Raman-Spectroscopic Observation of the Σ-diads of $^{12}C^{16}O^{18}O$ and $^{12}C^{16}O^{17}O$

K. Srinivasan [1], H. Finsterhölzl, H. W. Klöckner,
D. Illig, and H. W. Schrötter
Sektion Physik der LMU München, Lehrstuhl
J. Brandmüller

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The Fermi resonance doublets of $^{12}C^{16}O^{18}O$ and $^{12}C^{16}O^{17}O$ were identified as weak Q-branches in the Raman spectrum of natural CO_2.

Carbon dioxide and its isotopic variants have been the subject of many experimental (IR and Raman) and theoretical spectroscopic investigations [2, 3]. Surprisingly the Raman spectra of $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$ only have been measured [4] and only the former has been analysed for the vibration-rotational structure [5].

In our program of experimental and theoretical Raman spectroscopic studies [6–8] of gases we have also recorded rovibrational spectra of various isotopic species of CO_2. Our experimental setup has been described previously [6–8]. We also made use of a method for direct scanning of the isotropic part ($\sim 45\,\alpha'^2$) of the scattered light [9] in order to identify the Q-branches which may otherwise get submerged in the rotational wings.

In the isotropic part of the rovibrational spectrum of natural CO_2 in addition to several hitherto unobserved Q-branches of hot bands [10] we identified four lines, the positions of which are given in Table 1, as to be the Σ-diads of $^{12}C^{16}O^{18}O$ and $^{12}C^{16}O^{17}O$. Their intensities are in agreement with the natural abundance of 0.4% $^{12}C^{16}O^{18}O$ and 0.07% $^{12}C^{16}O^{17}O$. The position of the lines was determined relative to the neighbouring rotational lines, the wavenumbers of which were calculated with rovibrational constants given by Dupré-Maquaire and Pinson [3]. Thus an accuracy of $\pm 0.05\ \text{cm}^{-1}$ could be obtained, with exception of the weakest line at $(1376.2 \pm 0.2)\ \text{cm}^{-1}$. One section of the spectrum has been published earlier [9], therefore we restrict ourselves to present in Fig. 1 another section showing the lower wavenumber components of the Σ-diads. The spectrum was obtained by subtracting 4/3 of the $I_\perp$ component, which is proportional to $3\,\gamma'^2$, from the $I_{||}$ component, which is proportional to $45\,\alpha'^2 + 4\,\gamma'^2$, thus resulting in a spectrum showing only the polarized Q-branches. It is interesting to note that both lines of $^{12}C^{16}O^{18}O$ are also discernible in the spectrum photographed by Stoicheff [5], however, one was labelled as a ghost and the other one escaped attention.

Table 1. Observed and calculated wavenumbers of the Σ-diads of $^{12}C^{16}O^{18}O$ and $^{12}C^{16}O^{17}O$.

	exp.	calc.
$^{12}C^{16}O^{18}O$	1259.40 (±0.05)	1259.42
	1365.88 (±0.05)	1365.84
$^{12}C^{16}O^{17}O$	1272.29 (±0.05)	1272.31
	1376.23 (±0.2)	1376.05

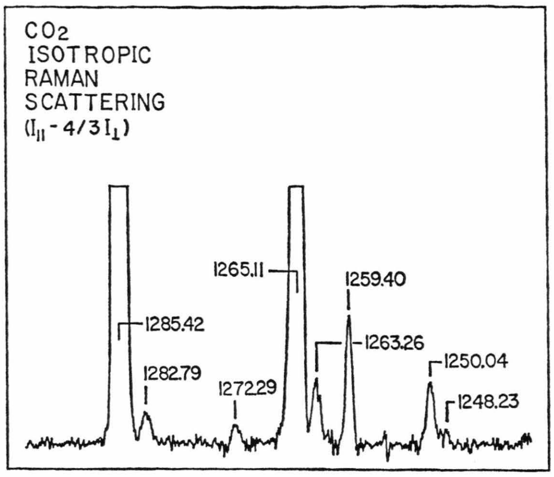

Fig. 1. Section of the purely isotropic part ($I_{||} - 4/3\,I_\perp \sim 45\,\alpha'^2$) of the vibrational-rotational Raman spectrum of natural CO_2. Gas pressure 1 atm., excitation 514.5 nm, 7 W. Slit width 1 cm^{-1}. Wavenumbers in cm^{-1}.

Using the spectroscopic constants given by Jobard and Chedin [11] for $^{12}C^{16}O^{18}O$ and $^{12}C^{16}O^{17}O$ we calculated the Σ-diad wavenumbers [12]. Table 1 shows that they are in excellent agreement with our observation. A comparison with a preliminary scan of enriched $^{12}C^{16}O^{18}O$ lends strong support to our assignments.

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Reprint requests to Dr. H. W. Schrötter, Sektion Physik der LMU, Schellingstr. 4, *D-8000 München 40,* Germany.

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[1] DAAD Post-doctoral fellow 1975–1977. Permanent address: Post-Graduate Physics Department, The American College, Madurai-625002, India.

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[12] Although using Berney and Eggers [13] constants one arrives at almost the same values for $^{12}C^{16}O^{18}O$, we preferred Jobard and Chedin's numbers, because their derivation overcomes earlier inconsistencies pointed out by Amat and Pimbert [14].

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