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The microwave spectrum of the rubidium monoxide RbO radical

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The rotational spectra of ⁸⁵RbO in the ground- and the first excited vibrational states and of ⁸⁷RbO in the ground vibrational state were observed in the millimeter- and submillimeter-wave region. The RbO radical was generated in a high-temperature absorption cell by the reaction of N₂O with Rb vapor, which was produced in the cell by heating a mixture of RbCl and lithium metal to 500– 550 °C. Analysis of the observed spectra yielded the rotational and centrifugal distortion constants, spin–rotation interaction constants, and hyperfine interaction constants. The bond length and the vibrational frequency were calculated from the rotational and centrifugal distortion constants to be 2.254 193 1 (15) Å and 387.22 (20) cm⁻¹, respectively, for ⁸⁵RbO. The ground electronic state of RbO was confirmed to be ${}^{2}\Sigma$, and the low-lying ${}^{2}\Pi$ state was estimated to be located at 650–700 cm⁻¹ above the ground state by using a second-order perturbation expression with the vibrational energy in the denominator for the spin–rotation interaction constant. The observed hyperfine interaction constants indicated that the RbO radical is essentially an ionic molecule. (© *1999 American Institute of Physics*. [S0021-9606(99)01306-9]

I. INTRODUCTION

Alkali monoxides have attracted much interest because they play important roles in many fields, including atmospheric chemistry. We have carried out a systematic study on these radicals by using microwave and infrared diode laser spectroscopy, in order to clarify their molecular structure in detail and also to provide a means of unambiguously identifying them in various environments. We have already reported the results on the first two members: LiO^{1,2} and NaO,³ and have briefly described those for the remaining three, KO RbO, and CsO, in a review paper.⁴ One of the interesting features of the series is that the ground electronic state is ${}^{2}\Pi$ for the first two members, as we have clearly established,^{1,3} whereas the ${}^{2}\Sigma$ state was inferred to be the ground state for the last two: RbO and CsO. The case of KO is crucial and has in fact been subject to controversy. The present paper describes the results obtained for RbO.

Little has been reported on the RbO radical in the gas phase. Spiker and Andrews⁵ attempted to observe the infrared spectrum of RbO by the reaction of Rb atoms with N₂O in a matrix, but the spectrum was too weak to observe. Lindsay, Herschbach, and Kwiram⁶ reported electron spin resonance (ESR) spectra of RbO and CsO isolated in a lowtemperature matrix and interpreted the observed data in terms of the ² Σ ground electronic state. They determined hyperfine interaction constants in addition to *g*-factors.

A number of *ab initio* calculations have been performed on alkali monoxides, and three of them reported the separation between the ${}^{2}\Pi$ and ${}^{2}\Sigma$ electronic states of RbO; Allison and Goddard^{7,8} obtained 114 cm⁻¹ by an eight-electron configuration interaction (CI) calculation, Langhoff *et al.*⁹ obtained 515 and 650 cm⁻¹ by an HF and a 15-electron CI, respectively, and So and Richards¹⁰ obtained 606 cm⁻¹ by a self-consistent-field (SCF) method, all identifying the ² Σ state as the ground state. Allison *et al.*^{7,8} have explained the energy difference between the ² Π and ² Σ ⁺ states in terms of two competing factors; the quadrupole attraction of the oxygen ion, which favors the ² Π state, and the Pauli repulsion, which favors the ² Σ ⁺ state. The three studies yielded also the bond length and the vibrational frequency of RbO, which may be compared with the present results.

II. EXPERIMENT

Because the vapor pressure of rubidium is quite high, as its melting point (39 °C) indicates, it was somewhat awkward to apply the reaction of alkali metal vapor with N₂O to the present case, although the reaction was successfully employed for the generation of LiO^{1,2} and NaO.³ Instead, we obtained rubidium vapor by the reaction of Li metal with RbCl; we loaded 6 g of Li and 25 g of RbCl in a stainlesssteel absorption cell, which, as drawn in Fig. 1, was almost identical to that used for NaO.³ The microwave spectrometer employed in the present study was described in detail in Ref. 11. Spectral lines which were supposed to be caused by RbO started to appear when the temperature of the cell reached 350 °C and became strong at 500 to 550 °C; N₂O was continuously pumped through the cell at the pressure of about 20 mTorr (2.7 Pa).

III. OBSERVED SPECTRA

Two groups of doublets appeared at around 351 847 and 353 000 MHz, and were tentatively assigned to the fine structure components of the $N=23\leftarrow22$ transition of ⁸⁵RbO in

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FIG. 1. Absorption cell.

the ground vibrational state. In fact, the lines corresponding to $N=24\leftarrow 23$ and $25\leftarrow 24$ were subsequently observed at the expected frequencies. The measurement was then extended to cover the transitions of $N=7 \leftarrow 6, 8 \leftarrow 7$, from $13 \leftarrow 12$ up to $26 \leftarrow 25$, and also a part of $6 \leftarrow 5$. Figure 2 reproduces the F_1 component of the $N=7 \leftarrow 6$ transition, which is clearly resolved into six hyperfine components corresponding to the nuclear spin quantum number I = 5/2 of ⁸⁵Rb. Table I lists a part of the observed transition frequencies. A similar set of spectra appeared in a lower frequency region than that of the main species did, and was assigned to ⁸⁵RbO in the first excited vibrational state. The measured frequencies of this set are also given in Table I. A comparison of the corresponding transition frequencies of the two vibrational states reveals that fine structure splittings increase greatly from the ground state to the excited state, almost twice as large in the latter state as in the former. The natural abundance of ⁸⁷Rb is 27.85%, and in fact the lines of ⁸⁷RbO were observed. In accordance with the nuclear spin quantum number I=3/2 of ⁸⁷Rb, each fine structure line was found split into four hyperfine component lines at most. Some of the observed transition frequencies are included in Table I. The $N = 16 \leftarrow 15$ transitions of the three species are displayed in Fig. 3 for comparison, where F_1 and F_2 fine structure components are exhibited in the left and right insets, respectively.





IV. ANALYSIS

We have analyzed all the observed spectra by a leastsquares method using a Hund's case (b) Hamiltonian,¹² which consists of the rotational and fine structure Hamiltonian \mathbf{H}_{rso} and of the hyperfine Hamiltonian \mathbf{H}_{hfs}

$$\mathbf{H} = \mathbf{H}_{rso} + \mathbf{H}_{hfs},\tag{1}$$

$$\mathbf{H}_{\mathbf{rso}} = B\mathbf{N}^2 - D\mathbf{N}^4 + H\mathbf{N}^6 + \gamma \mathbf{N} \cdot \mathbf{S},\tag{2}$$

$$\mathbf{H}_{\mathbf{hfs}} = b\mathbf{I} \cdot \mathbf{S} + cI_z S_z + \mathbf{H}_{\mathbf{O}} + \mathbf{T}_{00} \mathbf{N} \cdot \mathbf{I}, \tag{3}$$

where the spin-rotation interaction constant includes the effect of centrifugal distortion in the following way:

$$\gamma = \gamma_{\nu} - \gamma_D \mathbf{N}^2 + \gamma_H \mathbf{N}^4. \tag{4}$$

 H_Q denotes the nuclear quadrupole interaction Hamiltonian, and the last term of H_{hfs} stands for the nuclear spin-rotation interaction Hamiltonian.

Hyperfine structure was not completely resolved for high-*N* transitions. For such lines the weight was reduced accordingly. We have paid special attention to the sign of the spin-rotation interaction constant. Both the positive and negative signs of the γ constant reproduced the global feature of the observed spectra almost equally well, but the details of the hyperfine pattern could be explained only by a negative γ constant. The rotational and centrifugal distortion constants, spin-rotation interaction constants, and hyperfine interaction constants, which were thus determined, are summarized in Table II. The standard deviation of the fit was 0.026 MHz for the main species, which is of the same order of magnitude as the estimated uncertainty 0.030 MHz of the frequency measurement.

V. DISCUSSION

The observed spectra conform nicely to those expected for a diatomic molecule in a ${}^{2}\Sigma^{+}$ electronic state, which may be reasonably assigned to the ground electronic state. The molecular parameters derived from the spectra provide us with invaluable information on the rubidium monoxide radical, as follows.

A. Molecular structure and vibrational frequency

When the Born–Oppenheimer approximation is assumed to hold, the rotational constant may be expressed as a linear combination of the terms in μ^{-1} and $\mu^{-1.5}$, where μ denotes the reduced mass

$$B_{\nu} = B_{e} - \alpha (\nu + \frac{1}{2})$$

with $B_{e} = h / [8 \pi^{2} \mu r_{e}^{2}]$ and $\alpha = \mu^{-1.5} [\alpha_{red}].$ (5)

Here, r_e denotes the equilibrium internuclear distance and α_{red} stands for the part of α that is independent of μ . The three observed constants were fitted to these expressions. The fitting was quite satisfactory; the calculated rotational constant in the ground state was reproduced within 0.0059 MHz from the observed value, which was an order of magnitude larger than the standard deviation of the rotational constant, as shown in Table II. The equilibrium rotational constants B_e thus obtained are 7389.3299 (97) and

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TABLE I. Part of the observed transitions of ⁸⁵RbO in the $\nu=0$ and 1 and of ⁸⁷RbO in the $\nu=0$ (in MHz).

						⁸⁵ RbO, <i>v</i> =0			⁸⁵ RbO, <i>v</i> =1			87 RbO, $\nu = 0$		
$N' \leftarrow N''$		$J' \! \leftarrow \! J''$		$F' \leftarrow \overline{F''}$		obs	0-c	wt	obs	0-C	wt	obs	0-с	wt
7	6	6.5	5.5	9.0	8.0	103 509.687	0.000	1.00	103 092.823	-0.061	1.00			
				8.0	7.0	103 507.058	-0.050	1.00	103 090.594	0.182	1.00	103 120.378	-0.022	1.00
				7.0	6.0				103 089.990	0.153	1.00	103 119.877	-0.033	1.00
				6.0	5.0	103 508.360	0.022	1.00	103 091.316	0.166	1.00	103 128.006	-0.028	1.00
				5.0	4.0	103 511.745	-0.043	1.00	103 094.382	0.032	1.00	103 141.593	-0.082	1.00
				4.0	3.0	103 516.950	-0.041	1.00	103 099.355	-0.074	1.00			
		7.5	6.5	10.0	9.0	102 436.621	0.005	1.00	101 024.537	0.111	1.00			
				9.0	8.0	102 443.180	0.030	1.00	101 030.222	0.047	0.76	102 064.045	-0.075	1.00
				8.0	7.0	102 446.346	0.002	1.00	101 033.129	-0.038	0.64	102 083.480	-0.064	1.00
				7.0	6.0	102 446.981	0.027	1.00	101 034.054	-0.043	1.00	102 085.867	-0.018	1.00
				6.0	5.0	102 445.498	-0.019	1.00	101 033.129	-0.038	0.36	102 079.246	0.096	1.00
				5.0	4.0	102 442.437	0.029	1.00	101 030.222	0.047	0.24			
8	7	7.5	6.5	10.0	9.0	118 217.230	0.013	1.00	117 671.133	-0.101	1.00			
				9.0	8.0	118 215.244	0.059	1.00	117 669.349	0.039	1.00	117 777.667	-0.003	1.00
				8.0	7.0	118 214.887	0.048	1.00	117 668.905	0.065	1.00	117 776.899	0.019	1.00
				7.0	6.0	118 216.073	0.032	1.00	117 669.925	0.094	1.00	117 783.045	0.040	1.00
				6.0	5.0	118 218.684	-0.017	1.00	117 672.255	-0.035	1.00	117 793.719	-0.067	1.00
				5.0	4.0	118 222.731	-0.029	1.00	117 676.106	-0.115	1.00			
		8.5	7.5	11.0	10.0	117 140.547	0.009	1.00	115 594.691	0.074	1.00			
				10.0	9.0	117 145.507	0.017	1.00	115 599.100	0.085	0.73	116 714.666	-0.090	1.00
				9.0	8.0	117 147.992	0.010	1.00	115 601.301	-0.021	0.62	116 729.442	-0.028	1.00
				8.0	7.0	117 148.525	0.014	1.00	115 602.062	0.012	1.00	116 731.674	0.012	1.00
				7.0	6.0	117 147.446	-0.003	1.00	115 601.301	-0.021	0.38	116 726.720	0.087	1.00
				6.0	5.0	117 145.103	0.036	1.00	115 599.100	0.085	0.27			
16	15	15.5	14.5	18.0	17.0	235 760.944	0.047	0.39	234 181.945	0.035	0.39			
				14.0	13.0	235 760.944	0.047	0.30	234 181.945	0.035	0.30	234 905.958	-0.064	1.00
				17.0	16.0	235 760.221	-0.012	0.36	234 181.301	0.002	0.36	234 902.256	0.182	0.10
				16.0	15.0	235 760.221	-0.012	0.34	234 181.301	0.002	0.34	234 901.681	0.122	0.10
				15.0	14.0	235 760.221	-0.012	0.32	234 181.301	0.002	0.32	234 903.005	0.012	0.10
				13.0	12.0	235 762.079	-0.080	1.00	234 182.993	-0.088	0.28			
		16.5	15.5	19.0	18.0	234 653.574	-0.027	1.00	232 012.628	-0.059	0.38			
				18.0	17.0	234 654.826	-0.006	0.36	232 013.952	0.126	0.36	233 801.677	-0.086	1.00
				14.0	13.0	234 654.826	-0.006	0.28	232 013.952	0.126	0.28			
				17.0	16.0	234 655.565	0.037	0.34	232 014.516	0.046	0.34	233 805.345	0.108	0.34
				16.0	15.0	234 655.565	0.037	0.32	232 014.516	0.046	0.32	233 806.320	0.094	1.00
				15.0	14.0	234 655.565	0.037	0.30	232 014.516	0.046	0.30	233 805.345	0.108	0.30

7362.4107 (97) MHz for ⁸⁵RbO and ⁸⁷RbO, respectively. These rotational constants, when inserted in the expression for B_e given in Eq. (5), led to the equilibrium bond length of 2.254 193 1 (15) Å, where the error given in parentheses corresponds to that of B_e . This result may be compared with an *ab initio* value of 2.333 Å (SCF) or 2.287 Å (single plus double CI:SDCI).⁹

The centrifugal distortion constants were analyzed in a similar way, where the first and the second terms were proportional to μ^{-2} and $\mu^{-2.5}$, respectively. The equilibrium centrifugal distortion constants were thus obtained to be 0.011 976 (13) and 0.011 889 (12) MHz for the two species, respectively. The constants calculated for the ground state differed from the observed values by 0.000 007 6 MHz, which was about seven times larger than the standard deviation of the ground-state centrifugal distortion constant, as shown in Table II. The harmonic frequency ω_e is given by $(1/2\pi)(k/\mu)^{1/2}$ with k denoting the force constant and the equilibrium centrifugal distortion constant D_e by $h^3/[32\pi^4k\mu^2r_e^6]$, and these two formulas, when combined with the expression for B_e given in Eq. (5), lead to the following well-known relation:

$$\omega_e = (4B_e^3/D_e)^{1/2}.$$
 (6)

The observed values of B_e and D_e were inserted in this relation to calculate the harmonic vibrational frequency ω_e to be 387.22 (20) and 386.52 (20) cm⁻¹ for the two isotopic species. These values may be compared with *ab initio* data: 363 (SCF) or 373 (SDCI) cm⁻¹ (Ref. 9).

It is not easy to estimate the effects of Born– Oppenheimer breakdown. So, the spectroscopic data on a molecule closely related to RbO, namely RbF, Ref. 13 are cited here as references; Y_{01} =6315.5438 (16) MHz may be compared with B_e =6315.5326 (16) MHz and Y_{10} = 373.444 98 (62) cm⁻¹ with ω_e =373.444 86 (59) cm⁻¹.

B. Lowest excited electronic state

The observed spin-rotation interaction constant γ may be used to estimate the excitation energy of the lowest Π state. The ground-state γ value is -1072.598 MHz, which, when inserted in the formula $\gamma = -4AB/\Delta E$, led to the excitation energy $-\Delta E$ of 2771 cm⁻¹, where the effective



FIG. 3. The $N=16 \leftarrow 15$ transitions of ⁸⁵RbO in the $\nu=0$ and 1 states and of ⁸⁷RbO in the $\nu=0$ state. The left and right insets show the F_1 and F_2 fine structure spectra, respectively.

spin-orbit coupling constant *A* was assumed to be -101 cm⁻¹ by referring to the results on LiO¹, and the ground-state rotational constant was used for *B*.

As listed in Table II, the spin–rotation interaction constant increases in magnitude to -2051.828 MHz in the first excited vibrational state. When a simple expression $\gamma_{\nu} = \gamma_e$ $-\alpha^{\gamma}(\nu + \frac{1}{2})$ is used with ν denoting the vibrational quantum number, the "equilibrium" spin–rotation interaction constant γ_e is -582.983 MHz, which leads to the excitation energy of 5098 cm⁻¹.

These two estimated values are much larger than the *ab initio* results of 114 to 606 cm⁻¹ (Refs. 7–10). The smallest value, 114 cm⁻¹, can be ruled out because spectral lines in the excited vibrational state were clearly observed, whereas those in the Π state were not. The Boltzmann population in

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the excited vibrational state at 387 cm⁻¹ above the ground state is 0.499 at the temperature of 527 °C. On the other hand, the abundance of ⁸⁷RbO relative to that of ⁸⁵RbO is 0.386. The observed intensities are consistent with these relative populations, confirming that the distribution of RbO radicals in the absorption cell was close to the thermal one at the cell temperature of 527 °C. Because we could not observe any spectral lines in the excited Π state, its excitation energy must be larger than 529 cm^{-1} (the relative population of ⁸⁷RbO corresponds to the Boltzmann factor of an excited vibrational state at 529 cm^{-1} above the ground state). But, it may not be as large as 2771 cm⁻¹. If the large increase of γ with vibrational excitation is entirely ascribed to the reduction in energy separation, $-\Delta E$ is calculated to be 811.36 cm^{-1} . This assumption requires, at the same time, the reduction in Franck-Condon factor, or in A constant, by a factor of 0.293. It is also possible that higher excited electronic states make positive contributions to the spin-rotation interaction constant, making its magnitude smaller and thus, the energy separation apparently larger.

It has been demonstrated¹⁴ that the formula, $\gamma = -4AB/\Delta E$, employed above to estimate the energy separation ΔE between the Σ and Π states, holds only when an identical potential applies to the both states, each described by a single electron configuration. When the potential function is quite different for the two states, we must take into account the Franck–Condon factor to calculate properly the contribution of each vibrational state in the upper electronic state. We have made such a calculation by using *ab initio* values⁹ for the vibrational frequencies and the equilibrium internuclear distances of the two states, which were fitted to Morse potentials for the sake of simplicity. We have also included the vibrational energy in the denominator, because the energy separation between the two states is not much larger than the vibrational energy.

The upper part of Fig. 4 shows the γ constants for the $\nu''=0$ and 1 states thus calculated as functions of the excitation energy $-\Delta E$. As is usually done in most other cases, we also assumed the spin-orbit coupling constant and the rotational constant to be taken out as constants from the vibrational integrals. We have found that the effective spin-orbit coupling constant of -50 cm^{-1} , rather than -101 cm^{-1} as first assumed, gave a good fit to the observed data. The

TABLE II. Molecular constants of the rubidium monoxide radical (in MHz).^a

Constant	85 RbO, $\nu = 0$	⁸⁵ RbO, $\nu = 1$	87 RbO, $\nu = 0$
В	7356.726 17 (42)	7291.536 28 (86)	7329.9967 (14)
D	0.012 632 4 (11)	0.013 967 6 (22)	0.012 554 4 (38)
$H/10^{-6}$	-0.004 12 (84)	-0.1912 (17)	0.0052 (31)
γ_{ν}	-1072.598 (30)	-2051.828 (32)	-1068.40 (11)
γ_D	0.045 837 (50)	0.149 921 (75)	0.045 17 (18)
$\gamma_{H}/10^{-5}$	-0.1512 (37)	-0.9651 (61)	-0.176 (14)
b	180.88 (38)	[180.88]	610.7 (34)
С	42.4 (13)	[42.4]	150.3 (96)
eQq	-28.0 (22)	[-28.0]	-17.0 (12)
T_{00}	0.0326 (56)	[0.0326]	0.102 (23)
$\sigma_{ m fit}$	0.026	0.052	0.071

^aValues in parentheses denote standard deviations and apply to the last digits of the constants; those in square brackets are fixed.

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FIG. 4. The upper part shows the spin–rotation coupling constants for the $\nu''=0$ and 1 states calculated as functions of the excitation energy $-\Delta E$. The effective spin-orbit coupling constant *A* was assumed to be -50 cm^{-1} . The lower part displays γ_1 / γ_0 , which indicates that $-\Delta E$ lies between 650 and 700 cm⁻¹.

lower part of Fig. 4 plots the ratio of the γ constants for $\nu''=1$ and 0, γ_1/γ_0 , which may be regarded to be exempt from the ambiguity of the spin-orbit coupling constant. We have finally concluded from this calculation that the energy difference $-\Delta E$ lies between 650 and 700 cm⁻¹.

C. Electronic structure

Lindsay *et al.*⁶ reported hyperfine constants, isotropic as well as anisotropic, of ⁸⁷RbO in a matrix, a = 166 G and T_{\parallel}

=34 G, which are converted to the Fermi term $b_F = b + c/3$ = 465 MHz, and a dipolar interaction constant c = 143 MHz in order to directly compare with the present results: 660.8 and 150.3 MHz, respectively.

When the Fermi term is compared with the ⁸⁵Rb atomic value 1037 MHz, as compiled by Morton and Preston¹⁵ for a 5s electron, the *s* character becomes quite large, 18.8%. However, this is probably not the case; according to Lindsay *et al.*,⁶ we should consider a 4s electron, rather than 5s electron, and then the *s* character would be close to 1% or so. It is difficult to estimate the spin density from the observed *c* constant, but the contribution of a 4p orbital would be of the order of several thousand MHz and thus the observed *c* constant would correspond to a spin density of a few percent, at most.

The nuclear quadrupole coupling constant -28.0 MHz determined for ⁸⁵Rb may be compared with -70.3415 MHz of ⁸⁵RbF (Ref. 16), which is well known as an ionic molecule.

All of the observed hyperfine parameters are consistent with the ionic configuration Rb^+O^- , with the unpaired electron predominantly occupying a p_σ orbital mainly localized at the oxygen ion.

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