TIME-RESOLVED INFRARED DIODE LASER SPECTROSCOPY OF THE $Co(CO)_2$ RADICAL

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Rovibrational transitions of the ν_3 band (C-O anti-symmetric stretch) of the $Co(CO)_2$ radical were observed in the frequency region of 1944 - 1964 cm^{-1}. The $Co(CO)_2$ radical was produced by the 248 nm excimer laser photolysis and the transient absorption signal was detected by time-resolved infrared diode laser spectroscopy.

More than 160 absorption lines were assigned to the ν_3 fundamental band. The ν_3 band consists of two series of spectral lines spaced approximately by four times the rotational constant, due to the spin statistics of identical C and O nuclei, and the electronic ground state was confirmed to be $X^2\Delta_g$. Molecular constants including the band origin ν_0, rotational constant, and centrifugal distortion constant were derived from the observed transitions. Hot bands originating from the ν_7 and $2\nu_7$ vibrational excited states, where ν_7 refers to the C-Co-C bending mode, were also observed. Because of the rovibronic interaction, each of the observed lines for the $\nu_3 + \nu_7 \leftarrow \nu_7$ and $\nu_3 + 2\nu_7 \leftarrow 2\nu_7$ hot bands was split into two and three components, respectively.

Ab initio calculation in BP86/6-311+G* level suggests that the $Co(CO)_2$ radical is slightly bent and has the X^2A_1 electronic ground state. The present experiment shows that the $Co(CO)_2$ radical is linear in average, and it may probably be a quasi-linear molecule in which the ground state has energy higher than the top of the potential bump.