I. INTRODUCTION

The two lowest electronic states of K₂ (X ¹Σ₉⁺ and a ³Σ₈⁺) dissociate to the same asymptotic limit, two ground state 4s ¹S atoms. If the potential curves of both molecular states are known precisely up to near dissociation (see Fig. 1), they can be used to determine Coulomb and exchange energies as a function of internuclear distance \( R \). This provides a direct empirical determination for the description of covalent chemical bonding in terms of the fundamental concepts of electronic Coulomb (dispersion) and exchange contributions. This type of analysis has previously been applied to the case of two Li(2s) atoms \(^1\) and two Na(3s) atoms. \(^2\)

At long range where the atomic overlap is small, the potential energies \( \Delta V_X(R) \) and \( \Delta V_a(R) \) with respect to dissociation [i.e., \( \Delta V_X(\infty) = \Delta V_a(\infty) = 0 \)] can be described in terms of the Coulomb contribution \( \Delta V_c(R) \) (dispersion) and the exchange contribution \( \Delta V_E(R) \). In particular

\[
\Delta V_X(R) = \Delta V_c(R) + \Delta V_E(R),
\]

and

\[
\Delta V_a(R) = \Delta V_c(R) - \Delta V_E(R),
\]

where it might be noted that both \( \Delta V_c \) and \( \Delta V_E \) are negative quantities. Alternatively, one can readily determine the values of \( \Delta V_c \) and \( \Delta V_E \) from the sum and difference of the (empirical) potentials,

\[
\Delta V_c(R) = 1/2[\Delta V_X(R) + \Delta V_a(R)],
\]

\[
\Delta V_E(R) = 1/2[\Delta V_X(R) - \Delta V_a(R)].
\]

In the literature, of course, potentials are often given with respect to the potential minimum, not the separated atom (dissociation) limit, i.e., \( V(R) = D_e + \Delta V(R) \). Thus one obtains

\[
\Delta V_c = 1/2(V_X + V_a) - D_e,''
\]

\( \Delta V_E = 1/2(V_X - V_a) \).

Two simple analytical representations for these energy contributions are the second-order long range multipolar expansion in terms of separated atoms\(^3\)

\[
\Delta V_c^{(2)}(R) = -C_6 R^{-6} - C_8 R^{-8} - C_{10} R^{-10} - \ldots
\]

and the exponential\(^4\)

\[
\Delta V_E(R) = Ae^{-aR},
\]

which vanishes rapidly at very large \( R \). We will compare these approximations and also a variety of other theoretical results with our empirical results, as previously done for Li₂ and Na₂.\(^1,2\) It might be noted that hyperfine structure is ignored, but it should only be important at distances much greater than those considered here.

Our procedure is as follows. In Secs. II and III we describe the spectroscopic data and the hybrid potential curves for the X ¹Σ₉⁺ and a ³Σ₈⁺ states of K₂, respectively. In Secs. IV and V we determine and discuss the long-range Coulomb and exchange interactions, respectively. In Sec. VI we describe dissociation energy estimates and recommend an improved value. Conclusions are presented in Sec. VII.

II. THE X ¹Σ₉⁺ STATE

From laser induced spectroscopic studies of the \( A ¹Σ₉⁺ \rightarrow X ¹Σ₉⁺ \) and \( B ¹Π₆⁺ \rightarrow X ¹Σ₉⁺ \) systems, Amiot\(^5\) was able to construct a ground state potential energy curve that goes up to within 0.7% of the dissociation limit, two K(4s) atoms. Amiot recorded more than 3000 rovibrational transitions by Fourier transform infrared (FTIR) spectroscopy. Because of the extent and high resolution (≈0.004 cm⁻¹) of his data, we consider this inverse perturbation analysis (IPA) potential energy curve the best experimental curve available.

Since there is a paucity of information characterizing the uppermost portion of the inner wall of the ground state, we fit the innermost turning points of the IPA curve to obtain an
exponential function $Be^{-bR}$ which permits us to extrapolate the ground state well above the dissociation limit [see Table I (X state, region I) for the exact exponential].

The long-range portion of the ground state curve (beyond the last Amiot turning point $R_{73+}=9.335 \text{ Å}$) is best represented by the dispersion coefficients of Mari
cenu$ et al.$ and exchange energy exponential based on the ab initio calculations of Magnier. The long range potential curve is fully described in Table I (region III).

The theoretical dispersion (van der Waals) coefficients for the $X \, 1\Sigma_g^+$ state (and the $a \, 3\Sigma_u^+$ state) of $K_2$ are given in Table II. The most precise calculations for $C_6$ in our opinion are those of Mari
cenu$ et al.$ which are coincidentally very close to the average ($3803 \text{ a.u.})$ of other results (excluding Bussyery and Aubert-Frecon$). Moreover, the Mari
cenu$ et al.$ calculations have been slightly scaled to agree exactly with the experimental dipole polarizability ($292.8 \pm 6.1 \text{ a}_0^2$) of Molof$ et al.$ Since the uncertainty in the dipole polarizability ($292.8 \pm 6.1 \text{ a}_0^2$) is best represented by the dispersion coefficients of Mari
cenu$ et al.$ and exchange energy exponential based on the ab initio calculations of Magnier. The long range potential curve is fully described in Table I (region III).

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cenu$ et al.$ and exchange energy exponential based on the ab initio calculations of Magnier. The long range potential curve is fully described in Table I (region III).

The perturbation facilitated optical–optical double resonance spectroscopic studies of Li$ et al.$ yielded resolved fluorescence spectra to the $a \, 3\Sigma_u^+$ state which, in turn, yielded an $a$ state potential energy curve that covered nearly 93% of the well.

With the very recent $a \, 3\Sigma_u^+$ state calculations of a very complete potential curve$^2$ and more accurate $C_6$ dispersion coefficients$^5$ (Li$ et al.$ used earlier less reliable values from Refs. 9 and 15), we were able to construct a new and improved hybrid potential energy curve. The approach used for the construction of the $a$ state hybrid potential is similar to that used for the $X$ state hybrid potential; region II (the well)

![FIG. 1. Long range regions of the experimentally-based curves for the $X \, 1\Sigma_g^+$ and $a \, 3\Sigma_u^+$ states of $K_2$. The dashed line is $D_0^+$ plus the negative Coulomb energy $\Delta V_C$. The splitting between the $X$ and $a$ states is twice the exchange energy ($\sim 2\Delta V_C$). $D_0^+$=4449.1±1.0 cm$^{-1}$. The $a \, 3\Sigma_u^+$ state RKR potential shown is given with respect to the $X \, 1\Sigma_g^+$ state minimum (i.e., $\Delta\left\langle a \, 3\Sigma_u^+\right\rangle$ $+ V_c(R)$).](image-url)
TABLE II. Dispersion coefficients (in atomic units) for the X \(1\Sigma^+\) and a \(3\Sigma^+\) states of K.

<table>
<thead>
<tr>
<th>Reference</th>
<th>(C_6)</th>
<th>(C_8)</th>
<th>(C_{10})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dalgarnc(^{\text{f}})</td>
<td>3820</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dalgarnc and Davis(^{\text{g}})</td>
<td>4100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dalgarnc and Davis(^{\text{h}})</td>
<td>3680</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tang, Norbeck, and Certo(^{\text{i}})</td>
<td>3890</td>
<td>446 000</td>
<td>54 900 000</td>
</tr>
<tr>
<td>Maeder and Kutzelnig(^{\text{k}})</td>
<td>3945</td>
<td>383 400</td>
<td>45 220 000</td>
</tr>
<tr>
<td>Miller, Fiesch, and Meyer(^{\text{m}})</td>
<td>(\Delta/4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manakov and Ovsiannikov(^{\text{n}})</td>
<td>3780</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bussery and Aubert-Frecou(^{\text{o}})</td>
<td>4721</td>
<td>389 400</td>
<td>40 690 000</td>
</tr>
<tr>
<td>Spelsberg, Lorenz, and Mayer(^{\text{p}})</td>
<td>3637</td>
<td>401 100</td>
<td>54 310 000</td>
</tr>
<tr>
<td>Marinescu, Sadeghpour, and Dalgarnc(^{\text{q}})</td>
<td>3813</td>
<td>409 600</td>
<td>52 480 000</td>
</tr>
<tr>
<td>Recommended (used in this work)</td>
<td>3813</td>
<td>409 600</td>
<td>52 480 000</td>
</tr>
</tbody>
</table>

\(^{a}\)This \(C_6\) in hartree \(a_0^2\). Conversions to cm\(^{-1}\) and \(a_0\) are \(1_0=0.529 177 249\) Å and 1 hartree = 219.474.631.418 cm\(^{-1}\) (Ref. 17).

\(^{b}\)Also \(C_6=1.571 \times 10^{10}\) a.u.

\(^{c}\)Reference 6.

\(^{d}\)Reference 7.

\(^{e}\)Reference 8.

\(^{f}\)Reference 9.

\(^{g}\)Reference 10.

\(^{h}\)Reference 11.

\(^{i}\)Reference 12.

\(^{j}\)Reference 13.

\(^{k}\)Reference 14.

\(^{l}\)Reference 15.

\(^{m}\)Reference 16.

\(^{n}\)Reference 17.

\(^{o}\)Reference 18.

\(^{p}\)Reference 19.

\(^{q}\)Reference 20.

\(^{r}\)Reference 21.

\(^{s}\)Reference 22.

\(^{t}\)Reference 23.

IV. COULOMB ENERGY

The Coulomb energies at various internuclear distances determined herein using the equation

\[ \Delta V_{c}(R) = 1/2 [V_x(R) + V_a(R)] - D_s \]

are given in Table III and plotted in Fig. 2. For comparison, the expansion

\[ \Delta V_{c}^{2}(R) = - C_6/R_6 - C_8/R_8 - C_{10}/R_{10} \]

with the dispersion coefficients of Marinescu et al.\(^{\text{g}}\) (Sec. II) is also given and plotted. The agreement between these values is

<table>
<thead>
<tr>
<th>(R)</th>
<th>Experiment (this work)</th>
<th>(ab) initio Ref. 7(^{*})</th>
<th>(ab) initio Ref. 23(^{b})</th>
<th>Expanded power series Ref. 6(^{c})</th>
</tr>
</thead>
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<tr>
<td>(a_0)</td>
<td>Å</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.5</td>
<td>6.086</td>
<td>676.76</td>
<td>631.98</td>
<td>940.38</td>
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<tr>
<td>12.0</td>
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<td>304.96</td>
<td>503.69</td>
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<td>7.408</td>
<td>203.06</td>
<td>189.52</td>
<td>324.82</td>
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<tr>
<td>15.0</td>
<td>7.938</td>
<td>126.99</td>
<td>121.70</td>
<td>212.89</td>
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<tr>
<td>16.0</td>
<td>8.467</td>
<td>81.25</td>
<td>81.32</td>
<td>81.29</td>
</tr>
<tr>
<td>17.0</td>
<td>8.996</td>
<td>53.37</td>
<td>56.30</td>
<td>53.27</td>
</tr>
<tr>
<td>17.64</td>
<td>9.335</td>
<td>41.19</td>
<td>45.34</td>
<td>41.29</td>
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<td>18.0</td>
<td>9.525</td>
<td>40.38</td>
<td>35.99</td>
<td></td>
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<td>19.0</td>
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<td>29.74</td>
<td>24.96</td>
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<tr>
<td>20.0</td>
<td>10.584</td>
<td>22.50</td>
<td>17.71</td>
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</tr>
<tr>
<td>22.0</td>
<td>11.642</td>
<td>13.72</td>
<td>9.45</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)\(\Delta V_{c}=1/2(V_x+V_a)-D_s\).

\(^{b}\)\(\Delta V_{c}^{2}-C_6/R_6-C_8/R_8-C_{10}/R_{10}\), where \(C_n\) coefficients are tabulated in Table II.

\(^{c}\)The \(a_0=73\) outer turning point for the \(X \ 1\Sigma^+\) state, Ref. 5.

\(^{d}\)Interpolated.
FIG. 2. Magnitude of the empirical Coulomb energy $-\Delta V_c$ (cm$^{-1}$) in the region 6–9.3 Å is indicated by the solid line. The expanded dispersion energy ($-\Delta V_c = -\sum C_n R^n$) is based on the $C_n$ coefficients of Ref. 6 (see Table III) and indicated by the dashed line from 6 to 11.6 Å. Ab initio $\Delta V_c$ values are those of Ref. 7 (A) and Ref. 23 (+). See also Table III.

The theoretical $X^1\Sigma^+_u$ and $a^3\Sigma^+_g$ potential curves of Magnier$^7$ and Jeung and Ross$^{23}$ can also be used to compute $\Delta V_c$ (Table III; Fig. 2), although the number of significant figures in Ref. 7 limit the accuracy at the larger distances. It is clear that the agreement with experiment is very good for the calculations of Magnier$^7$ and somewhat less good for the calculations of Jeung and Ross.$^{23}$

V. EXCHANGE ENERGY

The exchange energies at various internuclear distances determined herein using the equation

$$\Delta V_E(R) = 1/2[V_x(R) - V_d(R)]$$

are given in Table IV and plotted in Fig. 3. Note that, as previously found for Li$_2$ and Na$_2$, the decay of $\Delta V_E$ with increasing $R$ is very nearly exponential. The dashed line in Fig. 3 is an exponential fit to several ab initio $\Delta V_E$ points based on Magnier.$^7$ It does appear that $\Delta V_E(R)$ falls below the exponential significantly at shorter $R$ and also at larger $R$. Again the results of Jeung and Ross$^{23}$ deviate more significantly from our experimental results than those of Magnier.$^7$

VI. DISSOCIATION ENERGY

The dissociation energy values of the $X^1\Sigma^+_u$ and $a^3\Sigma^+_g$ states of K$_2$ were recently reviewed by Li et al.,$^{20}$ who recommended $D_e[X^1\Sigma^+_u] = 4450 \pm 2$ cm$^{-1}$ and $D_e[a^3\Sigma^+_g] = 254 \pm 2$ cm$^{-1}$. However, the more recent work of Amiot$^5$ and this work provide additional information which can be used to estimate improved $D_e$ values. These new results are summarized in Fig. 4.

Amiot$^5$ in four different ways estimated $D_e$ values between 4449.7 and 4455 cm$^{-1}$; he concluded by recommend-
FIG. 4. Estimates of the dissociation energy \(D_e^+\) of the \(X^1\Sigma^+_g\) state of \(K_2\). The solid curve (with occasional error bars) is based on the RKR curve of Ref. 5 for the \(X^1\Sigma^+_g\) state. The points at \(R = 0.8 \pm 0.02\) Å (Δ with error bars) are based on the new curve for the \(a^3\Sigma^+_u\) state, which is based on the data of Ref. 20. Our overall recommended \(D_e^+\) value, based primarily on the solid curve, is 4449.1 ± 1.0 cm\(^{-1}\) (dashed line).

\[
D_e^+ = 4451 \pm 1.5 \text{ cm}^{-1}.
\]

In our opinion, the most accurate estimate of \(D_e^+\) based on this data alone would be that for \(R_{33}^{+}\) as shown in Table V (\(D_e^+ = 4449.9 \pm 1.8 \text{ cm}^{-1}\)), where the uncertainty in \(\Delta V_C\) is taken as 4% and in \(\Delta V_F\) as 5%.

The same approach applied to the data alone is also shown in Table VI and Fig. 4. The most accurate estimate would be that based on \(R_{17}^{+}\) (\(D_e^+ = 4448.7 \pm 1.0 \text{ cm}^{-1}\)). Note that \(R_{17}^{+}(a) = 10.514 \pm 0.02\) Å, so the \(a^3\Sigma^+_u\) value is derived from data at longer range and is thus less uncertain (although this is partially offset by the higher precision of Amiot’s FTIR spectra\(^a\) compared to the spectrally resolved fluorescence of Li et al.\(\text{^20}\)).

However, the consideration of both \(X^1\Sigma^+_g\) and \(a^3\Sigma^+_u\) data simultaneously (i.e., through determination of \(V_C\)) allows a third determination of \(D_e^+\), namely 4449.1 ± 1.0 cm\(^{-1}\), based on the dotted curve in Fig. 4. In particular, \(\Delta V_C\) should be accurately described by \(\Delta V_C(R)^{2\text{w}}\) well inside the LeRoy radius, since the exchange \(\Delta V_F\) interaction cancels out. The dominant uncertainty in this \(D_e^+\) (as noted in Sec. II) is due to the uncertainty in \(C_6\) (and hence in \(\alpha_K\)). The excellent agreement among the \(X, a,\) and combined \(D_e^+\) values suggests a recommended value of 4449.1 ± 1.0 cm\(^{-1}\). This is inside the earlier 4430±2 cm\(^{-1}\) bounds and suggests both the \(C_6\) and \(\alpha_K\) values may in fact be less uncertain than is quoted above.

Finally, we note the corresponding value for \(D_o^+ = D_0(X^1\Sigma^+_g) = 4449.1 - 46.1 = 4403.0 \pm 1.0 \text{ cm}^{-1}\), and for the \(a^3\Sigma^+_u\) state. \(D_e(a^3\Sigma^+_u) = D_o^+ - T_o^+ = 252.9 \pm 1.1 \text{ cm}^{-1}\) and \(D_o(a^3\Sigma^+_u) = 252.9 - 10.7 = 242.2 \pm 1.2 \text{ cm}^{-1}\).

VII. CONCLUSIONS

Our recommended \(X^1\Sigma^+_g\) and \(a^3\Sigma^+_u\) potential energy curves for \(K_2\) have been combined to empirically determine Coulomb energies, exchange energies, and dissociation energies. These results strongly support the high quality of dispersion calculations (e.g., by Marinescu et al.\(^2\)) and of molecular electronic structure calculations (e.g., by Magner\(^7\)).

\[
\begin{array}{cccccc}
\hline
\nu & 70 & 71 & 72 & 73 \\
\hline
R^a & 8.5739 & 8.7768 & 9.0486 & 9.3353 \pm 0.001 \\
V(R)^b & 4362.729 & 4378.596 & 4392.634 & 4404.877 \pm 0.004 \\
-\Delta V_C^c & 74.426 & 62.218 & 51.167 & 41.293 \pm 1.65 \\
-\Delta V_F^d & 11.898 & 8.471 & 5.771 & 3.728 \pm 0.19 \\
E_{\text{total}}^f & 4449.053 & 4449.284 & 4449.571 & 4449.898 \pm 1.84^g \\
\hline
\end{array}
\]

\(\text{a}\) Values are the outermost RKR turning points from Ref. 5; these points have been shifted to slightly shorter distances (see text).

\(\text{b} V(R)=G(v)\equiv Y_\infty\) and \(T_o=4196.1587 \text{ cm}^{-1}\) from Ref. 20.

\(\text{c} \Delta V_C(R)=\Sigma C_n R^n\), using \(C_n\) coefficients from Ref. 6.

\(\text{d} \Delta V_F(R)=a e^{-BR}\), based on our fit to the \(ab\) initio \(\Delta V_F=1/2(V_C-V_F)\) values, Ref. 7.

\(\text{f} E_{\text{total}}=V(R)-\Delta V_C(R)-\Delta V_F(R)\).

\(\text{g} 0.38 of the total 1.16 \text{ cm}^{-1}\) uncertainty is because of uncertainty in \(R\).

\(0.38 of the total 1.00 \text{ cm}^{-1}\) uncertainty is because of uncertainty in \(R\).
Such high accuracy at long-range is critical to understanding collisions of ultracold atoms (see e.g., Ref. 24, and references therein).

ACKNOWLEDGMENTS

Helpful discussions with G. Jeung, F. Masnou-Seeuws, and A. Dalgarno are gratefully acknowledged, as is the support received from the National Institute of Standards and Technology and the National Science Foundation.