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The K_2 $2^3\Pi_g$ State: New Observations and Analysis

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Totally 3045 transitions into the $2^3\Pi_g$ $v = 0-42$, $J = 0-103$, $\Omega = 0, 1, 2$ rovibrational levels have been observed by infrared–infrared double resonance fluorescence excitation and two-photon spectroscopy. Molecular constants including the spin–orbit interaction parameters are obtained. Although the K_2 $2^3\Pi_g$ state dissociates to the $4s + 3d$ atomic limit, it is strongly mixed with the 3P ionic states in the range of the potential well. This mixing results in a relatively large equilibrium internuclear distance $R_e = 5.254$ Å and a larger spin–orbit constant $A_0 \sim 14.17$ cm $^{-1}$ than that of the atomic limit -2.33 cm $^{-1}$. Strong perturbations of the $2^3\Pi_g$ levels observed are attributed to the spin–orbit coupling with the $4^1\Sigma_g^+$ state.

1. Introduction

The $2^3\Pi_g$ state of alkali metal dimers has received much attention both experimentally and theoretically.^{1–8} This state has a relatively large equilibrium internuclear distance, R_e , and exhibits strong fluorescence to the lowest triplet state $a^3\Sigma_u^+$. Although the $2^3\Pi_g$ state of the Na_2 and Li_2 molecules was observed^{3,9–11} 20 years ago by the perturbation facilitated optical–optical double resonance (PFOODR) excitation spectroscopy via the $A^1\Sigma_u^+ \sim b^3\Pi_u$ mixed intermediate window levels, the $2^3\Pi_g$ state of the K_2 molecule was observed much later because of experimental difficulties (two infrared lasers are required to reach this state in K_2 , in place of the visible and near-ultraviolet lasers in the case of Na_2 and Li_2). Besides, the accurate molecular constants of the $A^1\Sigma_u^+$ and $b^3\Pi_u$ states of the K_2 molecule had become available only recently.¹² The observations of the $v = 4-14$, $\Omega = 0, 1$ levels of the K_2 $2^3\Pi_g$ state by perturbation facilitated infrared–infrared (IR–IR) double resonance and two-photon $2^3\Pi_g \leftarrow X^1\Sigma_g^+$ spectroscopy (101 transitions total) along with the corresponding analysis were reported.¹³ The strong $2^3\Pi_g \rightarrow a^3\Sigma_u^+$ fluorescence spectrum, peaking at 573 nm, was used to determine the potential energy curve of the K_2 $a^3\Sigma_u^+$ state.¹⁴

At the moment we have observed many more vibrational–rotational levels of the $^{39}K_2$ $2^3\Pi_g$ state (3045 transitions total), including the $v = 0-3$ levels and the $\Omega = 2$ component. The current paper reports the new observations and their analysis. The data on the $^{39}K_2$ $4^1\Sigma_g^+$ state, obtained in a similar

experiment, and the deperturbation of the $2^3\Pi_g \sim 4^1\Sigma_g^+$ mixed levels will be published separately.

2. Experimental Techniques

The experimental details were described in ref 13. Briefly, potassium vapor was generated in a heatpipe oven at 300 °C with 1 Torr argon buffer gas. Two single-mode tunable Toptica DL 100 diode lasers were used as the pump and probe lasers. The pump laser selectively excited an $A^1\Sigma_u^+ \sim b^3\Pi_u$ mixed intermediate level and the probe laser frequency was scanned. The IR–IR double resonance signals of the $2^3\Pi_g$ state were detected by monitoring the $2^3\Pi_g \rightarrow a^3\Sigma_u^+$ yellow-green fluorescence. A Spex 1404 monochromator was used to resolve the fluorescence from the $2^3\Pi_g$ state.

3. Observations

Accurate molecular constants of the intermediate $A^1\Sigma_u^+$ and $b^3\Pi_u$ states as well as of the ground $X^1\Sigma_g^+$ state were reported in refs 12 and 15 correspondingly. With these constants, pump transition frequencies from the ground-state levels into the $A^1\Sigma_u^+ \sim b^3\Pi_u$ mixed levels can be predicted with the accuracy better than 0.08 cm $^{-1}$. Since the $A^1\Sigma_u^+$ and $b^3\Pi_u$ states strongly perturb each other, many $A^1\Sigma_u^+ \sim b^3\Pi_{\Omega_u}$ ($\Omega' = 0, 1$) mixed levels have been used as the intermediate window levels for double resonance excitation into triplet states. We also found five $A^1\Sigma_u^+ \sim b^3\Pi_{\Omega_u}$ $\Omega' = 2$ mixed levels, which have been used as the intermediate window levels to observe the $2^3\Pi_g$ $\Omega = 2$ levels.

The Doppler linewidth of $^{39}K_2$ at 300 °C is about 0.02 cm $^{-1}$. To set the pump laser frequency at the Doppler line center, we first tuned the pump laser frequency to the predicted frequency

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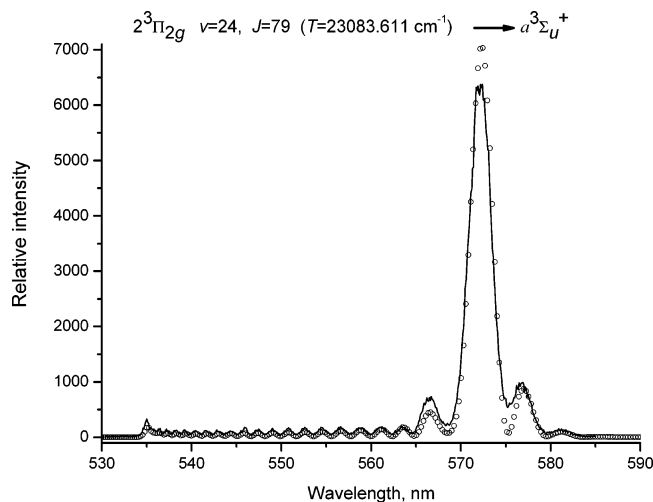


Figure 1. Resolved fluorescence of the ³⁹K₂ 2³Π_g $v = 24$, $J = 79 \rightarrow a^3\Sigma_u^+$ transition: experimental (solid line) and simulated (circles). The fragment of the spectrum at $\lambda < 536.7$ nm is the fluorescence into the bound levels of the $a^3\Sigma_u^+$ state that are not resolved in the figure.

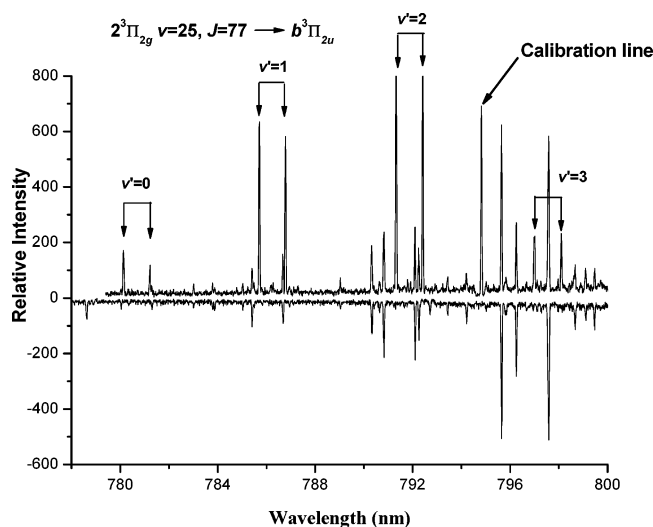


Figure 2. Resolved fluorescence of the ³⁹K₂ 2³Π_g $v = 25$, $J = 77 \rightarrow b^3\Pi_{2u}$ transition. The upper spectrum was recorded when the pump (11 732.215 cm⁻¹) and probe (10 652.772 cm⁻¹) lasers excited the 2³Π_g $v = 25$, $J = 77 \leftarrow b^3\Pi_{2u}$ $v' = 25$, $J' = 78 \leftarrow X^1\Sigma_g^+$ $v'' = 4$, $J'' = 77$ transition. The lower spectrum was recorded without the probe laser. Fluorescence lines from the 2³Π_g $v = 25$, $J = 77$ level into the $b^3\Pi_{2u}$ $v' = 0-3$ vibrational levels are assigned in the upper spectrum.

and scanned the probe laser frequency to find a double resonance signal and then adjusted the pump laser frequency up-down with a 0.002 cm⁻¹ step and repeated the probe laser frequency scan to optimize the double resonance signal. When the signal was the strongest, the pump laser frequency was at the Doppler line center of the pump transition and held fixed there.

Figure 1 displays one of the resolved fluorescence spectra measured in the experiment, namely, the 2³Π_g $v = 24$, $J = 79 \rightarrow a^3\Sigma_u^+$ transition, along with its simulation (see the section “Analysis” below). The part of the spectrum at $\lambda \leq 536.7$ nm is the fluorescence into the bound levels of the shallow well of the $a^3\Sigma_u^+$ state (unresolved in Figure 1).

Figure 2 shows the resolved fluorescence in the 778–800 nm region when the pump (11 732.215 cm⁻¹) and the probe (10 652.772 cm⁻¹) lasers excited the 2³Π_g $v = 25$, $J = 77 \leftarrow b^3\Pi_{2u}$ $v' = 25$, $J' = 78 \leftarrow X^1\Sigma_g^+$ $v'' = 4$, $J'' = 77$ transition. Besides the 2³Π_g $v = 25$, $J = 77 \rightarrow b^3\Pi_{2u}$ $v' = 0-3$ fluorescence lines, many additional lines appear in the spectrum.

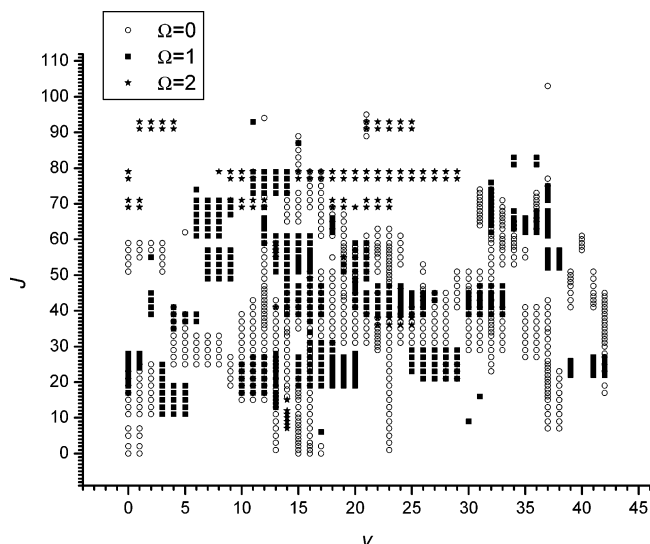


Figure 3. Data field of the ³⁹K₂ 2³Π_g state rovibrational levels observed by the IR–IR double resonance excitation.

Although the pump and probe laser frequencies were in the frequency range of the $A^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ transitions, the $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ fluorescence would have much longer wavelength. The lower spectrum was recorded when the probe laser was blocked. Because the density of the accessible rovibronic levels of K₂ was high under our experimental conditions, the pump laser itself excited a two-photon transition and gave rise to a fluorescence in this wavelength region.¹³ The probe laser itself did not induce a fluorescence in this wavelength region.

On the whole, 2944 new IR–IR double resonance transitions into levels of the K₂ 2³Π_g state have been observed and assigned (Appendix A, Supporting Information) in addition to 101 double resonance and two-photon transitions reported in ref 13. The newly observed levels span a greater range of the vibrational quantum number ($v = 0-42$ in place of $v = 4-14$) and the rotational quantum number ($J = 0-103$ in place of $J = 19-41$). The levels observed in ref 13 belonged only to $\Omega = 0$ and $\Omega = 1$ components, while the new data include 211 transitions to the $\Omega = 2$ component. Figure 3 shows the v – J distributions of the three Ω components.

4. Analysis

The 2³Π_g state has case a coupling at low J with a spin–orbit splitting of ~ 14 cm⁻¹.¹³ Using the ³Π₀, ³Π₁, ³Π₂ case a basis, the effective Hamiltonian matrix elements are¹⁶

$$\langle {}^3\Pi_0, v, J | H | {}^3\Pi_0, v, J \rangle = T_e + G_v + B_v(X+1) - D_v(X^2 + 4X + 1) - \tilde{A}_v$$

$$\langle {}^3\Pi_1, v, J | H | {}^3\Pi_1, v, J \rangle = T_e + G_v + B_v(X+1) - D_v(X^2 + 6X - 3)$$

$$\langle {}^3\Pi_2, v, J | H | {}^3\Pi_2, v, J \rangle = T_e + G_v + B_v(X-3) - D_v(X^2 - 4X + 5) + \tilde{A}_v$$

$$\langle {}^3\Pi_0, v, J | H | {}^3\Pi_1, v, J \rangle = -(2X)^{1/2}[B_v - 2(X+1)D_v]$$

$$\langle {}^3\Pi_0, v, J | H | {}^3\Pi_2, v, J \rangle = -2D_v[X(X-2)]^{1/2}$$

$$\langle {}^3\Pi_1, v, J | H | {}^3\Pi_2, v, J \rangle = -(2X-4)^{1/2}[B_v - 2D_v(X-1)]$$

where $X = J(J+1)$.

TABLE 1: Molecular Constants of the $^{39}\text{K}_2$ $2^3\Pi_g$ State^a

| | this work | ab initio ⁸ |
|----------------|--|------------------------|
| $T_e + Y_{00}$ | 21 601.740 7(16 6) | 21 583 |
| Y_{10} | 55.017 891 (13 517) | 53.40 |
| Y_{20} | -0.169 836 2(3 679 7) | |
| Y_{30} | 0.005 304 245 (443 247) | |
| Y_{40} | -3.156 548 (272 688) $\times 10^{-4}$ | |
| Y_{50} | 1.074 823 0(89 488 0) $\times 10^{-5}$ | |
| Y_{60} | -1.898 627 (149 138) $\times 10^{-7}$ | |
| Y_{70} | 1.341 395 (99 188) $\times 10^{-9}$ | |
| Y_{01} | 0.031 348 83(7 16) | 0.031 3 |
| Y_{11} | 4.739 2(81 0) $\times 10^{-5}$ | |
| Y_{21} | -2.214 24(46 82) $\times 10^{-6}$ | |
| Y_{31} | 1.893 9(80 4) $\times 10^{-8}$ | |
| Y_{02} | -4.100 2(80 5) $\times 10^{-8}$ | |
| Y_{12} | -1.013 3(40 0) $\times 10^{-9}$ | |
| A_0 | 14.168 2(4 4) | |
| A_2 | -6.362 (69) $\times 10^{-4}$ | |
| R_e (Å) | 5.253 8 | 5.26 |
| Y_{00} | -0.040 0 | |

^a Measurement units are cm^{-1} and angstrom. The value of A_1 is statistically insignificant.

All v -dependent constants of the above equations have been represented by the Dunham-like polynomial expressions

$$G_v = \sum_{i=0} Y_{i0}(v + 1/2)^i$$

$$B_v = \sum_{i=0} Y_{i1}(v + 1/2)^i$$

$$D_v = -\sum_{i=0} Y_{i2}(v + 1/2)^i$$

$$\tilde{A}_v = \sum_{i=0} A_i(v + 1/2)^i$$

By numerically diagonalizing the resulting matrix for each v , J and performing a nonlinear least-squares fit to the entire set of the observed unperturbed terms, the values of Y_{ij} and A_i have been obtained. The resulting values are presented in Table 1 along with the ab initio estimates reported in ref 8. The final value $D_e = -Y_{02} = 4.10 \times 10^{-8} \text{ cm}^{-1}$ is very close to the semiclassical estimate¹⁷ $4B_e^3/\omega_e^2 = 4Y_{01}^3/Y_{10}^2 = 4.07 \times 10^{-8} \text{ cm}^{-1}$, confirming that the result is self-consistent.

TABLE 2: RKR Potential Curve of the K_2 $2^3\Pi_g$ State with the Constants of Table 1^a

| R_{\min} | R_{\max} | $T_e + G_v$ | v | R_{\min} | R_{\max} | $T_e + G_v$ | v |
|------------|------------|---------------|-----|------------|------------|---------------|-----|
| 5.078 03 | 5.432 93 | 21 629.207 78 | 0 | 4.137 97 | 6.625 74 | 22 774.445 06 | 22 |
| 4.950 84 | 5.567 32 | 21 683.901 74 | 1 | 4.115 88 | 6.663 20 | 22 823.802 92 | 23 |
| 4.864 04 | 5.661 79 | 21 738.295 45 | 2 | 4.094 40 | 6.700 34 | 22 872.933 56 | 24 |
| 4.794 01 | 5.739 98 | 21 792.408 13 | 3 | 4.073 47 | 6.737 18 | 22 921.836 94 | 25 |
| 4.733 86 | 5.808 74 | 21 846.254 19 | 4 | 4.053 07 | 6.773 75 | 22 970.512 61 | 26 |
| 4.680 47 | 5.871 18 | 21 899.844 20 | 5 | 4.033 16 | 6.810 08 | 23 018.959 64 | 27 |
| 4.632 08 | 5.929 06 | 21 953.185 63 | 6 | 4.013 71 | 6.846 19 | 23 067.176 71 | 28 |
| 4.587 58 | 5.983 46 | 22 006.283 58 | 7 | 3.994 69 | 6.882 12 | 23 115.162 13 | 29 |
| 4.546 24 | 6.035 11 | 22 059.141 39 | 8 | 3.976 07 | 6.917 87 | 23 162.913 99 | 30 |
| 4.507 53 | 6.084 53 | 22 111.761 08 | 9 | 3.957 84 | 6.953 47 | 23 210.430 28 | 31 |
| 4.471 05 | 6.132 12 | 22 164.143 81 | 10 | 3.939 96 | 6.988 94 | 23 257.709 18 | 32 |
| 4.436 50 | 6.178 16 | 22 216.290 20 | 11 | 3.922 42 | 7.024 28 | 23 304.749 30 | 33 |
| 4.403 63 | 6.222 88 | 22 268.200 62 | 12 | 3.905 20 | 7.059 50 | 23 351.550 11 | 34 |
| 4.372 27 | 6.266 47 | 22 319.875 31 | 13 | 3.888 29 | 7.094 60 | 23 398.112 39 | 35 |
| 4.342 24 | 6.309 08 | 22 371.314 62 | 14 | 3.871 69 | 7.129 58 | 23 444.438 75 | 36 |
| 4.313 42 | 6.350 83 | 22 422.519 02 | 15 | 3.855 39 | 7.164 42 | 23 490.534 32 | 37 |
| 4.285 70 | 6.391 82 | 22 473.489 16 | 16 | 3.839 39 | 7.199 08 | 23 536.407 48 | 38 |
| 4.258 98 | 6.432 13 | 22 524.225 89 | 17 | 3.823 71 | 7.233 52 | 23 582.070 71 | 39 |
| 4.233 19 | 6.471 84 | 22 574.730 20 | 18 | 3.808 37 | 7.267 68 | 23 627.541 59 | 40 |
| 4.208 25 | 6.511 00 | 22 625.003 19 | 19 | 3.793 39 | 7.301 47 | 23 672.843 89 | 41 |
| 4.184 11 | 6.549 68 | 22 675.045 98 | 20 | 3.778 81 | 7.334 81 | 23 718.008 80 | 42 |
| 4.160 70 | 6.587 91 | 22 724.859 64 | 21 | 3.764 68 | 7.367 55 | 23 763.076 30 | 43 |

^a $R_e = 5.2538 \text{ Å}$, $T_e = 21 601.781 \text{ cm}^{-1}$, $v_{\min} = -0.49927$, $Y_{00} = -0.0400 \text{ cm}^{-1}$.

The RKR curve computed from the constants of Table 1 is presented in Table 2.

As an independent check of the quality of the results we have simulated the experimental fluorescence spectra of the $2^3\Pi_g \rightarrow a^3\Sigma_u^+$ transitions. To do that we have implemented the split-operator computational technique^{18–20} and used the RKR potential functions of the $2^3\Pi_g$ state constructed from the molecular constants of this work, the modified Lennard-Jones (MLJ)²¹ potential function of the $a^3\Sigma_u^+$ state from ref 14, and the ab initio^{7,8} dipole moment function of the $2^3\Pi_g \rightarrow a^3\Sigma_u^+$ transition. All the simulated spectra have reproduced the experimental ones with a reasonably good accuracy. As an example, the simulation of the $2^3\Pi_{2g} v = 24, J = 79 \rightarrow a^3\Sigma_u^+$ fluorescence is shown in Figure 1 along with the experimental spectrum.

Due to perturbations some part of the experimental term values could not be fitted with a satisfactory accuracy. Those outliers have been excluded from the fit in a following procedure: (i) an initial set of the term values has been fitted, (ii) the averaged standard deviation σ of the calculated and experimental term values has been estimated, (iii) those term values that had deviated by more than 3σ have been excluded from the initial set (and are designated “perturbed”), and (iv) the procedure has been iterated until all the remaining term values are within the range of $\pm 3\sigma$ (and are designated “unperturbed”). The resulting errors of the reproduction of the remaining “unperturbed” term values are shown in Figure 4. Their histogram is compared with the normal distribution density in Figure 5. No significant systematic errors can be observed.

The “perturbed” values excluded from the fit are a set of 446, including 397 transitions to the $\Omega = 0$ component, 39 transitions to the $\Omega = 1$ component, and 10 transitions to the $\Omega = 2$ component. Their deviations from the approximate values based on molecular constants are shown in Figure 6. Many of these deviations exhibit a characteristic behavior of resonantly perturbed terms. As the majority of the perturbed terms belong to the $\Omega = 0$ component, it can be concluded from the selection rules that the main perturber is a state of the $1^1\Sigma_g^+$ symmetry. Obviously, it is the $4^1\Sigma_g^+$ state, whose levels have been also observed by us in the same energy range. Results of the analysis

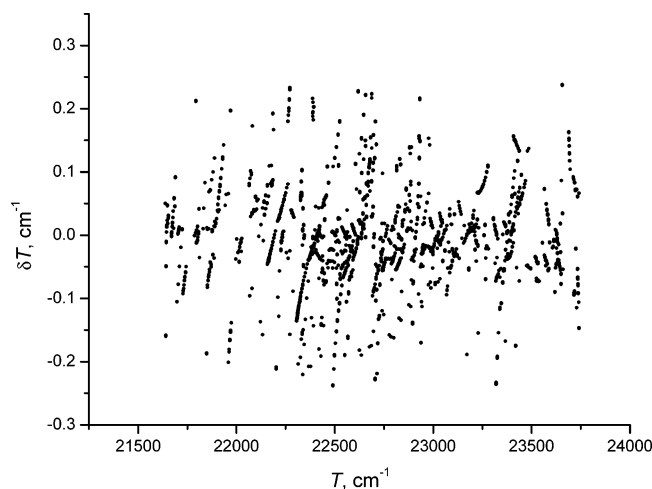


Figure 4. Errors in reproducing “unperturbed” experimental term values of the $^{39}K_2$ $2^3\Pi_g$ state with the molecular constants determined in the current work.

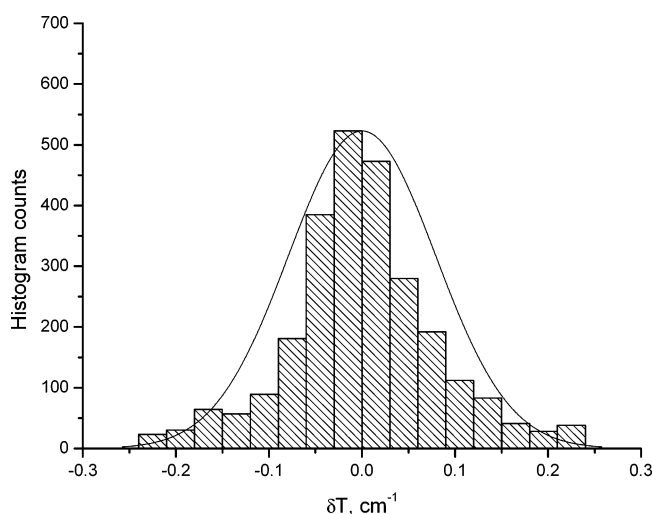


Figure 5. Histogram of the errors of the unperturbed experimental term values of the $^{39}K_2$ $2^3\Pi_g$ state reproduction with the molecular constants determined in the current work compared with the probability density of the corresponding normal distribution.

of the $4^1\Sigma_g^+$ state and the deperturbation of the $4^1\Sigma_g^+ \sim 2^3\Pi_g$ spin–orbit interaction will be published separately.

5. Discussion

Figure 7 shows the ab initio K_2 $2^3\Pi_g$ potential curve intersecting with several curves of the ionic 3P states. Important configurations in the electronic wave function of the $2^3\Pi_g$ state include $4s4p$, $4s5p$, $4s6p$, and $4s7p$. The analysis based on the ab initio computations⁸ shows that the K_2 $2^3\Pi_g$ state between 3.5 Å (7 au) and 6.5 Å (13 au) is built mainly from the ionic $4p7p$ and covalent $6p3d$ configurations, and in this range it can be considered as an ionic state.

Three experimental observations testify to this inference. (i) The K_2 $2^3\Pi_g$ state dissociates to the $4s + 3d$ atomic limit. The ~ 14.17 cm^{-1} spin–orbit constant of the $2^3\Pi_g$ state is much larger than the spin–orbit splitting of the $3d$ atom, -2.33 cm^{-1} . (ii) The dependence of the rotational constant B_v on the vibrational quantum number v has a nontrivial nonmonotonic character (see Figure 8). The standard deviations shown in the same figure confirm that this behavior is statistically significant. In our opinion, such an unusual dependence suggests that the K_2 $2^3\Pi_g$ electronic state configuration changes with the inter-

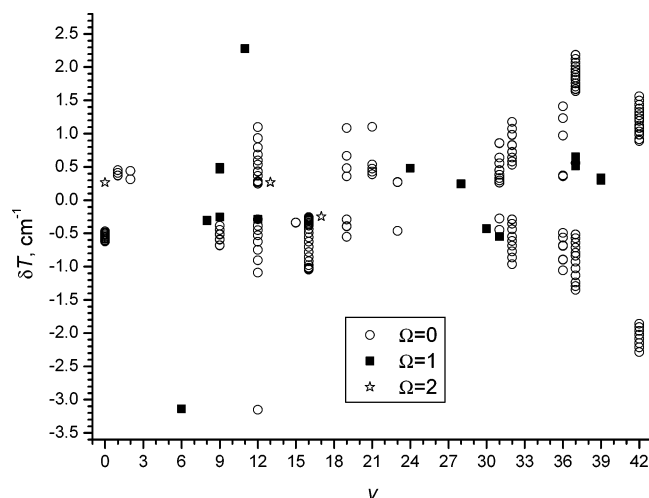


Figure 6. Errors in reproducing “perturbed” experimental term values of the $^{39}K_2$ $2^3\Pi_g$ state with the molecular constants determined in the current work.

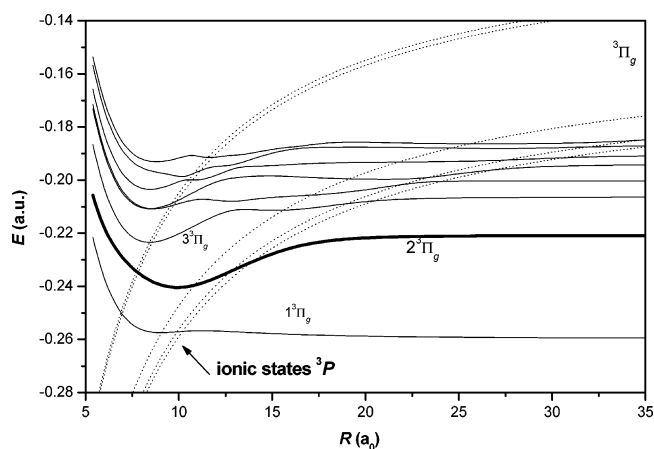


Figure 7. Influence of the potential energy curves of the ionic 3P states (dissociating to the $K^+ + K^-$ ($^3P(nh'l')$) limits) on potential energy curves of the $^3\Pi_g$ states of K_2 from the $K(4s) + K(4p)$ limits up to the $K(4s) + K(5d)$ limits at intermediate and large R .

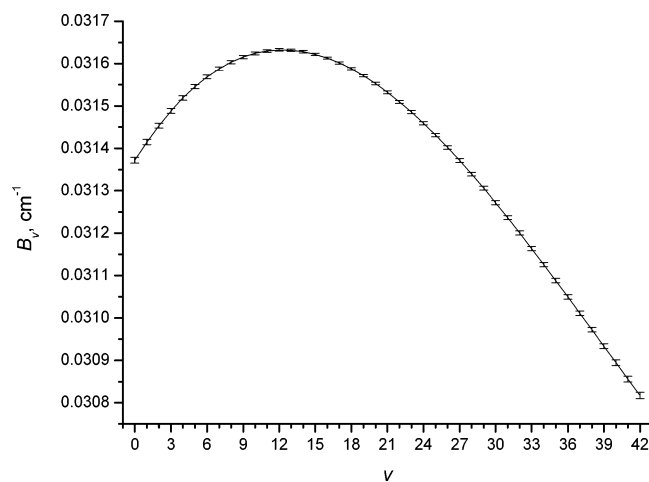


Figure 8. Rotational constant B_v of the $^{39}K_2$ $2^3\Pi_g$ state vs the vibrational quantum number v . Standard deviations computed from the estimated covariance matrix of the Y_{il} values are also shown.

nuclear distance. (iii) A relatively large equilibrium internuclear distance $R_e \sim 5.25$ Å can also be explained by mixing the covalent $6p3d$ and ionic configurations. Calculations on ionic resonance states of K^- and their influence on potential energy curves of K_2 molecular states will be published separately.

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Supporting Information Available: Data of the K_2 $2^3\Pi_g$ state by infrared–infrared double resonance: Intermediate levels, probe transition frequencies, the ν , J , Ω assignments, and term values of the $2^3\Pi_g$ state. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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