \Sigma_u^+ \) state. An analogous picture can be observed for other perturbed levels as well. For example, Fig. 3(b) shows the resolved fluorescence spectrum from another perturbed \( 2^3 \Sigma_g^+ \) level \( (v=39, N=83, J=83) \).

Figure 2(c) is an expanded portion of Fig. 2(a) showing transitions into the bound levels of the \( a^3 \Sigma_u^+ \) state. Unlike the rotational pattern from unperturbed \( 2^3 \Pi_0^0 \) and \( 2^3 \Sigma_g^+ \) levels, where the \( P-R \) lines have nearly the same intensities, in Fig. 2(c), the \( P-R \) lines have quite different intensities into each \( a^3 \Sigma_u^+ \) level.

It is well known that when probabilities of transitions from two interacting states to a common level are comparable in value, rotational line intensity anomalies can occur due to quantum-mechanical interference effects. This type of rotational line intensity anomaly has been observed both in the \( 2^3 \Pi_0^0 \rightarrow 2^3 \Sigma_g^+ \rightarrow b^3 \Pi_u^0 \) excitation spectra and in the \( 2^3 \Pi_0^0 \rightarrow 2^3 \Sigma_g^+ \rightarrow a^3 \Sigma_u^+ \) resolved fluorescence spectra of \( \text{K}_2 \).

The \( 2^3 \Pi_0^0 \rightarrow 2^3 \Sigma_g^+ \) \( (v=15, J=71) \) level. (b) Fluorescence spectrum from the \( 2^3 \Sigma_g^+ \) \( (v=39, N=83, J=83) \) level.

**FIG. 3.** (a) Fluorescence spectrum from the very weakly perturbed \( 2^3 \Pi_0^0 \) \( (v=15, J=87) \) level. (b) Fluorescence spectrum from the \( 2^3 \Sigma_g^+ \) \( (v=39, N=83, J=83) \) level.
The nuclear spin of the $^{39}$K atom is $3/2$, so the total nuclear spin of the $^{39}$K$_2$ molecule, $I$, is $3, 2, 1, 0$. For $I = 3$ and 1, the nuclear spin wave functions are symmetric; they are antisymmetric for $I = 2$ and 0. Since the total wave function has to be antisymmetric following the Pauli principle, the odd $N$ levels of the 2 $^{3}S^+$ state of $^{39}$K$_2$ must combine with the symmetric nuclear wave functions with $I = 3$ and 1 and the even $N$ rotational levels must combine with the antisymmetric nuclear wave functions with $I = 2$ and 0. The hyperfine structure of the 2 $^{3}S^+$ state is expected to follow the case $b_{GS}$ coupling scheme for low rotational levels. In this coupling scheme, the total nuclear spin $I$ couples with total electron spin $S$ to form $G(=S+I)$, and $G$ couples with rotation $N$ to form $F$. The odd $N$ rotational levels should split into six hyperfine levels, $I = 3, S = 1, G = 4, 3, 2$, and $I = 1, S = 1, G = 2, 1, 0$, with energies $3b_F, -b_F, -4b_F$, and $b_F, -b_F, -2b_F$, respectively, according to the expression

$$E_{G,I,S} = \frac{b_F}{2}[G(G + 1) - S(S + 1) - I(I + 1)],$$

where $b_F$ is the Fermi contact constant. Thus the excitation spectra should exhibit five line patterns (since two levels are expected to be degenerate) for transitions involving antisymmetric (odd $N$) 2 $^{3}S^+$ rotational levels. Similarly, the symmetric (even $N$) rotational levels should split into four levels, $I = 2, S = 1, G = 3, 2, 1, 0$, and $I = 0, S = 1, G = 1$, with energies $2b_F, -b_F, -3b_F$, and 0, respectively. Therefore, the even $N$ levels should display four line patterns.

Figure 5 shows excitation spectra corresponding to several transitions into unperturbed 2 $^{3}S^+$ levels. The pattern is similar to that of the case $b_{GS}$ coupling of the Na$_2$ triplet states. The Fermi contact constant of the $^{39}$K 4s ground state is much smaller than that of other alkali atoms: $^{23}$Li, 401.80 MHz; $^{23}$Na, 885.7 MHz; $^{39}$K, 231.54 MHz; $^{85}$Rb, 1011.90 MHz; and $^{133}$Cs, 2298.20 MHz. The HFS of several K$_2$ $b^3$Π$_{0u}$ levels has been resolved by laser excitation spectroscopy in a highly collimated molecular beam. However, even though several K$_2$ triplet Rydberg states have been observed, no HFS has been previously resolved. In our sub-Doppler IR-IR double resonance excitation spectra of the 2 $^{3}S^+$ state, the HFS is partially resolved, as seen in Fig. 5.

With a simple calculation from the $G$ splittings in Fig. 5, similar to that described in Ref. 28, we have obtained a primary Fermi contact constant, $b_F = 65 \pm 10$ MHz. This is in good agreement with 1/4 of the atomic potassium ground state Fermi contact constant [(1/4)231.54 = 58 MHz]. Detailed analysis and simulations of the hyperfine structure will be published separately.

Perturbations involving levels of the 2 $^{3}Π$ state affect the fine hyperfine splittings of the K$_2$ 2 $^{3}Σ_g^+$ levels similar to that observed for the Na$_3$, $^{3}Σ_g^+$ states. The hyperfine patterns of excitation lines into perturbed levels exhibit case $b_{GL}$ coupling. Figure 6 shows hyperfine patterns of perturbed K$_2$ 2 $^{3}Σ_g^+$ rotational lines displaying case $b_{GL}$ coupling. In all these cases, excitation lines associated with the $F_2$ component are narrower than the lines involving the $F_1$ and $F_3$ fine structure components. The energies of the $F_1$ and $F_3$ components can be either higher or lower than that of the $F_2$ component.
ponent due to these perturbations of the $2\Sigma^+_g$ levels by nearby $3\Pi_0$ levels of the same $J$. Since the $2\Sigma^+_g \sim 3\Pi_0$ perturbation comes from $L$ uncoupling $|(1/2\mu k^2)(J^* L^* + J' L')|$, all higher $2\Sigma^+_g$ rotational levels above the $2\Sigma^+_g$ $v=0$ level observed in our experiment have case $b_{\beta S}$ coupling (Fig. 6), while $2\Sigma^+_g$ rotational levels (up to at least $N=43$) which lie below the potential minimum of the $2\Sigma^+_g$ state and other relatively unperturbed $2\Sigma^+_g$ levels all have case $b_{\beta L}$ coupling (Fig. 5).

In addition to perturbations involving the $2\Pi_0$ state, the spin-rotation interaction, which is not important for low-$N$ $2\Sigma^+_g$ rotational levels, becomes inevitably stronger with increasing rotational quantum number and the coupling scheme is expected to evolve from case $b_{\beta S}$ toward case $b_{\beta L}$ as $N$ increases. This transition from case $b_{\beta S}$ to case $b_{\beta L}$ has not been observed in the unperturbed rotational levels up to $N=43$. For the perturbed levels, the observed splitting of a particular $2\Sigma^+_g$ level also depends on how strongly it interacts with a perturbing $3\Pi_0$ level. In Fig. 6(c) the $2\Sigma^+_g$ $v=42$, $N=63$, $J=63$, level is perturbed by the $2\Sigma^+_g$ $v=18$, $J=63$ level, which lies 2.349 cm$^{-1}$ below the $2\Sigma^+_g$ $v=42$, $N=63$, $J=63$ level.

D. Two-photon transition assignment

Many two-photon transitions into the $2\Pi_0$ state have been observed and some of them have been assigned.\textsuperscript{5,6} We observed a two-photon transition at 11 539.361 cm$^{-1}$.\textsuperscript{20} Fig.

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**FIG. 5.** Excitation line shapes of transitions: (a) $2\Sigma^+_g$ $v=42$, $N=2\rightarrow b^3\Pi_{0u} v'=21$, $J'=1$; (b) $2\Sigma^+_g$ $v=42$, $N=5\rightarrow b^3\Pi_{0u} v'=21$, $J'=6$; (c) $2\Sigma^+_g$ $v=23$, $N=21\rightarrow b^3\Pi_{0u} v'=20$, $J'=22$; (d) $2\Sigma^+_g$ $v=23$, $N=41\rightarrow b^3\Pi_{0u} v'=19$, $J'=42$; and (e) $2\Sigma^+_g$ $v=23$, $N=43\rightarrow b^3\Pi_{0u} v'=19$, $J'=42$. Labeled arrows give the term energies of the indicated peaks.
indeed K₂ rather than NaK, which is likely to be present in
samples containing K₂ impurities. The low concentration in the potassium heat pipe due to Na
impurities.

This two-photon transition spectrum looks very similar to the 2 \(^{3}\Sigma^+_g \rightarrow a \(^{3}\Sigma^+_u\) fluorescence of Figs. 2(a) and 3(b). The spectrum contains transitions into the bound levels of the \(^{a}\Sigma^+_u\) state as well as a diffuse band associated with the \(^{a}\Sigma^+_u\) state repulsive continuum. The fluorescence into the vibrational levels of the \(^{a}\Sigma^+_u\) state [Fig. 7(b)] consists of a series of doublets. The discrete lines in Fig. 7(b) have been assigned to transitions into vibrational levels of the \(^{a}\Sigma^+_u\) state, including (\(v > 10\)) rotationally predissociated shape resonance states.

Using the procedure of Ref. 5, we have determined that the two-photon transition at 11 359.361 cm\(^{-1}\) is the \(^{3}\Sigma^+_g\) \(^{2}\Sigma^+_g\) \(v = 53, N = 67\) transition of the \(^{a}\Sigma^+_u\) state.
two $^{3}\Sigma_{g}^{+}$ photons excited by the pump laser when the pump laser was set to 11 539.361 cm$^{-1}$.

The bound-bound fluorescence shown in Fig. 7(b) has been carefully corrected for the relative detection system efficiency versus wavelength. The $a \, ^{3}\Sigma_{u}^{+}$ potential energy function from Ref. 28 showed that the $a \, ^{3}\Sigma_{u}^{+}$ bound levels also confirm the energy of the upper $2 \, ^{3}\Sigma_{g}^{+}$ level.

While the highest vibrational level of the $2 \, ^{3}\Sigma_{g}^{+}$ state observed by IR-IR double resonance is $v = 47$, this two-photon excited level $v = 53$, $N = 67$ is the highest detected level of the $2 \, ^{3}\Sigma_{g}^{+}$ state.

E. Molecular constants and RKR potential curve

In total, we have observed 845 transitions into the $^{39}\text{K}_{2}$ $2 \, ^{3}\Sigma_{g}^{+}$ state. All quantities are in cm$^{-1}$ except $R_{e}$ which is in Å. semiclassical estimate (Ref. 17) $Y_{02} = 4 Y_{01}/Y_{11} = 6.563 \times 10^{-8}$ cm$^{-1}$. The numbers of digits presented are necessary for an accurate reproduction of the term values obtained in the fit and do not reflect the uncertainty in the individual molecular constants.

**TABLE I. Molecular constants of the $^{39}\text{K}_{2}$ $2 \, ^{3}\Sigma_{g}^{+}$ state.**

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**FIG. 8.** (a) Resolved fluorescence to the $a \, ^{3}\Sigma_{g}^{+}$ state with the pump laser frequency set to 11 539.361 cm$^{-1}$ while the probe laser excited the $2 \, ^{3}\Pi_{0g}$ $v = 15$, $J = 69 \rightarrow b \, ^{3}\Pi_{0u}$ $v = 19$, $J' = 68$ transition (10 704.765 cm$^{-1}$); (b) 524–528 nm fluorescence with and without the 10 704.765 cm$^{-1}$ probe laser when the pump laser was set to 11 539.361 cm$^{-1}$.

Note that the $2 \rightarrow 3$ transition has been carefully corrected for the relative detection system efficiency versus wavelength. The $a \, ^{3}\Sigma_{u}^{+}$ potential energy function has been reported in Ref. 28, and we have used this to predict rovibrational term values. From the $P$–$R$ fluorescence line separation, the upper level has been determined to have rotational quantum number $N = 67$. The fluorescence frequencies into the $a \, ^{3}\Sigma_{u}^{+}$ bound levels also confirm the energy of the upper $2 \, ^{3}\Sigma_{g}^{+}$ level.

While the highest vibrational level of the $2 \, ^{3}\Sigma_{g}^{+}$ state observed by IR-IR double resonance is $v = 47$, this two-photon excited level $v = 53$, $N = 67$ is the highest detected level of the $2 \, ^{3}\Sigma_{g}^{+}$ state.
Molecular constants of the $2^3\Sigma^+_g$ state are given in Table I. Table II gives the experimental $2^3\Sigma^+_g$ RKR potential curve determined from the global fitting procedure in this work. Figures 1 (spectrum D), 7(a) and 7(b) show final simulated resolved fluorescence spectra in comparison with observed spectra. From the direct Dunham fit we found the uncertainty of the $T_\epsilon$ value to be 0.7 cm$^{-1}$, since the lowest vibrational level observed is $v=23$. However, in Table I we list more digits for the constants than are needed to reflect the accuracy with which any particular constant has been determined, since these extra digits are needed to reproduce the observed term values and bound-free node positions to within experimental uncertainties.

IV. CONCLUSION

Ab initio calculations$^8$ indicate that the $K_2$ $2^3\Sigma^+_g$ state dissociates to the $4s+5s$ atomic limit and predict values $R_e$ = 4.258 Å and $T_\epsilon$ = 19 376 cm$^{-1}$ above the potential minimum of the ground state. Limited by the available laser wavelengths, the $v$ = 23–25, 27, 28, 31–33, 38–45, 47, and 53 levels have been observed by perturbation-facilitated IR-IR double resonance spectroscopy and two-photon excitation. Vibrational numbering has been determined from resolved fluorescence spectra into the $a^3\Sigma^+_u$ state. Molecular constants have been obtained using a global fit procedure based on a comprehensive set of experimental data, which includes node positions of the bound-free continua as well as term values.

Fine and hyperfine splittings have been resolved in the excitation spectra. The $2^3\Sigma^+_g$ state follows case $b_{gs}$ coupling for unperturbed levels up to $N=43$. Fermi contact is the dominant hyperfine interaction and a preliminary Fermi contact constant, $B_F = 65 \pm 10$ MHz, has been obtained.

Perturbations between the $2^3\Sigma^+_g$ and $2^3\Pi_u$ states were observed. The hyperfine patterns of the $2^3\Sigma^+_g$ levels are strongly affected by perturbation. Intensity anomalies of rotational lines due to quantum-mechanical interference effects appeared both in the $2^3\Sigma^+_g - 2^3\Pi_u$ excitation spectra and in the $2^3\Sigma^+_g - 2^3\Pi_g$ resolved fluorescence spectra.

ACKNOWLEDGMENTS

Support from the NSFC (20473042) and SRFDP of China, the RFBR (05-03-39012) of Russia, and NSF (USA) is gratefully acknowledged. The authors thank Dr. Patrick Burns for assistance with the mixed sodium-potassium heat pipe experiment.

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403, 262 (2005).


The \( 11 \) 539.361 cm\(^{-1} \) two-photon transition was first observed with Ti:sapphire laser (Coherent model 899-29) excitation with the laser frequency calibrated using a uranium hollow cathode lamp. In the experiment with diode lasers, the laser frequencies were measured using Burleigh WA-1600 wavemeters, which have a specified accuracy of 0.003 cm\(^{-1} \). The two-photon transition frequency was measured by a WA-1600 wavemeter to be \( 11 \) 539.365 cm\(^{-1} \). \( 11 \) 539.365 cm\(^{-1} \) is also the central frequency of the transition according to Refs. 32–34. 

See EPAPS Document No. E-JCPSA6-126-027717 for the PFOODR excitation data. This document can be reached via a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).

V. B. Sovkov, V. S. Ivanov, D. Li, F. Xie, L. Li, Opt. Spectrosc. (to be published).

