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Infrared diode laser spectroscopy of the CCO radical: The $2\nu_1-\nu_1$ and $\nu_1+\nu_3-\nu_3$ difference bands

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The $2\nu_1-\nu_1$ and $\nu_1+\nu_3-\nu_3$ difference bands of the CCO radical in the gas phase have been studied using a tunable infrared diode laser spectrometer. The CCO radical was produced using a flowing mixture of carbon suboxide and helium subjected to a hollow-cathode discharge. The spectral region between 1920–1960 cm^{-1} was probed. Ninety and seventy-five rovibrational transitions were measured in the $2\nu_1-\nu_1$ and $\nu_1+\nu_3-\nu_3$ bands, respectively. The analyses of these bands yielded spectroscopic constants for the (001), (200), and (101) vibrational states. The band origins for $2\nu_1-\nu_1$ and $\nu_1+\nu_3-\nu_3$ were determined to be 1941.85761(54) cm^{-1} and 1936.79402(56) cm^{-1}, respectively. © *1998 American Institute of Physics.*
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I. INTRODUCTION

The CCO radical is postulated to act as an intermediate in a variety of chemical reactions[1] and has been detected in interstellar space toward the dark molecular cloud TMC.[2] The first spectroscopic detection of this molecule was made in a matrix isolation study by Jacox *et al.*[3] who showed that CCO is an asymmetric linear molecule and determined the vibrational frequencies in the ground electronic state to be 381, 1074, and 1978 cm^{-1}. Devillers and Ramsay[4] reported the first gas-phase spectrum of CCO, observing the $\widetilde{A}\,^3\Pi_i-\widetilde{X}\,^3\Sigma^-$ electronic transition. From the analysis of the rovibronic spectra, the term energy (T_0), vibrational frequencies, rotational constants, and the Renner–Teller coupling constant for the $\widetilde{A}\,^3\Pi_i$ electronic state were determined. These earlier spectroscopic studies have been followed more recently by near-infrared diode laser spectroscopy to reinvestigate several bands of $\widetilde{A}\,^3\Pi_i-\widetilde{X}\,^3\Sigma^-$ electronic transition[5,6] and photoelectron spectroscopy to determine the energetics of the singlet electronic states.[7]

Several groups have investigated the spectra of CCO in the ground electronic state. Yamada *et al.*[8] have measured the ν_1 band of CCO using diode laser kinetic spectroscopy. Here, the CCO radical was generated by the 193 or 248 nm excimer laser photolysis of carbon suboxide. The molecular parameters obtained from the observed infrared spectrum were then used to search and successfully record the pure rotational spectrum of the radical both in laboratory and space.[9,2] The attempt by Yamada *et al.* to detect CCO by an electrical discharge of C_3O_2 was not successful.

Most recently, two of the low N-value transitions of CCO in the ground vibrational state were measured using a Fabry–Perot type Fourier-transform microwave spectrometer and a pulsed discharge nozzle.[10] An extended study of the ν_1 fundamental band and the first observation of the $\nu_1+\nu_2-\nu_2$ sequence band were reported by Moazzen-Ahmadi *et al.*[11] All the spectroscopic investigations have confirmed the structure of the ground electronic state of CCO.

In the present work, we used a hollow cathode discharge cell with a flowing mixture of carbon suboxide and helium to generate the CCO radical. The absorption of the $2\nu_1-\nu_1$ and $\nu_1+\nu_3-\nu_3$ difference bands were recorded using a tunable infrared diode laser spectrometer. Ninety and seventy-five rovibrational transitions were measured in the $2\nu_1-\nu_1$ and $\nu_1+\nu_3-\nu_3$ bands, respectively. Unambiguous N-numbering of the bands were made by combination differences and/or the observation of the weak low N-value lines near the band origin. The nonlinear least-squares analyses of the two bands yielded spectroscopic constants for the (001), (200), and (101) vibrational states. The results reported here and those of our earlier work[11] on the (000), (100), (010), and (110) vibrational states provide a more comprehensive set of spectroscopic constants for CCO in the ground electronic state. In the present study we highlight the usefulness of a hollow cathode discharge as a source for study of the hot band spectra of short-lived molecules.

II. EXPERIMENTAL DETAILS

The measurements were carried out using equipment and procedures very similar to those used in the infrared studies of C_3[12] and C_4.[13,14] The spectra were recorded using a tunable diode laser spectrometer and a multipass hollow cathode absorption cell. The cathode (70 cm long, 5 cm diam) was constructed from two concentric cylinders and was cooled to $-10\,°$C by flowing methanol from a refrigerated bath through the space between the cylinders.

Three diodes were used in order to get reasonably complete coverage of the 1920–1960 cm^{-1} region of interest. Wave numbers of the CCO lines were measured relative to known lines of allene[15] using fringes from a temperature-

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stabilized solid Ge étalon with a free spectral range of $0.0488 \, \text{cm}^{-1}$. The absolute uncertainty of the measured lines is $\pm 0.002 \, \text{cm}^{-1}$.

The CCO radicals were generated in a 1 kHz modulated discharge through a flowing mixture of carbon suboxide (0.2 Torr) and helium (1 Torr). The discharge modulation technique was employed for detection.[16] Carbon suboxide was prepared by dehydration of malonic acid with P_2O_5[17] or by hot-tube pyrolysis of molten diacetyltartaric anhydride[18] and purified by fractional distillation through traps cooled by dry-ice ($-78 \, ^\circ$C) and ethanol (-115 to $-110 \, ^\circ$C) slush baths, the latter retaining pure C_3O_2.

In contrast to the relatively high discharge current (~ 400 mA) required for the optimum production of C_3,[12] C_4,[13,14] and C_5,[19] the maximum signal for the CCO radical was achieved at a much lower current (40 mA). See Ref. 11 for more experimental details.

III. SPECTRA, ANALYSIS, AND RESULTS

The ground electronic state of CCO is $^3\Sigma^-$. Each rotational level, characterized by the rotational angular momentum quantum number N, is split into three fine structure levels F_1, F_2, and F_3 characterized by total angular momentum $J = N+1$, $J = N$, and $J = N-1$ (except for $N = 0$, where there is only a single component with $J = 1$), respectively. For all but the lowest values of N, almost all of the intensity of the vibration–rotation $P(N)$, $Q(N)$, or $R(N)$ transition is contained in the three components with $\Delta J = \Delta N$.

The general features of the difference bands $2\nu_1 - \nu_1$ and $\nu_1 + \nu_3 - \nu_3$ are similar to those for the ν_1 band.[11] For transitions with $N'' \geq 8$, each spectral line appears as a doublet with a 2:1 intensity ratio and an essentially constant spacing between the two components. This spacing which measures the difference between the values of the spin–spin parameter (λ) in the upper and lower states is about 205 MHz for the $2\nu_1 - \nu_1$ band and 175 MHz for the $\nu_1 + \nu_3 - \nu_3$ band. The corresponding spacing for the ν_1 band is slightly larger (248 MHz).[11]

The doubling of the spectral lines is due to the fact that the F_1 and F_3 components are close in energy and that the contribution to energy from the spin–rotation effect is nearly the same for both components. Moreover, the F_2 component is widely separated from the other two components and is at higher energy.[20] Since all three components are expected to have similar intensities, a doublet with the higher frequency component half as intense as the lower frequency component is observed. Figure 1 illustrates a small portion of the spectra recorded for the $2\nu_1 - \nu_1$ band. Here, the trace shows the observed spectrum near the $R(18)$ transition which exhibits a normal ("zeroth derivative") line shape due to the discharge modulation technique employed.[16] The stronger doublet to the higher frequency side of the $R(18)$ transition is the $P(19)$ transition of the ν_1 band.[11]

Table I lists the ninety lines measured for the $2\nu_1 - \nu_1$ band. As can be seen, large spin splittings ($0.01-0.03 \, \text{cm}^{-1}$) were observed for $P(2)-P(6)$ and $R(1)-R(7)$. The absolute N-numbering of the band was easily determined by com-
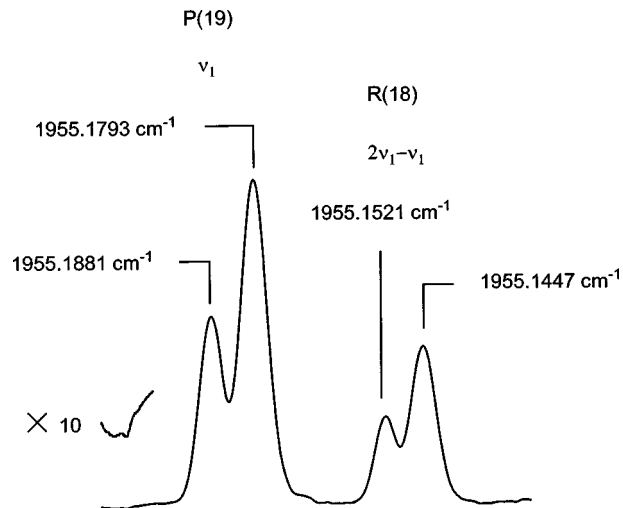

FIG. 1. The observed spectrum of CCO in the region of the $R(18)$ line of the $2\nu_1 - \nu_1$ difference band. For the identification of the individual components see Table I. The doublet to the higher frequency side of $R(18)$ is the $P(19)$ of the ν_1 band.

paring the lower level combination differences $R(N-1) - P(N+1)$ with those of the upper state combination differences $R(N) - P(N)$ derived from the ν_1 band. The data in Table I were analyzed using a full matrix treatment. The effective Hamiltonian and the matrix elements are given in Ref. 21. The lower state parameters were held fixed at the values given in Ref. 11. For the unresolved lines, the calculated frequencies were obtained from the average of the theoretical frequencies of the individual members. The resulting molecular parameters are listed in Table II; a comparison of the calculated and the measured frequencies are given in Table I.

The wave numbers for 75 lines observed in the $\nu_1 + \nu_3 - \nu_3$ band are listed in Table III. Since the ν_3 band of CCO in the gas phase has not been observed, the N-numbering of the band could not be assigned using the combination differences and had to be otherwise determined.

Initially, the high N-value transitions in the $\nu_1 + \nu_3 - \nu_3$ band were recorded. These lines appear as unresolved doublets with an F_3 component visible as a shoulder to the higher frequency side. An example of spectra recorded for this band is shown in Fig. 2. The unresolved doublet near $1944.09 \, \text{cm}^{-1}$ is the $R(9)$ of the $\nu_1 + \nu_3 - \nu_3$ band. Also shown in this figure are the $P(31)$ of the ν_1 band and $R(2)$ of the $2\nu_1 - \nu_1$ band which occur in the same frequency region. As can be seen, the triplet for $R(2)$ of the $2\nu_1 - \nu_1$ band is fully resolved and exhibits relative intensities within the triplet that are in accordance with the approximate theoretical values.[22] The weak unidentified doublet, which is almost certainly due to the CCO radical, has not been identified.

To establish the N-numbering of the band, a preliminary analysis of the high N-value transitions was made. The assignment was then chosen, and is given in Table II, so that it resulted in $\alpha_3 (= B_{000} - B_{001})$ which was positive and comparable in magnitude to $\alpha_1 (= B_{000} - B_{100})$. This assignment was later confirmed by the observation of the low N-value

TABLE I. Observed transitions in the $2\nu_1-\nu_1$ band of CCO (in cm^{-1}).[a]

N''	$P(N'')$	Obs.–Calc.	$R(N'')$	Obs.–Calc.
1			1943.3514	−0.0008
			1943.3707	−0.0004
2	1940.3301	0.0003	1944.1020	−0.0000
	1940.3301	0.0003	1944.1152	−0.0007
			1944.1365	−0.0004
3	1939.5511	0.0007	1944.8432	0.0006
	1939.5511	0.0007	1944.8558	−0.0010
	1939.5183	0.0014	1944.8558	−0.0011
4	1938.7662	0.0003	1945.5754	−0.0003
	1938.7662	0.0003	1945.5866	0.0005
	1938.7482	−0.0009	1945.5866	0.0005
5	1937.9739	−0.0017	1946.3012	−0.0007
	1937.9739	−0.0017	1946.3133	0.0018
	1937.9671	0.0029	1946.3087	−0.0005
6	1937.1783	−0.0007		
	1937.1783	−0.0007		
	1937.1693	−0.0008		
7	1936.3733	−0.0004	1947.7352	−0.0012
	1936.3775	−0.0012	1947.7447	0.0018
	1936.3700	0.0013	1947.7352	−0.0012
8	1935.5635	0.0011	1948.4403	−0.0020
	1935.5691	−0.0006	1948.4476	−0.0013
9	1934.7480	0.0009	1949.1413	−0.0005
	1934.7543	0.0001	1949.1486	0.0001
10	1933.9263	0.0009	1949.8352	0.0004
	1933.9331	0.0006	1949.8430	0.0014
11	1933.0967	−0.0006	1950.5216	0.0002
	1933.1033	−0.0010	1950.5288	0.0007
12	1932.2632	0.0005	1951.2015	0.0000
	1932.2697	−0.0000	1951.2074	−0.0008
13	1931.4227	0.0009	1951.8745	−0.0006
	1931.4284	−0.0004	1951.8809	−0.0010
14	1930.5745	−0.0001	1952.5433	0.0011
	1930.5810	−0.0005	1952.5503	0.0013
15	1929.7219	0.0010	1953.2026	−0.0002
	1929.7285	0.0007	1953.2094	−0.0002
16	1928.8618	0.0009	1953.8563	−0.0006
	1928.8681	0.0003	1953.8645	0.0007
17	1927.9930	−0.0015	1954.5050	0.0004
	1928.0014	−0.0001	1954.5116	0.0002
18	1927.1219	0.0001	1955.1447	−0.0010
	1927.1289	0.0002	1955.1521	−0.0004
20	1925.3579	0.0005		
	1925.3650	0.0007		
21	1924.4654	−0.0003		
	1924.4722	−0.0004		
22	1923.5684	0.0007	1957.6455	0.0005
	1923.5748	0.0002	1957.6529	0.0010
23	1922.6635	0.0002	1958.2537	0.0001
	1922.6702	−0.0000	1958.2606	0.0001
24	1921.7506	−0.0021	1958.8566	0.0010
	1921.7577	−0.0019	1958.8625	0.0000
25	1920.8355	−0.0002	1959.4512	0.0001
	1920.8409	−0.0017	1959.4592	0.0012

[a]For $N''<8$, the frequencies for F_1, F_2, and F_3 components are the first, second, and third entries, respectively. Otherwise, only two frequencies are given; the first entry corresponds to the unresolved F_1 and F_3 components and the second entry is for the F_2 component.

transitions whose wave numbers were predicted using the molecular parameters from the preliminary analysis. Figure 3 shows an example of the spectra recorded near the $\nu_1+\nu_3 -\nu_3$ band center. The weak triplet for $R(2)$ of the $\nu_1+\nu_3 -\nu_3$ band which partially overlaps with $R(25)$ of the ν_1 $+\nu_2-\nu_2$ band is shown. The lines labelled by $*$ have not been identified. The results of the least-squares fit of the data in Table III, based on the chosen assignment, are listed in Table II. Comparison of the calculated and the measured frequencies are given in Table III.

TABLE II. Molecular parameters for the ν_1, $2\nu_1-\nu_1$, and $\nu_1+\nu_3-\nu_3$ bands of CCO.[a]

Parameter	ν_1	$2\nu_1-\nu_1$	$\nu_1+\nu_3-\nu_3$
ν_0/cm^{-1}	1970.86332(41)	1941.85761(54)	1936.79402(56)
B'/MHz	11453.508(50)	11357.05(14)	11380.71(34)
D'/kHz	5.814(37)	5.71(21)	5.831(70)
λ'/MHz	11848(24)	12054(18)	12025(20)
λ_D'/MHz	-0.00537[b]	-0.00537[b]	-0.00537[b]
γ'/MHz	$-17.5(4.2)$	-17.5[c]	-17.5[c]
B''/MHz	11545.59684(61)	11453.508[c]	11479.62(36)
D''/kHz	5.819(67)	5.814[c]	5.814[c]
λ''/MHz	11600(18)	11848[c]	11848[c]
λ_D''/MHz	$-0.00537(46)$	-0.00537[c]	-0.00537[c]
γ''/MHz	$-17.8166(40)$	-17.5[c]	-17.5[c]

[a]The uncertainties in parentheses correspond to 1σ from the least-squares fit.
[b]This was held fixed at its value for (000) state. See Ref. 11.
[c]This was held fixed at its value for (100) vibrational state. See Ref. 11.

IV. RESULTS AND DISCUSSION

The molecular parameters resulting from the analyses of the two bands reported in this paper are compared with those of the ν_1 fundamental[11] in Table II. The band origin for $2\nu_1-\nu_1$ was determined to be 1941.85761(54) cm^{-1}, 29.01 cm^{-1} lower than that for the ν_1 fundamental. For comparison, the band origin for $\nu_1+\nu_3-\nu_3$ was 1936.79402(56) cm^{-1}, some 34 cm^{-1} below the band origin for the ν_1 band. This indicates that the excitation of v_3 by one quantum results in a larger red-shift in ν_1 frequency than the excitation of v_1 by one quantum. The change in B values with increasing v_1 exhibits a smooth trend, namely $\alpha_1(=B_{000}-B_{100})=92.09$ MHz and $B_{100}-B_{200}=96.45$ MHz. The difference in the B values between the upper and lower states of the $\nu_1+\nu_3-\nu_3$ is also in line with the above values; $B_{001}-B_{101}=98.91$ MHz.

From the lower state B values of the ν_1 and $\nu_1+\nu_3-\nu_3$ bands, we find that $\alpha_3(=B_{000}-B_{001})=65.98$ MHz. This indicates that the excitation of v_3 vibration causes a smaller decrease in B than the excitation of the v_1 vibration.
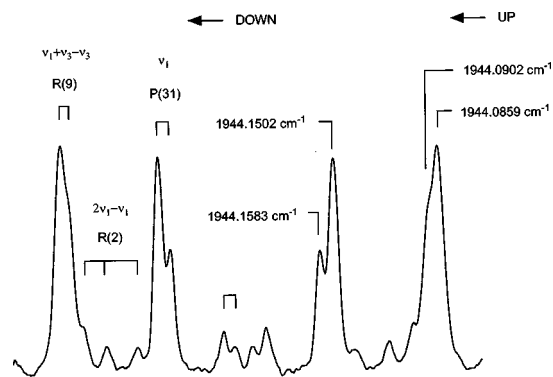

FIG. 2. The observed spectrum of CCO in the region of $R(9)$ of the $\nu_1+\nu_3-\nu_3$ difference band. Two scans (up and down) are shown. Because the difference between the spin–spin parameter in the lower and upper states for this transition are smaller than those for the ν_1 band, the F_2 component appears as a shoulder on the high frequency side. The $P(31)$ of the ν_1 band and $R(2)$ of the $2\nu_1-\nu_1$ band which occur in the same frequency region are also shown. The weak doublet, which is almost certainly due to CCO, has not been identified.
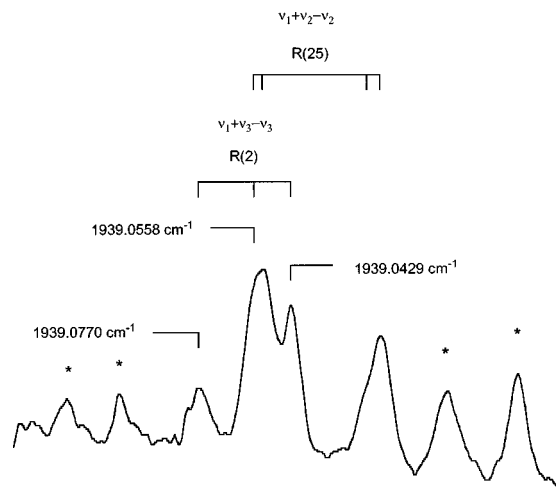

FIG. 3. The observed spectrum of CCO in the region of $R(2)$ of the $\nu_1+\nu_3-\nu_3$ difference band. For the identification of the individual components see Table III. The $R(25)$ transition of the $\nu_1+\nu_2-\nu_2$ band is also identified. The lines labeled by $*$ have not been identified.

The analogous quantities for other three-heavy-atom molecules follow the same trend, i.e. $\alpha_1=85.49$ MHz and $\alpha_3=76.16$ MHz for CCN[23] and $\alpha_1=103.5$ MHz and $\alpha_3=52.6$ MHz for N$_2$O.[24] Thus the values of $\alpha_1=98.91$ MHz for the v_3 vibration and $\alpha_3=65.98$ MHz obtained here provide further evidence in support of the N assignment for the $\nu_1+\nu_3-\nu_3$ band.

Although several low N-value transitions were observed for each of the two bands, the analyses of the data did not permit the determinations of λ_D and γ for the (200), (001), and (101) vibrational states. This indicates that the vibrational dependence of these parameters are too small. These parameters were, therefore, held fixed at their values for (100) vibrational state.[11] Furthermore, only one of the spin–spin parameters for the $\nu_1+\nu_3-\nu_3$ band could be determined. Since a value for λ_{001} is not available, this was held fixed at $\lambda_{100}=11848$ MHz.

The *normal* values of the centrifugal distortion constants observed here are indicative of the fact that none of the vibrational states analyzed here are strongly perturbed and that C$_2$O is a well behaved rigid molecule unlike C$_3$ which shows substantial nonrigidity.

Comparison of the intensities between transitions in the ν_1 band with those in the $2\nu_1-\nu_1$ band shows that the strength of the $2\nu_1-\nu_1$ band is only about two times smaller than that for the ν_1 band. See Fig. 1. The same is true for the relative intensity of $\nu_1+\nu_3-\nu_3$ and ν_1. This implies that a significant fraction of the CCO radicals are created in vibrationally excited states in a hollow cathode discharge. This might also be the case for the C$_n$ clusters, in which case many of the excited vibrational states of these species can be probed.

In summary, the $2\nu_1-\nu_1$ and $\nu_1+\nu_3-\nu_3$ difference bands of the CCO radical have been observed in a hollow-cathode discharge of a flowing C$_3$O$_2$+He mixture by means of a tunable diode laser spectrometer. Rovibrational transitions with N-values up to 34 were assigned and fitted. Analyses of the two bands yielded band centers of 1941.85761(54)

TABLE III. Observed transitions in the $\nu_1 + \nu_3 - \nu_3$ sequence band of CCO (in cm^{-1}).[a]

N''	$P(N'')$	Obs.−Calc.	$R(N'')$	Obs.−Calc.
2			1939.0429	−0.0001
			1939.0558	−0.0001
			1939.0770	−0.0010
3	1934.4803	−0.0006	1939.7847	0.0000
	1934.4803	−0.0006	1939.7970	0.0017
	1934.4474	−0.0005	1939.8003	−0.0011
4	1933.6945	0.0003	1940.5187	0.0000
	1933.6945	0.0003	1940.5291	0.0005
	1933.6778	0.0000	1940.5291	0.0005
5	1932.9029	0.0014		
	1932.9029	0.0014		
	1932.8917	0.0012		
6	1932.1021	−0.0003	1941.9662	0.0005
	1932.1021	−0.0003	1941.9725	−0.0001
	1932.0944	0.0004	1941.9725	−0.0001
8			1943.3872	−0.0002
			1943.3919	−0.0011
9			1944.0859	−0.0011
			1944.0902	−0.0025
10	1928.8377	0.0004		
	1928.8420	−0.0014		
11				
	1928.0114	−0.0005		
12	1927.1687	0.0010	1946.1460	0.0001
	1927.1745	0.0008	1946.1516	−0.0001
13	1926.3230	−0.0001	1946.8188	−0.0001
	1926.3282	−0.0009	1946.8241	−0.0006
14	1925.4732	0.0013	1947.4848	−0.0004
	1925.4792	0.0013	1947.4913	0.0002
15	1924.6150	0.0008	1948.1442	−0.0007
	1924.6207	0.0005	1948.1506	−0.0002
16	1923.7492	−0.0007	1948.7983	0.0004
	1923.7555	−0.0004	1948.8048	0.0010
17			1949.4449	0.0006
			1949.4510	0.0009
18	1922.0032	0.0013	1950.0835	−0.0004
	1922.0095	0.0017	1950.0897	−0.0001
19	1921.1182	0.0002	1950.7166	−0.0003
	1921.1232	−0.0008	1950.7222	−0.0006
20	1920.2266	−0.0019	1951.3437	0.0006
	1920.2317	−0.0020	1951.3491	0.0001
21			1951.9637	0.0010
			1951.9691	0.0005
22			1952.5750	−0.0006
			1952.5812	−0.0003
23			1953.1822	0.0005
			1953.1882	0.0006
24			1953.7816	0.0004
			1953.7877	0.0006
25			1954.3738	−0.0001
			1954.3791	−0.0007
28			1956.1107	−0.0010
			1956.1181	0.0005
33			1958.8738	0.0006
			1958.8803	0.0012
34			1959.4044	−0.0009
			1959.4113	0.0001

[a]For $N'' < 8$, the frequencies for F_1, F_2, and F_3 components are the first, second, and third entries, respectively. Otherwise, only two frequencies are given; the first entry corresponds to the unresolved F_1 and F_3 components and the second entry is for the F_2 component.

cm^{-1} and 1936.79402(56) cm^{-1} for $2\nu_1-\nu_1$ and $\nu_1+\nu_3-\nu_3$, respectively. The results obtained here and those of our earlier work[11] on the (000), (100), (010), and (110) vibrational states provide a more comprehensive set of spectroscopic constants for CCO in the ground electronic state.

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