AIP The Journal of Chemical Physics

What is the ground electronic state of KO?

Edmond P. F. Lee, Pavel Soldán, and Timothy G. Wright

Citation: J. Chem. Phys. **117**, 8241 (2002); doi: 10.1063/1.1511179
View online: http://dx.doi.org/10.1063/1.1511179
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v117/i18
Published by the American Institute of Physics.

JOURNAL OF CHEMICAL PHYSICS VOLUME 117, NUMBER 18 8 NOVEMBER 2002

What is the ground electronic state of KO?

Edmond P. F. Lee[a]
Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hung Hom, Hong Kong and Department of Chemistry, University of Southampton, Highfield, Southampton, United Kingdom, SO17 1BJ

Pavel Soldán[b]
Department of Chemistry, University of Durham, South Road, Durham, United Kingdom, DH1 3LE

Timothy G. Wright[c]
Spectroscopy of Complexes and Radicals (SOCAR) Group, Department of Chemistry, School of Chemistry, Physics and Environmental Science, University of Sussex, Falmer, Brighton, United Kingdom, BN1 9QJ

(Received 12 July 2002; accepted 12 August 2002)

High-level, restricted coupled cluster with singles, doubles, and perturbative triples calculations are performed to determine the ground electronic state of KO. In the absence of spin–orbit coupling, we find that the ground state is a $^2\Sigma^+$ state, with a $^2\Pi$ state lying just over 200 cm^{-1} higher in energy. We ascertain that basis set extension, higher-order correlation energy, mass-velocity, and Darwin relativistic terms do not change this ordering. We then calculate the low-lying Ω states when spin–orbit coupling is turned on. The $^2\Sigma^+_{1/2}$ state undergoes an avoided crossing with the $^2\Pi_{1/2}$ state, and we therefore designate the ground state as $X\frac{1}{2}$. This state is essentially $^2\Sigma^+_{1/2}$ at short R, but essentially $^2\Pi_{1/2}$ at long R; there is a corresponding $A\frac{1}{2}$ state with the opposite behavior. These states have significantly different shapes and so spectroscopy from the adiabatic states. Finally, we calculate the dissociation energy D_0, of KO as 66 ± 1 kcal mol^{-1} and derive ΔH_f(KO, 0 K) as 13.6 ± 1 kcal mol^{-1}. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1511179]

I. INTRODUCTION

The alkali-metal monoxides continue to attract interest both theoretically and spectroscopically. In part, this comes from their important roles in atmospheric,[1,2] combustion,[3,4] and energy[5,6,7] chemistry. Recently, we have performed a number of studies on these species, with reports on the thermodynamics and spectroscopy of LiO and LiO$^+$,[8] NaO,[9] and NaO$^+$,[9,10] the photoionization of NaO,[11] and in addition the spectroscopy and thermodynamics of RbO, CsO, and FrO and their cations.[12]

These species are also of interest as, like other series of molecules,[13] there is a change in the symmetry of the ground state. For LiO (Refs. 14 and 15) and NaO (Ref. 16), the electronic ground state has been established as $^2\Pi$, while it has been shown to be $^2\Sigma^+$ for RbO (Ref. 17) and CsO (Ref. 18); this changeover was explained by Allison *et al.*[19] as being due to the competing effects of the quadrupole attraction of O$^-$, which favors the $^2\Pi$ state, and Pauli repulsion, which favors the $^2\Sigma^+$ state. The changeover point comes at KO, and the identity of its ground electronic state has proved to be a controversial topic.

Early experiments on KO were inconclusive, with Herm and Herschbach initially concluding that the ground electronic state was $^2\Sigma^+$ on the basis of magnetic deflection experiments[20] and then concluding[21] that the nonobservation of an electron spin resonance (ESR) spectrum was consistent with its being $^2\Pi$. Allison *et al.*[19] calculated the ground state of KO to be $^2\Pi$ (with the $^2\Sigma^+$ state lying 830 cm^{-1} above) using configuration interaction (CI) calculations and a double-ζ basis set, with polarization functions on the oxygen atom. Later, however, Langhoff *et al.*, again employing the configuration interaction with single and double excitations (CISD) method, using very large basis sets and concluded[22] that the ground state of KO was in fact $^2\Sigma^+$. In 1991, Langhoff *et al.* published complete-active-space self-consistent-field (CASSCF) and CASSCF+multireference configuration interaction (MRCI) calculations,[23] which indicated that at the CASSCF level of theory, the ground state of KO was determined to be $^2\Pi$, but that at the CASSCF +MRCI level, it was $^2\Sigma^+$—a fact that they confirmed in a careful series of calculations in 1992 (Ref. 24) (as well as in a study of the photodetachment process on KO$^-$).[25] This latter conclusion was also confirmed in CASSCF calculations by Serrano-Andrés *et al.*[26,27] In 1993, two of the present authors were involved in an *ab initio* study of KO,[28] and in line with Allison *et al.*,[19] the ground state of KO was calculated[28] to be $^2\Pi$. One of the authors was also involved in a photoelectron study of KO (Ref. 29) (as well as LiO and NaO). The KO was formed by either the reaction K+N$_2$O or the reaction K+O$_3$: The reaction of K+N$_2$O was expected to yield KO in the $^2\Sigma^+$ state on the basis of correlation arguments[30] and molecular beam magnetic deflection experiments[31] as applied to the Na+N$_2$O reaction—a conclusion also inferred in Ref. 29 from the intensities of bands

---

[a] Electronic mail: E.P.Lee@soton.ac.uk
[b] Electronic mail: pavel.soldan@durham.ac.uk
[c] FAX: +44 1273 677196. Electronic mail: T.G.Wright@sussex.ac.uk

in the NaO photoelectron spectrum. (This preference for formation of the $A\,^2\Sigma^+$ state has been readdressed recently.[32]) If the $^2\Sigma^+$ state of KO is formed almost exclusively, then the appearance of features assigned to the $^2\Pi$ state in the photoelectron spectrum from the $K+N_2O$ route was taken to imply that the $^2\Pi$ state is the lower, populated by collisional deactivation.[29] Very recently, Hirota[13] has outlined the results of as-yet-unpublished microwave spectroscopic studies of the KO molecule, where it was concluded that the ground state is $^2\Pi$, with the $^2\Sigma^+$ state lying 200 cm^{-1} higher in energy. All of the above present a very confusing picture, but this situation is made all the more nebulous by the aforementioned study of Langhoff, Bauschlicher, and Dyall, who performed a very careful *ab initio* study,[24] taking into account basis set, level of theory, basis set superposition error (BSSE), and relativistic (spin–orbit) effects—their conclusion was that the ground state of KO was $^2\Sigma^+$, and they could not see any effect that could alter that conclusion. This is in apparent direct contradiction to the detailed microwave experiments,[13] which tend to yield very reliable results. Consequently, two apparently reliable studies reach opposite conclusions, and the conflicting conclusions of the other studies do not help.

It is the purpose of the present work to look into this matter further by performing state-of-the-art *ab initio* calculations and to try and give a definitive answer to the question posed in the title of this paper. A particular point of interest is how does the interaction between the $^2\Pi_{1/2}$ spin–orbit component and the $^2\Sigma^+_{1/2}$ spin–orbit state affect the picture? Finally, we further investigate the effects of relativity, as well as basis set extension and core-valence correlation energy.

II. COMPUTATIONAL DETAILS

First, we generated potential energy curves for the lowest $^2\Sigma^+$ and $^2\Pi$ states using the Feller misc. CVQZ basis set for K from the Gaussian basis set order form (GBSOF),[33] which in its original form has *s* and *p* functions from Partridge, with core and polarization functions from Feller, and has the contracted form $(23s19p6d4f2g)/[10s9p6d4f2g]$. In the present work, the contracted $[4s2p]$ functions of that basis set were taken and augmented with

nine *s*: $\zeta=9.0-0.00589824$, ratio$=2.5$;
ten *p*: $\zeta=19.0-0.00498073$, ratio$=2.5$;
six *d*: $\zeta=7.5-0.05227$, ratio$=2.7$;
four *f*: $\zeta=2.0-0.1016$, ratio$=2.7$;
three *g*: $\zeta=1.485-0.2037$, ratio$=2.7$;
two *h*: $\zeta=0.8$ and 0.2963,

giving a $[13s12p6d4f3g2h]$ basis set. For O, the standard aug-cc-pV5Z basis set was employed. These will be referred to as basis A below. This was used with the RCCSD(T) procedure,[34] as implemented in MOLPRO.[35] We performed a scan over short and long *R*, but were restricted in the long-*R* region by the emergence of multireference behavior, as the ionic-covalent avoided crossing[23,26] starts to occur.

A second set of calculations also employed the RCCSD(T) procedure, but this time employed the $(24s16p)$ basis set from Huzinaga and Klobukowski,[36] which was contracted to $[3s2p]$. This was augmented with the same uncontracted $(9s10p6d4f3g2h)$ basis functions as above, giving a $[12s12p6d4f3g2h]$ basis set. For O, the standard aug-cc-pV5Z basis set was again employed. These will be referred to as basis B below. For these calculations we also investigated the effect of the BSSE by performing the full counterpoise (CP) correction[37] at all points.

In the RCCSD(T) procedure, the $1s$ electrons on O and the $1s2s2p$ electrons on K were kept frozen. The RCCSD(T)/basis A and RCCSD(T)/basis B results were used to calculate spectroscopic constants employing LEVEL.[38]

Subsequently, single-point energy calculations at the minima of the $^2\Sigma^+$ and $^2\Pi$ curves from the RCCSD(T)/basis B calculations were performed using basis C and basis D, which were constructed as follows:

Basis C: this consisted of the $[12s12p6d4f3g2h]$ basis set from basis B, to which was added the following tight functions in order to allow core-valence correlation to be described:

four *s*: $\zeta=351.5625-22.5$, ratio$=2.5$;
three *p*: $\zeta=296.875$, 118.75 and 47.5;
three *d*: $\zeta=147.6225$, 54.675 and 20.25;
two *f*: $\zeta=50.0$ and 5.4;
one *g*: $\zeta=15.0$,

giving a $[16s15p9d6f4g2h]$ basis set. For these calculations, no electrons were frozen in the RCCSD(T) procedure. The standard aug-cc-pCV5Z basis set was used for O.

Basis D: this consisted of the $[12s12p6d]$ functions from the $[12s12p6d4f3g2h]$ K basis set in basis C, but augmented with the following even-tempered functions:

five *f*: $\zeta=5.488-0.089286$, ratio$=2.8$;
four *g*: $\zeta=2.43-0.09$, ratio$=3.0$;
three *h*: $\zeta=1.225$, 0.35 and 0.1;
two *i*: $\zeta=0.8$ and 0.2,

giving a $[12s12p6d5f4g3h2i]$ basis set. The standard aug-cc-pV6Z basis set was used for O.

In addition, we calculated the mass-velocity and Darwin contributions to the relativistic energy employing basis E at the Hartree–Fock (HF) level. This consisted of the uncontracted $(24s16p)$ functions from Huzinaga and Klobukowski as used in basis B for K, together with the six uncontracted *d* functions, giving a $(24s16p6d)$ K basis set. We took the uncontracted $(14s9p5d)$ standard functions from the aug-cc-pV5Z basis set for O. More details of the procedure used will be presented below.

The next stage of the calculations was to calculate the spin–orbit interaction. This was done by taking RCCSD(T)/basis B energies for the $^2\Pi$ and $^2\Sigma^+$ states and employing the state-interacting method (more details below).

III. RESULTS AND DISCUSSION

A. No spin–orbit coupling

In Fig. 1 are shown the RCCSD(T)/basis A curves. As may be seen, the $^2\Sigma^+$ curve is calculated to lie the lowest in energy. It has a minimum at $R_e=2.170$ Å and a calculated 0-1 separation of 422.1 cm^{-1}. For comparison, the results using RCCSD(T)/basis B are $R_e=2.170$ Å and 0-1 separa-

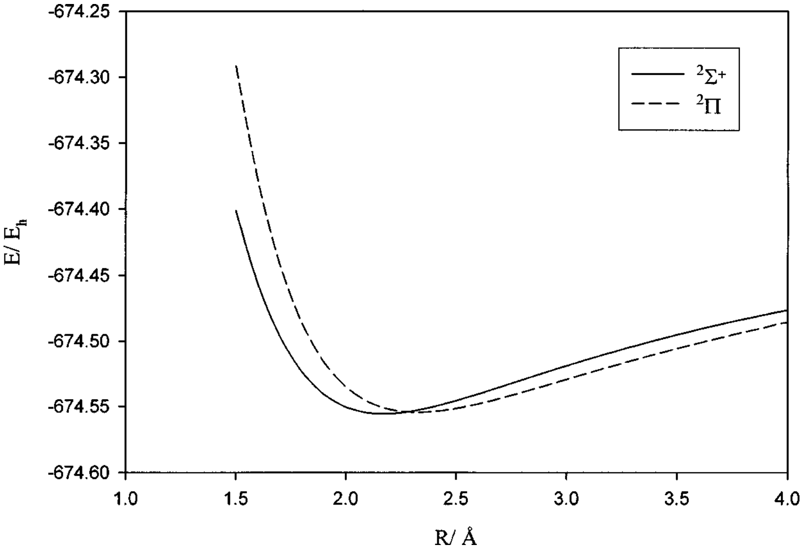

FIG. 1. Potential energy curves for the $^2\Sigma^+$ and $^2\Pi$ curves calculated at the RCCSD(T)/basis A level of theory.

tion of 422.0 cm^{-1}. The results are in good agreement with Bauschlicher *et al.*[24] who obtained a value of $R_e = 2.187$ Å and a harmonic frequency of $\omega = 422$ cm^{-1} using the modified coupled pair function (MCPF) approach. Similarly, from the RCCSD(T)/basis A curve for the $^2\Pi$ state $R_e = 2.323$ Å and the 0-1 separation was 387.9 cm^{-1}, while from the RCCSD(T)/basis B curve, $R_e = 2.323$ Å and the 0-1 separation was 388.4 cm^{-1}: These compare with the values of $R_e = 2.338$ Å and $\omega = 390$ cm^{-1} from the MCPF calculations in Ref. 24. The T_e values were 241.5 cm^{-1} using basis A and 243.1 cm^{-1} using basis B. The best value from Ref. 24 was 229 cm^{-1} at the CCSD(T) level. Of course, these results are under the approximation of no spin–orbit coupling. That the results from basis A and basis B are so similar indicates that the importance of the 4*s* contraction is small, since basis A has a contracted 4*s* function (based on the neutral K wave function), whereas basis B does not.

We also calculated BSSE-corrected curves at the RCCSD(T)/basis B level, where each point was corrected using the full CP correction.[37] Analysis of these BSSE-corrected potentials led to the following results. For the $^2\Pi$ state, $R_e = 2.325$ Å and the 0-1 separation was calculated as 387.3 cm^{-1}; for the $^2\Sigma^+$ state, $R_e = 2.172$ Å and the 0-1 separation was calculated as 421.0 cm^{-1}. Thus the effect of the BSSE is to lead to a very slight increase in the R_e value and very small change in the shape of the curve: we conclude that the basis sets we are using are large and flexible enough that the BSSE is not affecting the shape or position of the curves. It does, however, have an effect on the calculated T_e value between the two states: From the BSSE-corrected curves, we obtain a T_e value of 230.5 cm^{-1}, which is 13 cm^{-1} lower than the uncorrected curves. It is, however, small enough to conclude that the BSSE will not be able to lead to a reversal in the ordering of the curves. The BSSE difference is entirely due to K^+, owing to the difference in bond lengths between the two states: The calculated BSSE's were 40 cm^{-1} for O^- in both states, 55 cm^{-1} for K^+ in the $^2\Pi$ state, and 69 cm^{-1} for K^+ in the $^2\Sigma^+$ state.

1. Relativistic

In order to calculate the effect of relativity, calculations were performed as follows: First, we calculated the mass-velocity plus Darwin relativistic contributions at the HF level. For these calculations we used basis E uncontracted. We calculated the mass-velocity and Darwin contributions for K^+ and O^- using the full molecular basis set. We then calculated these relativistic terms for the KO molecule in each of the $^2\Pi$ and $^2\Sigma^+$ states, and hence could estimate the lowering of the potential energy curves owing to these two contributions.

We find that the $^2\Pi$ state increases in energy by 39.5 cm^{-1} and the $^2\Sigma^+$ state increases in energy by 25.0 cm^{-1}, so that the $^2\Pi$-$^2\Sigma^+$ separation increases by ~15 cm^{-1}. Thus these effects are relatively small and will certainly not lead to a reversal of the ordering of the states—a conclusion also reached in Ref. 24.

2. Core-valence correlation

As noted above, we constructed basis C so that it contained tight functions to describe the core-valence correlation. The result of full RCCSD(T) calculations was that the $^2\Pi$ state was at a T_e separation of 254 cm^{-1} compared to the $^2\Sigma^+$ state, which is very similar to the values obtained using basis A and basis B. We find that this separation reduces to 239 cm^{-1} when the CP correction is applied. We conclude that core-valence interactions will not change the ordering.

3. Further basis set extension and BSSE

Using the very large basis D and freezing the O 1*s* and K 1*s*2*s*2*p* electrons, we find that the T_e value at the RCCSD(T) level is 253 cm^{-1}, which is very close to that obtained at the RCCSD(T, full)/basis C level and is only changed by ca. +10 cm^{-1} compared to the RCCSD(T)/basis A and RCCSD(T)/basis B methods. Given this close agreement and also the agreement with the values obtained in Ref. 24, we conclude that the ordering of the $^2\Pi$ and $^2\Sigma^+$ states

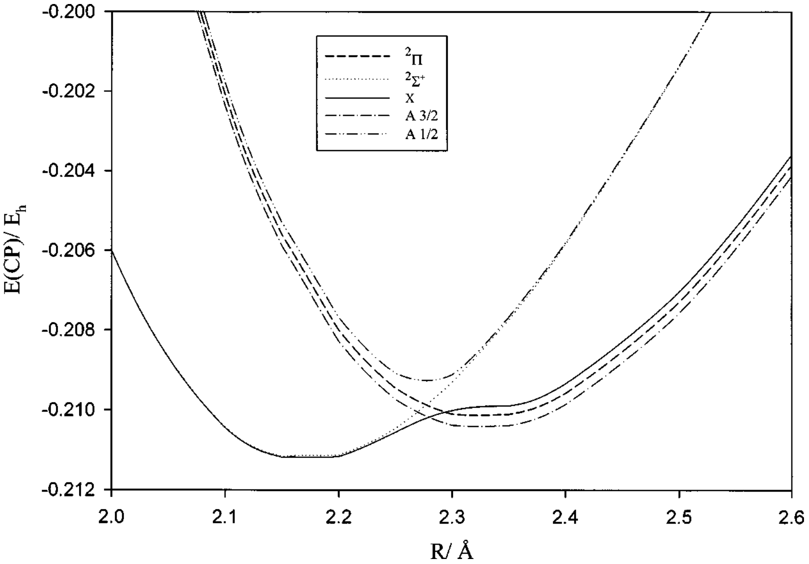

FIG. 2. Potential energy curves calculated at the RCCSD(T)/basis B level of theory for the $^2\Sigma^+$ and $^2\Pi$ states and the Ω states that arise from spin orbit coupling: the $X\frac{1}{2}$, $A\frac{1}{2}$, and $A\frac{3}{2}$ states. Note particularly the avoided crossing between the $X\frac{1}{2}$ and $A\frac{1}{2}$ states—see text for more details. The full counterpoise correction has been applied in a point-by-point manner.

will be unaltered by further increasing the basis set—indeed, if anything the separation will increase slightly. Again, as with basis B, we find that the BSSE is again almost entirely due to K^+ because of the difference in bond lengths. We calculate the following BSSE's: K^+ (77 cm^{-1}) and O^- (16 cm^{-1}) for the $^2\Pi$ state and K^+ (95 cm^{-1}) and O^- (14 cm^{-1}) for the $^2\Sigma^+$. Thus the correction for the BSSE leads to a decrease in the calculated T_e by 16 cm^{-1}, giving a value of 237 cm^{-1}, which is very close to the BSSE-corrected values from basis B.

B. Inclusion of spin–orbit coupling

For the first time, the spin–orbit interaction at each point in the potential and the interaction between the low-lying Ω states is calculated—this is in contrast to Ref. 24, where the spin–orbit coupling of O^- was used in a first-order model at a single point. In Fig. 2 are shown curves calculated for the $^2\Pi$ and $^2\Sigma^+$ states and the effect of including spin–orbit coupling employing the Breit-Pauli operator as implemented in MOLPRO.[39] In the latter calculations, CASSCF calculations are carried out with basis E (uncontracted), with the oxygen $1s$ and K $1s$, $2s$, and $2p$ electrons treated as core; the RCCSD(T)/basis B BSSE-corrected energies were used as the diagonal elements of the spin–orbit matrix.

If we look at $R = 2.1$ Å, the $^2\Pi$ states splits into two components, with $\Omega = 1/2$ and 3/2. The $\Omega = 1/2$ lies above the $^2\Pi$ state and is denoted $A\frac{1}{2}$, and the $\Omega = 3/2$ lies below and is denoted $A\frac{3}{2}$; the $^2\Sigma^+$ state becomes another $\Omega = 1/2$ state, denoted $X\frac{1}{2}$. There is now an avoided crossing between the $X\frac{1}{2}$ and $A\frac{1}{2}$ states, but the $A\frac{3}{2}$ state remains parallel to the $^2\Pi$ curve, but lying below. The interesting feature here is that although the $X\frac{1}{2}$ state is essentially the $^2\Sigma^+_{1/2}$ state at short R, after the avoided crossing, it becomes the $^2\Pi_{1/2}$ component of the $^2\Pi$ state and develops a shelf, as the result of the avoidance. The $A\frac{1}{2}$ state, which is essentially the $^2\Pi_{1/2}$ component of the $^2\Pi$ state at short R, becomes the $^2\Sigma^+_{1/2}$ state as the result of the avoided crossing; the avoidance also leads to a steepening of the potential at longer R. It is possible to analyze all of these curves by making use of LEVEL,[38] and the results are given in Table I. We summarize some of the main features for these states in the following paragraphs.

Looking first at the $X\frac{1}{2}$ state, the R_e value is almost unaffected by the avoided crossing, which is as expected from the shape of the curves in Fig. 2. The $v = 0$ vibrational level is found to be at 194.5 cm^{-1} above the minimum, which places it almost isoenergetic with the minimum of the $A\frac{3}{2}$ state. The $v = 0$ level lies just below the shelf, with the $v = 1$ level lying above it, and this feature is demonstrated in the calculated anomalous vibrational separations, which are 296.6, 281.4, 316.8, and 315.8 cm^{-1}, starting from the 0-1 separation. The separations are smaller than those in the $^2\Sigma^+$ state, as expected, since the avoided crossing leads to a flattening out of the $X\frac{1}{2}$ state potential compared to the $^2\Sigma^+$ state. The 0-1 value is somewhat smaller than that reported in a matrix isolation study, where 384 cm^{-1} was obtained.[40]

Looking at the $A\frac{1}{2}$ state, the R_e value is smaller than that of the $^2\Pi$ state, as expected from Fig. 2: in addition, the zero-point vibrational energy (ZPVE) of 301.7 cm^{-1} and the 0-1 separation of 559.9 cm^{-1} are very much higher than that of the $^2\Pi$ state, as expected from Fig. 2. Of interest is that the R_0 value is *smaller* than the R_e value, contrary to the usual situation—the reason for this is the steepening of the long-R region, which leads to the $v = 0$ vibrational wave function being more localized to short R, the opposite of the normal situation.

The $A\frac{3}{2}$ state is essentially unaltered by the presence of the avoided crossing, with R_e and 0-1 separation values almost identical to those of the $^2\Pi$ state.

TABLE I. Spectroscopic constants for the lowest Ω states of KO.

State	R_e (Å)	R_0 (Å)	ZPVE (cm^{-1})	0-1 separation (cm^{-1})
$X\frac{1}{2}$	2.170	2.261	194.5	296.6
$A\frac{3}{2}$	2.325	2.330	195.3	387.2
$A\frac{1}{2}$	2.277	2.275	301.4	559.9

C. T_e value for KO

From the above, we can estimate our best value for T_e for the ${}^2\Pi \leftarrow {}^2\Sigma^+$ separation in the absence of spin–orbit coupling. From the RCCSD(T)/basis D results, the value of 253 cm^{-1} is lowered to 237 cm^{-1} after correction for the BSSE. The mass-velocity and Darwin terms combine to raise the separation by $\sim$15 cm^{-1}, and the core-valence effect is to raise it by $\sim$10 cm^{-1}. Thus a T_e value of 250 ± 25 cm^{-1} is our best value, where the error is an estimate based upon the change in the separation upon application of the CP correction and basis set extension and further core-valence effects.

Once spin–orbit coupling has been included, then the T_e values obtained from LEVEL become $A\frac{3}{2} \leftarrow X\frac{1}{2}$ (178 cm^{-1}) and $A\frac{1}{2} \leftarrow X\frac{1}{2}$ (434 cm^{-1}).

D. Heat of formation

It is a straightforward matter to derive a heat of formation at 0 K for KO from the calculated energetics for the reaction

$$\mathrm{KO}(X\tfrac{1}{2}) \rightarrow \mathrm{K}^+ + \mathrm{O}^- \tag{1}$$

and employing the well-established $\Delta H_f(0\ \mathrm{K})$ values for K^+ (121.6 $\mathrm{kcal\,mol}^{-1}$) and O^- (25.3 $\mathrm{kcal\,mol}^{-1}$) from the JANAF Tables.[41] We employ the RCCSD(T)/basis D//RCCSD(T)/basis B energetics, as we have shown that the effects on R_e of the spin–orbit coupling are negligible. We obtain ΔH for reaction (1) as 132.1 $\mathrm{kcal\,mol}^{-1}$, which is simply the change in the electronic energy modified by the ZPVE of KO. This converts into a ΔH_f value of 13.6 $\mathrm{kcal\,mol}^{-1}$ for KO. The error on this value, from the results given above, is very much less than 1 $\mathrm{kcal\,mol}^{-1}$; in particular, we note that the corresponding RCCSD energetics yield a ΔH value only 0.2 $\mathrm{kcal\,mol}^{-1}$ lower. We cite a final value of $\Delta H_f(\mathrm{KO}) = 13.6 \pm 1$ $\mathrm{kcal\,mol}^{-1}$. This value is a large improvement on the estimated JANAF value of 17 ± 10 $\mathrm{kcal\,mol}^{-1}$.

It is also straightforward to calculate the dissociation energy of KO by employment of the ionization energy of K ($4.340\,066 \pm 0.000\,01$ eV), the electron affinity of O (1.461 eV),[42] and the calculated energetics of reaction (1). This yields values of $D_e = 66.3$ $\mathrm{kcal\,mol}^{-1}$ and $D_0 = 65.7$ $\mathrm{kcal\,mol}^{-1}$, and we cite $D_0(\mathrm{KO}) = 66 \pm 1$ $\mathrm{kcal\,mol}^{-1}$. These values are in almost perfect agreement with the CI value of $D_e = 66.0$ $\mathrm{kcal\,mol}^{-1}$ obtained in Ref. 22. Experimentally, values of the dissociation energy of KO have been reported as 71 ± 6 $\mathrm{kcal\,mol}^{-1}$ (Ref. 43) and 66 ± 3 $\mathrm{kcal\,mol}^{-1}$ (Ref. 44, also recommended in Ref. 45); a more recent value[6] is 62 ± 1 $\mathrm{kcal\,mol}^{-1}$, which seems slightly on the low side.

It is worth noting that in the absence of spin–orbit coupling, the ${}^2\Sigma^+$ state correlates to the excited $\mathrm{K}({}^2P) + \mathrm{O}({}^3P)$ asymptote, with the ${}^2\Pi$ state correlating to the ground state $\mathrm{K}({}^2S) + \mathrm{O}({}^3P)$ asymptote, which lies $\sim$13 000 cm^{-1} (37 $\mathrm{kcal\,mol}^{-1}$) higher in energy.[46] The presence of the avoided crossing means that the (essentially ionic) $X\frac{1}{2}$ state will dissociate to the ground-state atomic products, initially as a result of the first avoided crossing with the $A\frac{1}{2}$ state, and then at longer R as a result of the avoided crossing with a covalent state (*vide supra*). (Note that we have ignored the spin–orbit splitting in the $\mathrm{O}({}^3P)$ in the above. In fact the lowest spin–orbit state is ${}^3P_0$, with the ${}^3P_1$ lying 158 cm^{-1} above, with the $\mathrm{O}({}^3P_2)$-$\mathrm{O}({}^3P_0)$ splitting being 227 cm^{-1}—the largest splitting is still only 0.6 $\mathrm{kcal\,mol}^{-1}$, which scarcely affects the above numbers.[47])

IV. FURTHER DISCUSSION

The conclusion in the present work that the ${}^2\Sigma^+$ state is the lowest electronic state of KO is in agreement with the previous detailed study by Bauschlicher *et al.*[24] The two studies complement each other and reinforce each other's conclusions. Also in agreement with that work, but now after a far more detailed study, neither relativistic effects (including spin–orbit) nor basis set extension are going to change this ordering—our largest basis set (basis D) consisted of 397 basis functions, in contrast to the "big basis set" of 225 functions, used in Ref. 24. In addition, we find that the effect of the triple excitations, in all cases examined herein, is to lead to an *increase* in the T_e value for the ${}^2\Pi$-${}^2\Sigma^+$ separation—a conclusion also made in Ref. 24, but only as the result of a single-point calculation. The conclusions of the earlier *ab initio* studies[19] and of Ref. 28 are incorrect in concluding that the ${}^2\Pi$ state is lower in energy, probably as a result of too small a basis set and too low a level of theory. The magnitude of our BSSE is similar to that of the "big basis set" of Ref. 24, even though our basis set is larger: This is probably because of the larger number of polarization and diffuse functions used herein. The differential BSSE between the electronic states is, however, similar to that of Ref. 24 (note that the BSSE was only calculated at the MCPF level in that work).

The important conclusion from the present work is that the spectroscopy of the low-lying states of KO is affected by the spin–orbit coupling that leads to an avoided crossing between the ${}^2\Sigma^+_{1/2}$ state and the ${}^2\Pi_{1/2}$ component. It is thus more correct to label the states in terms of their Ω values rather than the standard Russell-Saunders term symbols. We conclude, therefore, that the ground electronic state of KO is the $X\frac{1}{2}$ state, which is essentially ${}^2\Sigma^+_{1/2}$ at short R, but ${}^2\Pi_{1/2}$ at long R: in between, the character is mixed. For the $A\frac{1}{2}$ state the situation is essentially reversed.

This mixed character of the $X\frac{1}{2}$ state could explain the conclusions of the microwave study:[13] As noted above, Hirota and co-workers concluded that the ground state was ${}^2\Pi$, with the ${}^2\Sigma^+$ state lying $\sim$200 cm^{-1} higher. However, it was noted in that work that the fit of the rotational structure for the ${}^2\Sigma^+$ state was far from satisfactory. We hypothesize that the mixed nature of the $X\frac{1}{2}$ state and its interaction with the $A\frac{1}{2}$ state lead to perturbation of the rotational levels. The perturbation of a ${}^2\Pi$ state by a ${}^2\Sigma$ state is well understood and is explained in detail in Ref. 48. However, the situation is a little more complicated than that treated therein, owing to the presence of the avoided crossing. In addition, the ${}^2\Pi$ state is expected to be close to a Hund's case (a) limit in the absence of spin–orbit coupling, and the ${}^2\Sigma^+$ state is, of course, Hund's case (b) in the absence of spin–orbit coupling; clearly, in the presence of spin–orbit coupling, Hund's case (c) will have to be considered.

We also noted in the above that photoelectron studies[29] concluded that the ground state of KO was $^2\Pi$ on the basis that both it and the $^2\Sigma^+$ state were observed in the photoelectron spectra. This conclusion relies heavily on the fact that the product of the $K+N_2O$ reaction would be $^2\Sigma^+$ and not $^2\Pi$. The present work has shown that these two states are mixed by the spin–orbit interaction, and consequently that the correlation rules[30] (based on Russell-Saunders coupling) are not applicable to KO.

V. CONCLUDING REMARKS

In the absence of spin–orbit coupling the ground state of KO is $^2\Sigma^+$: this conclusion is unlikely to be changed by relativistic effects, higher correlation effects, or basis set extension. The $^2\Pi$ state is, however, close in energy ($\sim$250 cm^{-1}) and the $^2\Sigma^+$ curve crosses it close to the minimum.

When spin–orbit coupling is turned on, the aforementioned crossing now becomes avoided between the two $\Omega = 1/2$ states. This has significant implications for the ground state, as it can now not be described as $^2\Sigma^+$ as it changes its character at long R, and we designate the ground state by $X\frac{1}{2}$. The effect of the avoided crossing is to flatten out the $X\frac{1}{2}$ state and to lead to a shelf at long R, both of which cause perturbations in the vibrational energy levels. The $A\frac{1}{2}$ state, which starts off at short R as the $^2\Pi_{1/2}$ state and evolves into the $^2\Sigma^+_{1/2}$ state at long R, is also affected significantly by the avoided crossing, becoming steeper on the long-R side. In contrast, the $A\frac{3}{2}$ state remains closely identified with the $^2\Pi_{3/2}$ state throughout.

The previous ambiguity in the identification of the ground electronic state can be traced to the complicated electronic structure. *Ab initio* calculations need to be of a very high quality to obtain the correct ordering. The interpretation of the microwave spectrum and the implications of the photoelectron study may both be affected by the avoided crossing in the spin–orbit curves and the consequent mixed identity of the states involved. In studies, there is also the complication that KO has to be produced for study, and the distribution of the molecules between these the $X\frac{1}{2}$, $A\frac{1}{2}$, and $A\frac{3}{2}$ states is far from clear.

This study has concentrated on the region of the curves close to the minima of the $^2\Sigma^+$ and $^2\Pi$ states. It is well known that the ionic nature of the alkali-metal monoxides leads to an avoided crossing at longer R than considered herein, in order to access the neutral dissociation products—the presence of this avoided crossing invalidates the single-reference RCCSD(T) procedure used herein. In order to gain a complete picture of the electronic states of KO, it will be necessary to perform a multireference study and also to include spin–orbit coupling.

Finally, the heat of formation of KO has been established to a high degree of accuracy as $13.6\pm1\ \mathrm{kcal\,mol}^{-1}$ at 0 K and $D_0(\mathrm{KO})=66\pm1\ \mathrm{kcal\,mol}^{-1}$.

ACKNOWLEDGMENTS

The authors are grateful to the EPSRC for the award of computer time at the Rutherford Appleton Laboratories under the auspices of the United Kingdom Computational Chemistry Working Party (UKCCWP), which enabled these calculations to be performed. E.P.F.L. is grateful to the Research Grant Council (RGC) of the Hong Kong Special Administration Region (HKSAR) and the Research Committee of the Hong Kong Polytechnic University for support. P.S. would like to thank the EPSRC for his present funding at Durham (Senior Research Assistantship). T.G.W. is grateful to the EPSRC for the award of an Advanced Fellowship. Useful e-mail correspondence with Dr. C. M. Western (Bristol) and Professor T. A. Miller (Columbus) is gratefully acknowledged.

[1] See, for example, J. M. C. Plane, Int. Rev. Phys. Chem. **10**, 55 (1991).
[2] See, for example, R. M. Cox and J. M. C. Plane, J. Geophys. Res. D **103**, 6349 (1998).
[3] D. E. Jensen, J. Chem. Soc., Faraday Trans. 1 **78**, 2835 (1982).
[4] M. S. Benilov, P. A. Pozdeev, B. V. Rogov, and V. A. Sinel'shchikov, Combust. Flame **98**, 313 (1994).
[5] M. Farber and R. D. Srivastava, High Temp.-High Press. **20**, 119 (1988).
[6] M. Farber, R. D. Srivastava, and J. W. Moyer, J. Chem. Thermodyn. **14**, 1103 (1982).
[7] J. L. Gole, Opt. Eng. (Bellingham) **20**, 546 (1981).
[8] E. P. F. Lee, P. Soldán, and T. G. Wright, Chem. Phys. Lett. **347**, 481 (2001).
[9] E. P. F. Lee, P. Soldán, and T. G. Wright, Chem. Phys. Lett. **295**, 354 (1998).
[10] P. Soldán, E. P. F. Lee, and T. G. Wright, J. Phys. Chem. A **102**, 9040 (1998).
[11] P. Soldán, E. P. F. Lee, S. D. Gamblin, and T. G. Wright, Phys. Chem. Chem. Phys. **1**, 4947 (1999).
[12] E. P. F. Lee, J. Lozeille, P. Soldán, S. E. Daire, J. M. Dyke, and T. G. Wright, Phys. Chem. Chem. Phys. **3**, 4863 (2001).
[13] E. Hirota, Bull. Chem. Soc. Jpn. **68**, 1 (1995).
[14] C. Yamada, M. Fujitake, and E. Hirota, J. Chem. Phys. **91**, 137 (1989).
[15] C. Yamada and E. Hirota, J. Chem. Phys. **99**, 8489 (1993).
[16] C. Yamada, M. Fujitake, and E. Hirota, J. Chem. Phys. **90**, 3033 (1989).
[17] C. Yamada and E. Hirota, J. Chem. Phys. **110**, 2853 (1999).
[18] C. Yamada and E. Hirota, J. Chem. Phys. **111**, 9587 (1999).
[19] J. N. Allison, R. J. Cave, and W. A. Goddard III, J. Phys. Chem. **88**, 1262 (1984); J. N. Allison and W. A. Goddard III, J. Chem. Phys. **77**, 4259 (1982).
[20] R. R. Herm and D. R. Herschbach, J. Chem. Phys. **52**, 5783 (1970).
[21] D. M. Lindsay, D. R. Herschbach, and A. L. Kwiram, J. Chem. Phys. **60**, 315 (1974).
[22] S. R. Langhoff, C. W. Bauschlicher, Jr., and H. Partridge, J. Chem. Phys. **84**, 4474 (1986).
[23] S. R. Langhoff, H. Partridge, and C. W. Bauschlicher, Jr., Chem. Phys. **153**, 1 (1991).
[24] C. W. Bauschlicher, Jr., H. Partridge, and K. G. Dyall, Chem. Phys. Lett. **199**, 225 (1992).
[25] C. W. Bauschlicher, Jr., H. Partridge, and L. G. M. Pettersson, J. Chem. Phys. **99**, 3654 (1993).
[26] L. Serrano-Andrés, A. Sánchez de Merás, R. Pou-Amérigo, and I. Nebot-Gil, Chem. Phys. **162**, 321 (1992).
[27] L. Serrano-Andrés, A. Sánchez de Méras, R. Pou-Amérigo, and I. Nebot-Gil, J. Mol. Struct.: THEOCHEM **254**, 229 (1992).
[28] E. P. F. Lee, T. G. Wright, and J. M. Dyke, Mol. Phys. **77**, 501 (1992); **82**, 1281(E) (1994).
[29] T. G. Wright, A. M. Ellis, and J. M. Dyke, J. Chem. Phys. **98**, 2891 (1993).
[30] D. R. Herschbach, C. E. Kolb, D. R. Worsnop, and X. Shi, Nature (London) **356**, 414 (1992).
[31] X. Shi, D. R. Herschbach, D. R. Worsnop, and C. E. Kolb, J. Phys. Chem. **97**, 2113 (1993).
[32] B. Friedrich and D. Herschbach, Phys. Chem. Chem. Phys. **2**, 419 (2000).
[33] EMSL Basis Set Library. (Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1/29/

01, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.)

[34] P. J. Knowles, C. Hampel, and H.-J. Werner, J. Chem. Phys. **99**, 5219 (1993); J. Chem. Phys. **112**, 3106(E) (2000).

[35] MOLPRO is a package of *ab initio* programs written by H.-J. Werner, P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, A. Berning *et al.*

[36] S. Huzinaga and M. Klobukowski, Chem. Phys. Lett. **212**, 260 (1993).

[37] S. F. Boys and F. Bernardi, Mol. Phys. **19**, 553 (1970).

[38] R. J. LeRoy, LEVEL 7.2, A computer program for solving the radial Schrödinger equation for bound and quasibound levels, and calculating various expectation values and matrix elements, University of Waterloo Chemical Physics Research Program Report CP-555R, 2000.

[39] A. Berning, M. Schweizer, H.-J. Werner, P. J. Knowles, and P. Palmieri, Mol. Phys. **98**, 1823 (2000).

[40] R. C. Spiker, Jr. and L. Andrews, J. Chem. Phys. **58**, 713 (1973).

[41] M. W. Chase, Jr., NIST-JANAF Themochemical Tables, 4th ed., J. Phys. Chem. Ref. Data Monogr. **1998**, 9.

[42] D. M. Neumark, K. R. Lykke, T. Anderson, and W. C. Lineberger, Phys. Rev. A **32**, 1890 (1985).

[43] A. V. Gusarov and L. N. Gorokhov, Teplofiz. Vys. Temp. **9**, 505 (1971).

[44] T. C. Ehlert, High. Temp. Sci. **9**, 237 (1977).

[45] R. H. Lamoreaux and D. L. Hildenbrand, J. Phys. Chem. Ref. Data **13**, 151 (1984).

[46] J. Sugar and C. Corliss, J. Phys. Chem. Ref. Data, Suppl. **14**, 1 (1985).

[47] C. E. Moore, *CRC Handbook of Chemistry and Physics*, 76th ed., edited by J. W. Gallagher (CRC, Boca Raton, FL, 1993), p. 336.

[48] H. Lefebvre-Brion and R. W. Field, *Perturbations in the Spectra of Diatomic Molecules* (Academic, Orlando, FL, 1986), p. 123.