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The ground state of KO revisited: the millimeter and submillimeter spectrum of potassium oxide

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The millimeter/sub-millimeter spectrum of the KO radical has been recorded in the frequency range 90–534 GHz using direct absorption methods. The radical was synthesized by reacting potassium vapor, produced with a Broida-type oven, with either N_2O or O_2 mixed in argon carrier gas. Twenty-seven rotational transitions of KO were measured, each exhibiting a doublet structure with a relatively small splitting (~100–200 MHz) that increased noticeably with frequency. A perturbation was apparent in the rotational lines at energies above ~120 cm^{-1}, which was more prominent in one doublet component. The data were successfully fit with a Hund's case (c) Hamiltonian, assuming that spectra arise from a $^2\Pi_i$ state, and rotational and effective lambda-doubling constants were determined. Higher order centrifugal distortion terms were needed to account for the perturbation. The spectra could also be fit as a $^2\Sigma^+$ ground state, but less successfully, and the resulting rotational constant of B = 8235.4 MHz disagreed significantly with that predicted by theory. On the basis of the experimental data, the ground electronic state of KO has been assigned as $^2\Pi_i$, although the $^2\Sigma^+$ assignment cannot be entirely ruled out.

Introduction

Diatomic alkali oxides are thought to be model systems for interpreting the bonding of metals to oxygen.[1] These species are highly ionic and can be described as M^+O^-, generated by the donation of the valence n*s* electron of the alkali atom to the oxygen. This transfer creates a $^2\Pi$ electronic state arising from a $\sigma^2\pi^3$ electron configuration. Spectroscopic studies over the decades have shown this simple scheme holds true for the lighter alkali oxides, LiO and NaO.[2–6] For example, molecular beam/electron resonance studies by Freund *et al.*[2] clearly demonstrated that the ground state of LiO is $^2\Pi_i$, which was later confirmed by microwave spectroscopy[3] and laser diode[5] studies. Yamada *et al.*[4] also measured the pure rotational spectrum of NaO and again found a $^2\Pi_i$ ground state, as did subsequent infrared electronic studies[6] of the A–X transition. CsO and RbO, in contrast, proved to not follow this trend. Early work involving kinetics and magnetic deflection experiments suggested that the ground state of both radicals is $^2\Sigma^+$.[7] These results were later verified by spectral measurements of these species in a solid matrix using electron spin resonance (ESR),[1] as well as by millimeter-wave studies.[8,9]

The shift in ground state from $^2\Pi_i$ to $^2\Sigma^+$ while descending the alkali column has been interpreted as arising from a change from valence to "inner shell" bonding.[1] The latter scheme arises from the $(n-1)$p orbitals of the alkali metal mixing with the 2p orbitals of oxygen. The bonding modification occurs because the metal $(n-1)$p orbitals shift from lying lower in energy relative to the oxygen 2p orbitals, for Li or Na, to being comparable, for Rb or Cs. In a more recent work, the shift has been attributed to the competition between Pauli repulsion and quadrupole interactions, favoring $^2\Sigma$ and $^2\Pi$, respectively.[10] These two forces scale as $1/R_e$ (Pauli repulsion) and $1/R_e^3$ (quadrupole), where R_e is the bond distance. Moving down the periodic table, the M^+ core increases in size, lengthening the bond distance, and shifting the dominant contribution to the Pauli repulsion term, thus favoring the $^2\Sigma$ state.

Because potassium lies between sodium and rubidium in the alkali column, the electronic ground state of KO has been the subject of studies for decades, with a long series of conflicting experimental and theoretical results. The early work of Herm and Herschbach suggested a $^2\Sigma$ state for KO.[7] This assignment was later revised to $^2\Pi$ by the same group, based on the lack of an ESR spectrum for KO in solid matrices.[1] Photoelectron spectroscopy conducted in the ultraviolet region determined the first vertical ionization energy of ~7.2 eV, but did not settle the ground state issue.[11] In 1995, a review article by Hirota reported the results of a millimeter-wave spectroscopic study

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of KO.[12] The article mentioned that both the $^2\Sigma^+$ and $^2\Pi_i$ states had been observed, giving rotational constants (B) for both states, and asserted that the ground state term was $^2\Pi_i$ with the $^2\Sigma^+$ lying approximately 200 cm^{-1} higher in energy. No further details of the experimental work were given, and additional data did not subsequently appear in the literature. Interestingly, the ground state of KS, the sulfur analog, has been determined to be $^2\Pi_i$ by pure rotational spectroscopy.[13]

Not surprisingly, the $^2\Sigma^+/^2\Pi_i$ electronic state ordering in KO has been the focus of many computational investigations. Earlier configuration interaction (CI) calculations using a double-ζ basis set yielded a $^2\Pi$ ground state,[14] while subsequent configuration interaction with single and double excitations (CISD) computations with a larger basis set predicted $^2\Sigma^+$.[15] These works were followed by complete active space self-consistent field (CASSCF) with and without multireference configuration interaction (MRCI) calculations.[16–18] Without MRCI, the ground state was computed to be $^2\Pi$, but with MRCI it was found to be $^2\Sigma^+$, as confirmed by additional CASSCF calculations.[19,20] Hartree–Fock and CISD studies utilizing a triple-ζ basis set and higher order corrections yielded a $^2\Pi$ ground state.[11] Most recently, calculations using couple cluster methods with single, double, and perturbative triple excitations (CCSD(T)), including relativistic corrections, were carried out by Lee *et al.*[21] Potential energy surfaces for the $^2\Sigma_{1/2}$, $^2\Pi_{1/2}$, and $^2\Pi_{3/2}$ states were constructed, considering spin–orbit coupling. It was concluded that, due to an avoided crossing, the ground state should be labeled $\Omega = 1/2$, signifying a $^2\Sigma^+$ state near the equilibrium bond length of 2.17 Å and $^2\Pi_{1/2}$ at longer ($r > 2.3$ Å) bond lengths.

Aside from the controversial chemical interest in KO, the free radical is also relevant to astronomy. Metal oxides such as TiO, ScO, and AlO have been known to be constituents in O-rich stellar photospheres for decades.[22–24] More recent studies have shown that molecules such as AlO, TiO, and VO are also present in ejected material around aging supergiant stars such as VY Canis Majoris.[25–27] Given the observation of strong, atomic potassium lines in many of these stars,[24,27] which are typically rich in oxygen, KO would appear to be a likely constituent both in the photosphere and in the circumstellar envelope of these objects. However, the dearth of electronic and rotational spectroscopic data for KO has hindered astronomical identification of this molecule.

With the goal of establishing the electronic ground state of KO, we have conducted a study of the pure rotational spectrum of this radical using millimeter/sub-mm direct absorption methods. We have identified a series of strong, harmonic transitions arising from the ground state of KO which deviate from the expected pattern at higher J. These data can be successfully fit as a $^2\Pi_{3/2}$ electronic state, although a $^2\Sigma_{1/2}$ state cannot be entirely dismissed. Here we present our spectral data and analysis, and our best determination of the ground state of KO.

Experimental

The pure rotational spectrum of KO was recorded using one of the millimeter/sub-mm wave direct absorption spectrometers of the Ziurys group.[28] Briefly, Gunn oscillators and Schottky diode multipliers are employed to produce millimeter/sub-mm wave radiation in the range of 65–850 GHz. The radiation is propagated quasi-optically through a water-cooled reaction chamber by a series of Teflon lenses, a polarizing grid, and a rooftop mirror. The reaction cell also contains a Broida-type oven for metal vaporization. The radiation passes through the cell twice before it is directed into the detector, a helium-cooled InSb bolometer. Phase sensitive detection is achieved by FM modulation of the Gunn source.

The KO radical was synthesized by the reaction of potassium vapor, produced by the Broida-type oven, with N_2O. Pure potassium metal, cleaned of its oxidation layer, was used in the oven. The strongest signals were produced using ~1–2 mTorr of N_2O, introduced through a tube over the top of the oven. Argon carrier gas (~20 mTorr) was flowed into the vacuum chamber from underneath the oven. A DC discharge was not needed to create the radical. KO could also be synthesized with O_2 instead of N_2O, but with weaker signals. The best reaction conditions resulted when the melted potassium had a shiny, mirror-like surface. Extreme caution had to be taken in handling residual potassium in the reaction cell.

Final frequency measurements were made by averaging two 5 MHz wide scans, one obtained in increasing frequency and the other in decreasing frequency. For the lower frequency transitions (<110 GHz), up to 20 scan pairs were necessary due to lower detector sensitivity. Each line was fit to a Gaussian profile to determine the center frequency.

Results

The 241–306 GHz frequency region was initially scanned continuously in 110 MHz intervals to locate KO rotational transitions. This range is ~8 times the rotational constants reported for either the $^2\Sigma^+$ or $^2\Pi$ states, based on the experimental and theoretical values.[12,21] The large region was searched in order to locate multiple electronic states, if present. At the onset, four harmonically-related doublets were observed, each with a splitting of approximately 100 MHz and indicating $B \sim 8200$ MHz – close to the theoretically-predicted rotational constant for the $^2\Pi_{3/2}$ state,[21] as well as the experimental value of ~8300 MHz reported by Hirota.[12] The doublet splitting also increased noticeably with increasing J, as also found for the lambda-doubling in the $^2\Pi_{3/2}$ ground state of KS, LiO, and NaO.[3,4,13] Additional doublets with similar splittings were not observed to either higher or lower frequency, suggesting that the measured rotational transitions arose from the $v = 0$ level. Hyperfine structure from the ^{39}K nucleus ($I = 3/2$) was not observed. Chemical tests proved the dependence of these lines on potassium and both N_2O or O_2, and therefore oxygen. Additional spectral features were present in the data, some of which were unidentified and others that were due to KOH. The harmonic doublets were then analyzed for preliminary constants assuming a $^2\Pi$ state and other rotational transitions then predicted. Additional transitions in the 90–240 GHz and

Table 1 Rotational transition frequencies for KO ($X^2\Pi_{3/2}$)[a]

$J' \leftarrow J''$	Parity[b]	ν_{obs}	$\nu_{\text{obs}} - \nu_{\text{obs}}$
$5.5 \leftarrow 4.5$	e	90578.265	−0.135
	f	90589.551	0.012
$6.5 \leftarrow 5.5$	e	107042.674	−0.037
	f	107058.319	0.031
$7.5 \leftarrow 6.5$	e	123504.951	−0.079
	f	123525.835	0.062
$8.5 \leftarrow 7.5$	e	139965.081	−0.038
	f	139991.716	−0.035
$9.5 \leftarrow 8.5$	e	156422.630	−0.116
	f	156456.041	0.056
$10.5 \leftarrow 9.5$	e	172877.620	−0.064
	f	172918.336	0.094
$11.5 \leftarrow 10.5$	e	189329.761	0.052
	f	189378.345	0.047
$12.5 \leftarrow 11.5$	e	205778.601	−0.006
	f	205836.063	0.128
$13.5 \leftarrow 12.5$	e	222224.182	0.013
	f	222290.982	0.035
$14.5 \leftarrow 13.5$	e	238666.234	0.041
	f	238743.142	0.003
$15.5 \leftarrow 14.5$	e	255104.530	0.042
	f	255192.289	−0.043
$16.5 \leftarrow 15.5$	e	271538.905	0.036
	f	271638.292	−0.072
$17.5 \leftarrow 16.5$	e	287969.226	0.062
	f	288081.030	−0.064
$18.5 \leftarrow 17.5$	e	304395.220	0.010
	f	304520.375	−0.036
$19.5 \leftarrow 18.5$	e	320816.936	0.077
	f	320956.176	−0.056
$20.5 \leftarrow 19.5$	e	337233.969	−0.007
	f	337388.409	−0.107
$21.5 \leftarrow 20.5$	e	353646.475	0.032
	f	353817.162	−0.105
$22.5 \leftarrow 21.5$	e	370054.163	−0.002
	f	370242.555	0.011
$23.5 \leftarrow 22.5$	e	386456.999	−0.067
	f	386664.525	0.048
$24.5 \leftarrow 23.5$	e	402855.013	−0.086
	f	403083.377	0.106
$25.5 \leftarrow 24.5$	e	419248.213	−0.037
	f	419499.368	0.138
$27.5 \leftarrow 26.5$	e	452019.986	−0.059
	f	452324.523	0.090
$28.5 \leftarrow 27.5$	e	468398.890	0.008
	f	468734.960	0.035
$29.5 \leftarrow 28.5$	e	484773.301	0.063
	f	485145.056	−0.072
$30.5 \leftarrow 29.5$	e	501143.448	0.069
	f	501556.013	−0.125
$31.5 \leftarrow 30.5$	e	517509.709	0.053
	f	517969.154	−0.138
$32.5 \leftarrow 31.5$	e	533872.445	−0.082
	f	534386.367	0.155

[a] In MHz. [b] Parity assignment is arbitrary, see text.

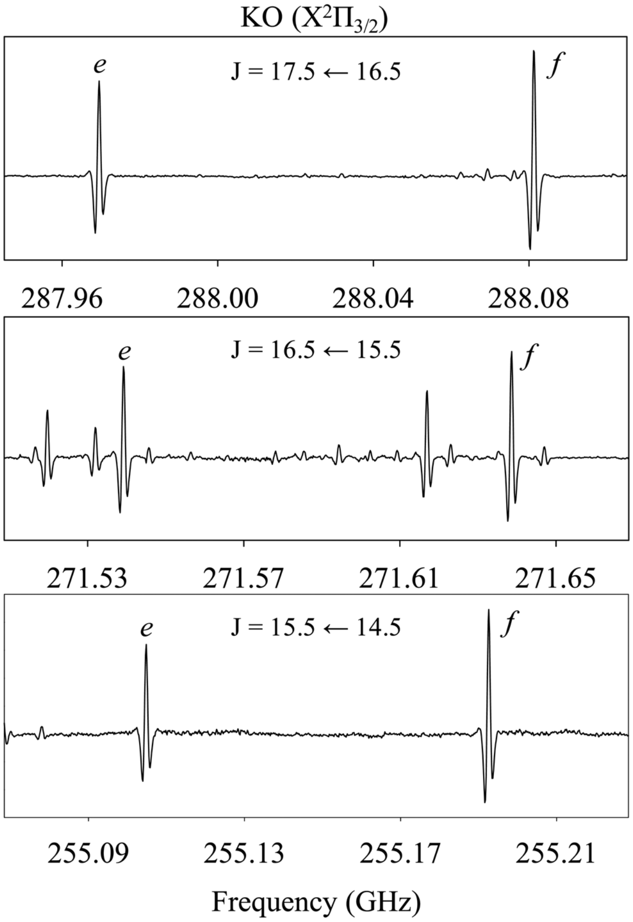

Fig. 1 Spectra of the $J = 15.5 \leftarrow 14.5$, $J = 16.5 \leftarrow 15.5$, and $J = 17.5 \leftarrow 16.5$ rotational transitions of KO near 255, 271, and 288 GHz, respectively, labeled assuming $X^2\Pi_i$. Each transition consists of lambda-doublets, indicated by e and f, whose splitting steadily increases in magnitude with frequency, indicative of a $^2\Pi_{3/2}$ sub-state. Each spectrum was created from combining two, 110 MHz wide scans, each acquired in ∼90 s, and then truncated to cover 160 MHz.

307–540 GHz ranges were subsequently measured. It became clear that transitions above 300 GHz systematically deviated from the preliminary fit with increasing frequency, indicating a local perturbation.

In total, 27 rotational transitions $J + 1 \leftarrow J$ in the range 90–534 GHz were recorded, as shown in Table 1, each consisting of doublets arbitrarily labeled e and f. The lines were assigned to half-integer J values, consistent with a $^2\Pi$ state. The doublet splitting increases from ∼11 MHz ($J = 5.5 \leftarrow 4.5$) to ∼514 MHz ($J = 32.5 \leftarrow 31.5$), comparable to that found for NaO and LiO in the $\Omega = 3/2$ spin–orbit component of the $X^2\Pi_i$ state.

Representative spectra for KO are presented in Fig. 1. Here the $J = 15.5 \leftarrow 14.5$, $J = 16.5 \leftarrow 15.5$, and $J = 17.5 \leftarrow 16.5$ transitions are shown near 255, 271, and 288 GHz, respectively. Each transition consists of (presumably) lambda doublets, labeled by e and f. The KO lines are quite strong for a radical species, suggesting they are due to the ground electronic state.

The data were fit to a Hund's case (c) effective Hamiltonian appropriate for a $^2\Pi_{3/2}$ state consisting of rotation and effective lambda-doubling terms:

$$H_{\text{eff}} = H_{\text{rot}} + H_{\text{LD}}. \tag{1}$$

In the case (c) formalism, the doubling is best described as omega doubling, as Λ and Σ are not good quantum numbers. However, as discussed later on, our experimental evidence shows that the ground state of KO is $^2\Pi_{3/2}$, and the splitting observed in this molecule is actual lambda doubling. The lambda doubling was characterized by an effective constant,

Table 2 Spectroscopic constants for KO[a]

	$^2\Pi_{3/2}$			$^2\Sigma_{1/2}$	
Parameter	90–300 GHz	90–530 GHz	Parameter	90–300 GHz	90–530 GHz
B	8235.5449(57)	8235.5460(46)	B	8235.3958(73)	8235.399(22)
D	0.010615(33)	0.010610(13)	D	0.010607(43)	0.010643(62)
H	$8.70(59) \times 10^{-7}$	$8.06(12) \times 10^{-7}$	H	$8.70(76) \times 10^{-7}$	$9.51(58) \times 10^{-7}$
L	—	5.33×10^{-11}[b]	L	—	-1.4×10^{-10}[b]
P	—	$2.076(31) \times 10^{-13}$	P	—	$2.76(15) \times 10^{-13}$
q_{eff}	−0.12541(86)	−0.12412(25)	γ	16 470.78 (23)	16 472.64(96)
$q_{\text{eff}\,D}$	$1.46(53) \times 10^{-5}$	$7.10(33) \times 10^{-6}$	γ_D	−0.1650(12)	−0.1769(30)
$q_{\text{eff}\,H}$	$1.74(90) \times 10^{-8}$	-1.29×10^{-9}[b]	γ_H	$7.6(2.1) \times 10^{-6}$	$3.97(42) \times 10^{-5}$
$q_{\text{eff}\,L}$	—	$-1.333(11) \times 10^{-11}$	γ_L	—	$-3.10(19) \times 10^{-8}$
rms	0.045	0.072	rms	0.058	0.356

[a] In MHz; uncertainties are 3σ. [b] Held fixed.

q_{eff}, including higher order centrifugal distortion terms, as described in Kingston *et al.*[29] and Yamazaki *et al.*[30]

$$E_{\text{LD}} = \pm\frac{1}{2}\left[\left[q_{\text{eff}} + q_{\text{eff}\,D}J(J+1) + q_{\text{eff}\,H}J^2(J+1)^2 + q_{\text{eff}\,L}J^3(J+1)^3\right]\left(J-\frac{1}{2}\right)\left(J+\frac{1}{2}\right)\left(J+\frac{3}{2}\right)\right] \tag{2}$$

Two approaches, shown in Table 2, were used to fit the spectra. First, the complete data set was analyzed, including the perturbed transitions above 300 GHz. In order to obtain an acceptable fit, several higher order centrifugal distortion terms (H, L, and P) and effective lambda-doubling terms ($q_{\text{eff}\,H}$ and $q_{\text{eff}\,L}$) were required. The value of the parameters L and $q_{\text{eff}\,H}$ had to be held fixed in the final fit; otherwise, they were slightly undefined within their 3σ uncertainties. The resulting rms of the fit with this approach is 72 kHz – below the experimental uncertainty of 100 kHz. The second method was to analyze only the data below 300 GHz, which presumably is not significantly perturbed. In this case, only the centrifugal distortion terms D, H, $q_{\text{eff}\,D}$, and $q_{\text{eff}\,H}$ were needed, producing a rms of the fit of 45 kHz. The use of the (unphysical) higher order distortion terms was simply a means to compensate for the perturbed lines.

The effect of this perturbation is illustrated in Fig. 2. Here, a Loomis–Wood plot of observed rotational transitions between 300 and 534 GHz is shown, as indicated by stick figures with triangles. Those with squares represent predicted transitions from the spectroscopic constants with data below 300 GHz only. The slowly increasing deviation is apparent in this plot, in particular for the higher frequency f components.

A deperturbation analysis was carried out in a Hund's case (c) basis, following the formalism of Gauyacq and Horani[31] and Yamazaki *et al.*,[30] assuming a $^2\Pi_{3/2}$ ground state and a perturbing $^2\Sigma$ state. However, unlike the previous perturbation analyses, no firm experimental data exists for the excited $^2\Sigma$ state. The analysis was thus carried out on the basis of the small perturbation observed in our rotational data, as described. Moreover, both the Π–Σ energy separation (~200 cm^{-1}) and the rotational constant of the excited Σ state (9486 MHz) had to be assumed using the values given by Hirota.[12] This lack of information leads to larger uncertainties than in previous deperturbation studies.[30,31]

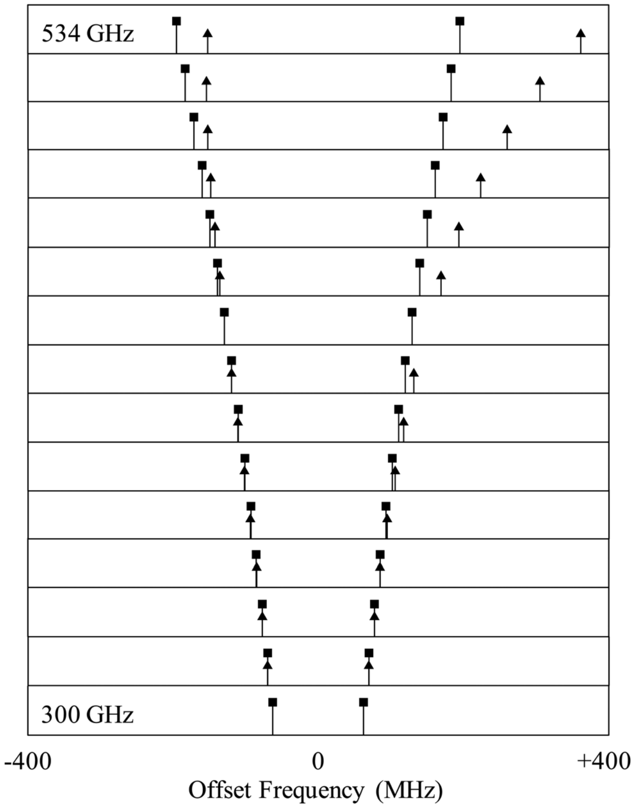

Fig. 2 Loomis–Wood plot of rotational transitions of KO between 300 GHz and 534 GHz. Triangles indicate the experimental data, while squares represent frequencies predicted using spectroscopic parameters obtained only from the data below 300 GHz. (There is a gap in the plot where the J = 26.5 ← 25.5 transition near 435 GHz would occur.) As shown in the figure, the observed lines deviate significantly from the predictions with increasing J, particularly for the higher frequency "f" lambda doublet. These data indicate a local perturbation, likely from a nearby $^2\Sigma$ state.

For the analysis, the off-diagonal perturbation term had the following form, where $\eta = \langle X^2\Pi_{3/2}|\mathbf{B}(\mathbf{r})|^2\Sigma_{1/2}\rangle$ (see ref. 30 and 31):

$$-2\eta[(J+1)^2 - 1]^{1/2}. \tag{3}$$

Table 3 Deperturbed spectroscopic constants for KO[a]

Parameter	$X^2\Pi_{3/2}$
B	8242(10)
D	0.0121(21)
H	$1.11(34) \times 10^{-6}$
P	$2.14(17) \times 10^{-13}$
q_{eff}	−0.12356(24)
$q_{\text{eff}\,D}$	$5.71(34) \times 10^{-6}$
$q_{\text{eff}\,L}$	$-1.377(11) \times 10^{-11}$
η	3300(2300)
B_{Σ}	9486[b]
$E_{\Pi-\Sigma}$ (cm^{-1})	200[b]
rms	0.071

[a] In MHz unless stated otherwise; uncertainties are 3σ. [b] Held fixed (see text).

The results of the analysis are given in Table 3. As shown in the table, a set of deperturbed rotational constants for the $^2\Pi_{3/2}$ ground electronic state of KO was obtained to within 3 sigma uncertainties. Two fewer parameters were needed to fit the deperturbed data set, as opposed to the ''perturbed'' analysis (see Table 2), with a comparable rms of the fit of 71 kHz. The deperturbed rotational constant is 8242(10) MHz. The large uncertainties for some of the fitted constants arise from the small magnitude of the observed perturbation, as well as the lack of experimental data for the excited perturbing state, as mentioned.

It should be noted that the KO spectra could also be fitted as a $^2\Sigma$ state in a case (b) analysis, assuming an integer rotational quantum number, as shown in Table 2. To do this, the lower frequency feature of each lambda (or omega) ''doublet'' was assigned an N value of $N = J - 1/2$ and the higher frequency one was given an N value of $N = J + 1/2$, where the values of J are those assigned in the $^2\Pi_{3/2}$ case (c) fit. For example, the doublets of the presumed $^2\Pi$, $J = 5.5 \leftarrow 4.5$ transitions at 90578.265 MHz and 90589.551 MHz were assigned as the $N = 5 \leftarrow 4, J = 5.5 \leftarrow 4.5$ line and the $N = 6 \leftarrow 5, J = 5.5 \leftarrow 4.5$ line, respectively. The resulting spin-rotation constant was consequently fitted to be $\gamma \sim 16$ GHz. However, using a comparable number of fitting parameters, a much larger rms of ∼350 kHz resulted from the analysis of all transitions. Fitting only the ''unperturbed'' data improved the rms, but still did not lower it to the value of the $^2\Pi$ analysis (58 kHz *vs.* 45 kHz).

Discussion

There are several reasons why the ground state of KO is assigned as $^2\Pi_i$. First, the rotational constant determined for the molecule is $B = 8235$ MHz, whether it is assigned as having a $^2\Pi$ or $^2\Sigma$ ground state. This value is in reasonable agreement with the previously reported experimental value of 8272.5 MHz for the $^2\Pi$ state (Hirota 1995).[12] This B presumably considers both spin–orbit ladders, and thus should be somewhat larger than the one for the $\Omega = 3/2$ component, as measured here. Our B value also is comparable to the computational value of 8209 MHz for the $^2\Pi_{3/2}$ state given by Lee *et al.*[21] Any previously reported rotational constants for the $^2\Sigma^+$ state are significantly larger. Hirota[12] reported a value of $B = 9486.5$ MHz, and the computational value[21] is 8718 MHz. Lee *et al.* calculated $B = 8610$ MHz for the $^2\Pi_{1/2}$ component – also clearly different.[21]

Another argument for the $^2\Pi_i$ assignment is the behavior of the assumed lambda-doublets of KO. The magnitude and increase of the splitting with J mimics that of the $\Omega = 3/2$ spin–orbit component of the $X^2\Pi_i$ state of both LiO and NaO.[3,4] Assignment as the $\Omega = 1/2$ component is highly unlikely, as the lambda-doubling in this ladder is significantly larger. For example, for LiO and NaO, the fine structure splitting in the $^2\Pi_{1/2}$ state is approximately 6 and 3 GHz, respectively. Furthermore, the rotational energy levels are approximately proportional to J^3 rather than J, consistent with $\Omega = 3/2$. Fitting the doublets as spin-rotation components in a $^2\Sigma^+$ state also results in higher rms values than as lambda-doublet components of a $^2\Pi$ state. The spin-rotation constant, if the observed KO lines arose from a $^2\Sigma$ state, is ∼16 GHz. This value is quite large but could result from strong second-order spin–orbit coupling to the nearby $^2\Pi$ state.

It is unlikely that the observed spectra for KO arise from anything other than the ground electronic state. The recorded lines were quite strong, and ∼64 GHz of continuous scanning produced no other strong, harmonically-related features. Use of the Broida oven to vaporize metals substantially heats the reaction mixture, unlikely leading to preferential population of a metastable state. Because of their relatively short lifetimes, observation of pure rotational transitions arising from excited electronic states are rare in mm-wave spectra, and would invariably produce weaker signals than the ground state. In rare cases where a low-lying excited electronic state is metastable, rotational spectra have been recorded. For example, in ZnO, pure rotational lines of the excited a $^3\Pi_i$ state were observed;[32] however, the signals were at least an order of magnitude weaker than those from the ground $X^1\Sigma^+$ state. In the case of KO, the nearby excited state, be it $^2\Sigma$ or $^2\Pi$, is not metastable because it shares the spin multiplicity of the ground state. Therefore, the excited state would readily decay to the ground state through the $\Delta S = 0$ selection rule. Large differences in the dipole moments of KO in the $^2\Sigma$ and $^2\Pi$ states could in principle preferentially favor observation of one state over the other, but are not expected. Unfortunately, such dipole moments have never been measured or calculated for KO.

It is clear from the plot in Fig. 2 that the rotational levels of the $^2\Pi_{3/2}$ state become increasingly perturbed as their energy above ground state increases. The deviation between the predicted and measured transition frequencies is greater in magnitude for the f (higher frequency) lambda-doublet than the e (lower frequency) component. The $J = 20.5$ level, where the perturbation becomes noticeable, lies approximately 120 cm^{-1} above ground state. Hirota placed the $^2\Sigma^+$ state about 200 cm^{-1} higher than the $^2\Pi$ – roughly comparable.[12] The nearby $^2\Sigma^+$ excited state is therefore the likely source of the perturbation, as the deperturbation analysis also suggests, and arises from the L-uncoupling operator, $-B(J_+L_- + J_-L_+)$.[33] This operator follows the selection rules $\Delta S = 0$ and $\Delta\Omega = \Delta\Lambda = \pm 1$, as found for a $^2\Pi$–$^2\Sigma$ interaction. Depending on their energies, the Σ_e $(N = J - 1/2)$

or Σ_f ($N = J + 1/2$) spin-rotation levels will affect the lambda-doubling components of the Π state differently. The L-uncoupling interaction thus explains the enhanced perturbation of the ''f'' lambda-doubling component. A similar effect is seen in the $^2\Sigma/^2\Pi$ system in CS^+.[31]

What is the electronic ground state of KO? These new measurements indicate that it is likely $^2\Pi_i$, as suggested by Hirota in 1995.[12] If the ground state is $^2\Sigma$, the experimentally determined rotational constant, which is quite accurate, deviates considerably from the most recent theoretical value given by Lee *et al.*:[21] 8235 MHz *vs.* 8718 MHz. It is clear that additional experimental and higher-level theoretical studies would be insightful.

Conclusions

The experimental work here strongly suggests that the ground state term for KO is $^2\Pi_i$, but the $^2\Sigma$ assignment is still possible, although less likely. The observed ground state spectra of KO, independent of the assignment, is experiencing perturbations at energies of ≥ 120 cm^{-1}, indicating that the nearest excited state is very low in energy. Additional experimental and theoretical studies would aid in fully addressing the ground state question.

Conflicts of interest

There are no conflicts to declare.

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References

1 D. M. Lindsay, D. R. Herschbach and A. L. Kwiram, *J. Chem. Phys.*, 1974, **60**, 315.
2 S. M. Freund, E. Herbst, R. P. Mariella and W. Klemperer, *J. Chem. Phys.*, 1972, **56**, 1467.
3 C. Yamada, M. Fujitake and E. Hirota, *J. Chem. Phys.*, 1989, **90**, 3033.
4 C. Yamada, M. Fujitake and E. Hirota, *J. Chem. Phys.*, 1989, **91**, 137.
5 C. Yamada and E. Hirota, *J. Chem. Phys.*, 1993, **99**, 8489.
6 S. Joo, D. R. Worsnop, C. E. Kolb, S. K. Kim and D. R. Herschbach, *J. Phys. Chem. A*, 1999, **103**, 3193.
7 R. R. Herm and D. R. Herschbach, *J. Chem. Phys.*, 1970, **52**, 5783.
8 C. Yamada and E. Hirota, *J. Chem. Phys.*, 1999, **110**, 2853.
9 C. Yamada and E. Hirota, *J. Chem. Phys.*, 1999, **111**, 9587.
10 J. N. Allison and W. A. Goddard III, *J. Chem. Phys.*, 1982, **77**, 4259.
11 T. G. Wright, A. M. Ellis and J. M. Dyke, *J. Chem. Phys.*, 1993, **98**, 2891.
12 E. Hirota, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 1.
13 J. Xin and L. M. Ziurys, *Astrophys. J.*, 1998, **495**, L119.
14 J. N. Allison, R. J. Cave and W. A. Goddard III, *J. Phys. Chem.*, 1984, **88**, 1262.
15 S. R. Langhoff, C. W. Bauschlicher Jr. and H. Partridge, *J. Chem. Phys.*, 1986, **84**, 4474.
16 S. R. Langhoff, H. Partridge and C. W. Bauschlicher Jr., *Chem. Phys.*, 1991, **153**, 1.
17 C. W. Bauschlicher Jr., H. Partridge and K. G. Dyall, *Chem. Phys. Lett.*, 1992, **199**, 225.
18 C. W. Bauschlicher Jr., H. Partridge and L. G. M. Pettersson, *J. Chem. Phys.*, 1993, **99**, 3654.
19 L. Serrano-Andrés, A. Sánchez de Merás, R. Pou-Amérigo and I. Nebot-Gil, *J. Mol. Struct.*, 1992, **254**, 229.
20 L. Serrano-Andrés, A. Sánchez de Merás, R. Pou-Amérigo and I. Nebot-Gil, *Chem. Phys.*, 1992, **162**, 321.
21 E. P. F. Lee, P. Soldán and T. G. Wright, *J. Chem. Phys.*, 2002, **117**, 8241.
22 G. H. Herbig, *Astrophys. J.*, 1974, **188**, 533.
23 G. Wallerstein, *Astrophys. J.*, 1971, **169**, 195.
24 G. Wallerstein, *Astron. Astrophys.*, 1986, **164**, 101.
25 E. D. Tenenbaum and L. M. Ziurys, *Astrophys. J.*, 2009, **694**, L59.
26 T. Kamiński, C. A. Gottlieb, K. M. Menten, N. A. Patel, K. H. Young, S. Brünken, H. S. P. Müller, M. C. McCarthy, J. M. Winters and L. Decin, *Astron. Astrophys.*, 2013, **551**, A113.
27 R. M. Humphreys, L. M. Ziurys, J. J. Bernal, M. S. Gordon, L. A. Helton, K. Ishibashi, T. J. Jones, A. M. S. Richards and W. Vlemmings, *Astrophys. J.*, 2019, **874**, L26.
28 L. M. Ziurys, W. L. Barclay Jr., M. A. Anderson and D. A. Fletcher, *Rev. Sci. Instrum.*, 1994, **65**, 1517.
29 C. T. Kingston, A. J. Merer and T. D. Varberg, *J. Mol. Spectrosc.*, 2002, **215**, 1062.
30 E. Yamazaki, T. Okabayashi and M. Tanimoto, *J. Chem. Phys.*, 2004, **121**, 162.
31 D. Gauyacq and M. J. Horani, *Can. J. Phys.*, 1978, **56**, 587.
32 L. N. Zack, R. L. Pulliam and L. M. Ziurys, *J. Mol. Spectrosc.*, 2009, **256**, 186.
33 H. Lefebvre-Brion and R. W. Field, *Perturbations in the Spectra of Diatomic Molecules*, Academic Press, Orlando, 1986.