Spectroscopy and Thermodynamics of KO^+

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High-level RCCSD(T) calculations are employed to generate potential energy curves for the $^3\Sigma^-$ and $^3\Pi$ states of KO^+. First, these curves are employed to obtain spectroscopic constants for the two cationic states. Second, the curves are employed together with our previous results on KO, to obtain accurate ionization energies for the $KO^+ \leftarrow KO$ processes, for the states involved. We conclude that the first adiabatic ionization energy of KO is 6.98 ± 0.05 eV, with $D_0(KO^+) = 1460 \pm 20$ cm^{-1}.

I. Introduction

Much work has been performed on the alkali metal monoxides. These species are interesting not only because of the occurrence of the species in the upper atmosphere[1] and flames[2−4] but also because of the change in ground electronic state from $^2\Pi$ for LiO[5,6] and NaO[7] to $^2\Sigma^+$ for RbO,[8,9] CsO,[9,10] and FrO.[9] KO has proven to be especially interesting, with various experiments and calculations concluding the ground state to be either $^2\Pi$ or $^2\Sigma^+$ (see Introduction to ref 11). Recently,[11] we calculated the potential energy curves for the $^2\Pi$ and $^2\Sigma^+$ states of KO both in the absence and presence of spin−orbit coupling. It was found that the presence of an avoided crossing between the $^2\Sigma_{1/2}{}^+$ state and the $^2\Pi_{1/2}$ state close to the $v = 0$ level of the lower $^2\Sigma^+$ state leads to the lowest $\Omega = {}^1/_2$ state having $^2\Sigma^+$ character at short R, but $^2\Pi$ character at long R, which could explain some of the conflicting experimental results.

Regarding the ionization energy of KO, Wright et al. recorded photoelectron spectra of the products of the $K + N_2O$ and the $K + O_3$ reactions[12] and assigned the spectra to a mixture of KO and KO_2 products. We previously[13] tackled the ionization of KO_2 and found that there was a very large geometry change between the C_{2v} $KO_2(\tilde{X}^2A_2)$ state and the $C_{\infty v}$ $KO_2{}^+$ cation. The calculated adiabatic ionization energy (AIE) of 5.98 eV was slightly higher than the onset of the photoelectron band (5.7 ± 0.1 eV),[12] and this was attributed to internal excitation of the KO_2. The photoelectron bands assigned to KO_2 were only seen from the $K + O_3$ reaction and were deduced to arise from the secondary reaction $KO + O_3 \rightarrow KO_2 + O_2$; the reaction $K + N_2O$ should produce KO, but the secondary reaction $KO + N_2O \rightarrow KO_2 + N_2$ is too slow for significant production of KO_2. Consequently, the onset of the photoelectron band from the $K + N_2O$ reaction was taken as being the adiabatic ionization energy of KO; however, there are still questions as to what ionization process this corresponds to—see next paragraph. Also in ref 12, SCF and CISD calculations were employed to calculate the AIE and vertical ionization energies (VIEs) of the various $KO^+ \leftarrow KO$ ionization processes.

KO is largely ionic and, consequently, may be written K^+-O^-. As has been discussed a number of times previously,[14] there are two orientations of the $2p^5$ O^-, with the hole in the 2p shell either pointing along the intermolecular axis, giving rise to a $^2\Sigma^+$ state, or pointing perpendicular to it, giving rise to a $^2\Pi$ state. The electronic configurations may be written

$$^2\Pi \cdots \sigma^2\pi^3$$

$$^2\Sigma^+ \cdots \sigma^1\pi^4$$

Assuming one-electron ionizations only are possible, and that Russell−Saunders coupling applies, then ionization from the $^2\Pi$ state can give rise to five cationic states, whereas ionization from the $^2\Sigma^+$ state can only give rise to three:

$$(1)\ {}^1\Sigma^+, {}^1\Delta, {}^3\Sigma^- \xleftarrow{\pi^{-1}} {}^2\Pi$$

$$^{1,3}\Pi \xleftarrow{\sigma^{-1}} {}^2\Pi$$

$$^{1,3}\Pi \xleftarrow{\pi^{-1}} {}^2\Sigma^+$$

$$(2)\ {}^1\Sigma^+ \xleftarrow{\sigma^{-1}} {}^2\Sigma^+$$

Note that it is the same $^{1,3}\Pi$ states that are accessed from each neutral state. One can see, therefore, that the $^3\Sigma^-$ cationic state may only be accessed from the $^2\Pi$ state. Intensity arguments, as well as the results of the ab initio calculations, were taken as evidence in ref 12 that the $^2\Pi$ state was the ground state of KO, and that the first photoelectron band onset corresponded to the process $^3\Sigma^- \leftarrow {}^2\Pi$. However, as noted above, in fact it is the $^2\Sigma^+$ state that is the lowest. Consequently, there is some doubt as to the assignment of the photoelectron features in ref 12. The purpose of the present work is 3-fold:

(i) calculate accurate potential energy curves for the lowest two triplet states of KO^+, which we expect to be the lowest on the basis of Hund's rules and by comparison to NaO^+ (ref 15);

(ii) derive spectroscopic parameters from these curves; and

(iii) calculate ionization energies and compare to the values obtained in the photoelectron spectrum.

II. Theoretical Details

The basis set employed for potassium was the (33s26p6d4f3g2h)/[12s12p6d4f3g2h] basis set described in full

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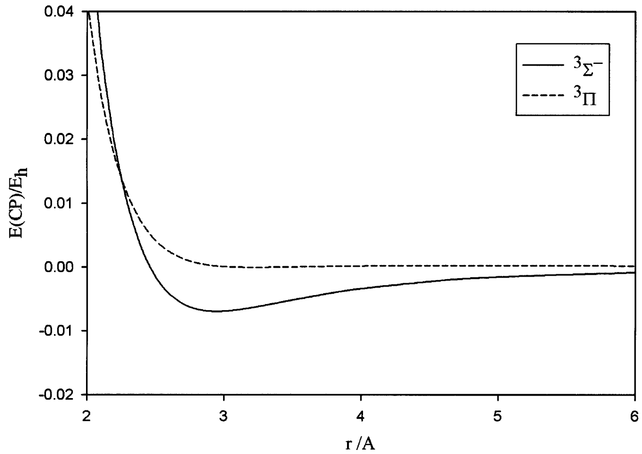

Figure 1. Calculated Potential energy curves for the two lowest lying triplet states of KO^+. Calculations are performed at the RCCSD(T) level and are counterpoise corrected. See text for details.

TABLE 1: Calculated Equilibrium Bond Lengths and Fundamental Vibrational Frequencies of the Lowest States of KO and KO^+

state	r_e/Å	0−1 separation/cm^{-1}	D_e/cm^{-1}	D_0/cm^{-1}
KO $^2\Sigma_{1/2}{}^+$ [a]	2.170	296.6	46 367[b]	46 172[b]
KO $^2\Pi_{3/2}$[a]	2.325	387.2	46 190[b]	45 994[b]
KO^+ $X^3\Sigma^-$	2.972	122.2	1520	1460[c]
KO^+ $A^3\Pi$	3.219	[d]	10	~0[d]

[a] From ref 11. [b] Relative to $K^+(^1S) + O^-(^2P)$. [c] Relative to $K^+(^1S) + O(^3P)$. [d] Likely unbound; see text.

in ref 11; for oxygen, the standard aug-cc-pV5Z basis set was employed. We employ the RCCSD(T) procedure[16] as implemented in MOLPRO[17] to scan the potential energy curves of the $^3\Sigma^-$ and $^3\Pi$ states over a range of bond lengths from 1.7 to 6 Å. These curves are all corrected for basis set superposition error (BSSE) at each point by performing a full counterpoise (CP) correction. In the RCCSD(T) calculations, the oxygen 1s and the potassium 1s2s2p orbitals were frozen. The potential energy curves were then employed to obtain spectroscopic parameters by employing LeRoy's LEVEL[18] program. Finally, the latter results combined with ab initio energies allowed the derivation of the AIEs and VIEs.

III. Results and Discussion

(a) Spectroscopic Parameters. The potential energy curves of the $X^3\Sigma^-$ and $A^3\Pi$ states of KO^+ are shown in Figure 1. As may be seen, both curves are very shallow, with the $^3\Pi$ state being almost flat. In fact, it was concluded to be dissociative from the SCF and CISD calculations of ref 12. The weak bonding in the cation relative to the neutral (see Table 1) occurs because the ionization process is essentially a removal of an electron from O^- in $K^+{-}O^-$, to give rise to $K^+{-}O$, and so the Coulombic attraction is lost. The spectroscopic parameters of the $X^3\Sigma^-$ and $A^3\Pi$ states as derived from LEVEL are given in Table 1, together with the corresponding values for the neutral states. The analysis of the $^3\Pi$ potential energy curve indicated that this state is very weakly bound and is unlikely to support any bound levels. The $^3\Sigma^-$ state is bound, albeit weakly, with $D_e = 1518$ cm^{-1} (0.19 eV), which may be corrected to $D_0 = 1456$ cm^{-1} (0.18 eV). The first few vibrational energy levels could be very well fitted to a Morse potential with $\omega_e = 129.2$ cm^{-1} and $\omega_e x_e = 3.5$ cm^{-1}.

The present results (see Table 1) are in fair agreement with the CISD results of ref 12, where the $^3\Sigma^-$ state was calculated to have $r_e = 3.00$ Å and $\omega_e = 111$ cm^{-1}. The dissociation energy of KO^+ was also derived in ref 12, but the percentage error was large, with a derived value of 0.15 ± 0.14 eV being reported. The only other experimental value that appears to have been obtained is that from Rol et al.[19] of 0.3 ± 0.3 eV. The calculated BSSE for the $X^3\Sigma^-$ state close to the potential energy minimum is only 20 cm^{-1}, and we employ this as the error in our calculated dissociation energy, and so cite $D_0(KO^+) = 1460 \pm 20$ cm^{-1}. This value may be straightforwardly converted to a ΔH^{298} value of 5.1 ± 0.1 kcal mol^{-1}, and use of the heat of formation of K^+ and O from the JANAF tables[20] allows $\Delta H_f^{298}(KO^+)$ to be derived as 177.3 kcal mol^{-1}. We cite a final value of 177 ± 2 kcal mol^{-1} to take into account the error in D_0 and the small errors in the use of the rigid-rotor harmonic oscillator approximation. Finally, we calculate S^{298}, obtaining a value of 57 cal K^{-1} mol^{-1}.

TABLE 2: Rotational Constants of $KO^+(X^3\Sigma^-)$ for the Lowest Vibrational Energy Levels (cm^{-1})

v	$E(v,J{=}0)$	B_v	$10^6 D_v$	r_v/Å[a]
0	0	0.1689	1.123	0.297
1	122.2	0.1638	1.301	0.301
2	237.4	0.1587	1.374	0.306
3	345.7	0.1536	1.454	0.311
4	447.2	0.1483	1.540	0.317

[a] Calculated from the B_v value.

In Table 2, we report the rotational constants, B_v, for the lowest rotational energy levels, as well as the corresponding first centrifugal distortion terms, D_v (these results should help to guide a possible microwave experiment: the calculated dipole moment is −1.45 D at 2.97 Å, with respect to the center of mass). Fitting these B_v values to the standard expression, gives $B_e = 0.171$ and the vibration−rotation parameter, $\alpha = 0.0051$; note that the distortion terms have been ignored in deriving the latter two parameters. In addition, we report the r_v values for these lowest vibrational energy levels.

(b) Ionization Energies. We assume that one-electron ionizations only are allowed and consider the spin−orbit states for the neutral, $^2\Sigma_{1/2}{}^+$ and $^2\Pi_{3/2}$ as calculated in ref 11. We also assume that the ionizations occur from the $v = 0$ level of these states, at the r_0 bond lengths (2.261 and 2.330 Å, respectively) derived in that work. Note that for the $^2\Sigma_{1/2}{}^+$ state, the r_e and r_0 values were significantly different, because the $v = 0$ level was almost degenerate with a "shelf" that formed as the result of the spin−orbit-induced avoided crossing. Note that for the $^3\Sigma^-$ and $^3\Pi$ states, there is a crossing at short bond lengths (see Figure 1), above the dissociation asymptotes. We conclude that spin−orbit coupling in the cation is not important in the bound regions of these curves, and in particular that the $^3\Sigma^-$ state will essentially maintain that character around the bound region. Any interaction that does occur will be between the $^3\Sigma_1{}^-$ and the $^3\Pi_1$ components and will lead to an avoided crossing in the repulsive region. It is also likely that these two curves will push apart slightly, and this may well lead to the $^3\Pi_1$ component being totally repulsive. The AIEs and VIEs could therefore straightforwardly be calculated using the spin−orbit curves reported in ref 11 for the neutral states, and the Russell−Saunders curves for the cation. Note that we have also calculated the AIE and VIE for the $^3\Sigma^- \leftarrow {}^2\Sigma^+$ process (which is forbidden in the absence of spin−orbit coupling), because the $v = 0$ of the lowest $\Omega = {}^1/_2$ state of KO has been shown to have contributions from both the $^2\Sigma^+$ state at short r,and the $^2\Pi$ state at longer r, thus this ionization will become allowed under the influence of spin−orbit coupling. The calculated results are given in Table 3. It is clear that the present results are superior

TABLE 3: Calculated AIEs and VIEs for Various Ionizations (eV)

	AIE			VIE		
ionization	ref 12[a]	present work	expt[12]	ref 12[a]	present work	expt[12]
$^3\Sigma_1^- \leftarrow {}^2\Pi_{3/2}$	5.81	6.98	6.9 ± 0.1	6.13	7.36	7.21 ± 0.08
$^3\Sigma_1^- \leftarrow {}^2\Sigma_{1/2}^+$ [b]		7.00			7.54	
$^3\Pi \leftarrow {}^2\Pi_{3/2}$	6.13	7.16		6.25	7.43	7.43 ± 0.09
$^3\Pi \leftarrow {}^2\Sigma_{1/2}^+$	5.24	7.18		6.38	7.55	7.71 ± 0.10

[a] CISD. [b] One-electron forbidden in Russell−Saunders picture; spin−orbit allowed (see text).

to those of ref 12, being much closer to the values measured in the photoelectron study.

Of note is that the lowest adiabatic ionization energy corresponds to the process $^3\Sigma^- \leftarrow {}^2\Pi_{3/2}$ with a value of 6.98 eV, which is in very good agreement with the photoelectron band onset of 6.9 ± 0.1 eV from the reaction K + N_2O in ref 12. The calculated VIE for this ionization process, 7.36 eV, is slightly higher than the experimental determination of 7.21 ± 0.08 eV and is clearly to unbound regions of the cationic curve. The two ionizations that access the $^3\Pi$ state are calculated to have AIEs that are very close, because they only differ by the spacing between the $^2\Sigma_{1/2}^+$ and $^2\Pi_{3/2}$ states. In the photoelectron spectrum, therefore, we expect these two features to be almost completely overlapped at low energy; the differing VIEs, however, suggest that two band maxima will appear. Again, the main contribution of these two features is expected to be mainly unbound ← bound, because the $^3\Pi$ state supports at most one vibrational level, and it can be easily seen from the potential energy curves that the vertical excitation accesses the region above the dissociation asymptote in the cationic curves. The presence of the avoided crossing at short r will affect the appearance of the photoelectron bands slightly. The other features in the photoelectron spectrum are due to the accessing of higher cationic states and are not considered further in the present work. The Russell−Saunders forbidden ionization, $^3\Sigma^- \leftarrow {}^2\Pi$, may be seen to contribute over a wide range of ionization energies; its importance to the appearance of the spectrum will depend on "how allowed" it becomes.

There have been other determinations of the first ionization energy of KO from mass spectrometric studies. Ehlert[21] obtained a value of 7.0 ± 0.2 eV, Farber et al.[22] obtained a value of 8 ± 1 eV, and Butman et al.[23] obtained a value of 7.1 ± 0.1 eV. Consequently, it can be seen that the present calculations, previous mass spectrometric data, and the photoelectron spectroscopic study are all essentially in agreement.

With regard to the error in our calculated value, we calculate the electron affinity of O using the aug-cc-pV5Z basis set, obtaining 1.424 eV, which is 0.04 eV lower than the experimental value of 1.461 eV.[24] Because KO is very ionic, we conclude that our ionization energies will be accurate to 0.05 eV.

IV. Conclusions

High-level RCCSD(T) calulcations have been performed on the two lowest triplet states of KO^+, and this has allowed spectroscopic parameters to be derived. We report $r_e = 2.972$ Å and $D_0 = 1460 \pm 20$ cm^{-1} for the $^3\Sigma^-$ state. In addition, making use of previously calculated curves for the neutral KO, adiabatic, and vertical ionization energies have been calculated. We report the first AIE of KO to be 6.98 ± 0.05 eV. This result is in good agreement with previous mass spectrometric and photoelectron spectroscopic results. Finally, despite the different conclusions regarding the identity of the ground state of KO, the assignments of the bands presented in the photoelectron study are consistent with the AIEs and VIEs calculated herein.

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