Cavity ring-down spectroscopy measurements of $l$-type doubling of hot bands in $\Delta$ vibrational states of OCS near 5.2 $\mu$m

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Abstract
We investigated the $l$-type doubling in the $(14^2\Omega) \leftrightarrow (02^2\Omega)$ weak hot band transition of carbonyl sulphide (OCS) for $l = 2$ (i.e. $\Delta$ state) vibrational state. High-resolution spectroscopic measurements of $l$-doublet splittings of OCS were carried out using cavity ring-down spectroscopy (CRDS) technique employing a continuous-wave (cw) external-cavity quantum cascade laser (EC-QCL) operating at $\sim 5.2 \mu$m. The rotationally resolved spectra of $l$-doublet splittings between the parity doublet e and f sub-states of OCS were recorded by probing the rotational lines from $J = 22$ to $J = 29$ in the R branch belonging to the weak hot band transition. Subsequently, we determined the $l$-type doubling constant, transition dipole moment, rotational constant and centrifugal distortion constant for both e and f components of the $(14^2\Omega)$ vibrational state with relatively high rotational states of OCS. As the measurement of $l$-doublet splitting in $l = 2$ or higher states of OCS remains challenging due to extremely small splitting, therefore our findings suggest that the observation of the $l$-type doubling in $\Delta$ vibrational state ($l = 2$) with new values of the several spectroscopic parameters as mentioned above will be useful for better understanding of linear polyatomic molecular properties in general from high-resolution spectroscopic data.

1. Introduction

It is well known that each bending or perpendicular mode of vibration in a non-rotating linear polyatomic molecule is doubly degenerate with exactly same frequency of oscillation. However, molecular rotation introduces a new phenomenon known as $l$-type doubling, $l$ being the quantum number of vibrational angular momentum so that the vibration-rotation interaction induces the splitting of the degenerate energy levels. It is noteworthy to mention that the $l$-type doubling of a linear polyatomic molecule is analogues to the Lambda ($\Lambda$) doubling of a linear diatomic molecule with different origin of splitting in rotational energy levels. Lambda doubling is observed in a diatomic molecule having an unpaired electron in the outermost orbital [e.g. Nitric oxide (NO)] and the coupling between the unpaired electronic motion and the rotational motion of molecule results in a splitting of the individual rotational energy level. In contrast, $l$-type doubling of a linear polyatomic molecule arises from the interaction between bending vibration and rotational motion of the molecule. In brief, the degenerate bending vibration of a rotating linear polyatomic molecule can be either parallel or perpendicular to the direction of angular momentum which eventually causes slightly splitting of two degenerate bending vibrations and this is known as $l$-type doubling. Several decades ago, Herzberg [11] first introduced the concept of $l$-type doubling and suggested that this splitting is caused by a Coriolis-type interaction between one component of a doubly degenerate bending mode and stretching vibrations of the molecule. Subsequently, the existence of $l$-type doubling transitions was theoretically demonstrated by Neilsen and Shaffer [2] and pointed out the importance of this effect for better understanding of linear polyatomic molecular properties from spectroscopic data. In addition, accurate measurements of $l$-type doubling transitions can provide a variety of information about the bending mode of linear molecules with rotational constants, centrifugal distortion constants and
Coriolis interaction. However, the effect of $l$-type doubling is usually significant only in the first excited state i.e. where $v_1 = v_2 = 0$, $v_2 = 1$, $l = \pm 1$ ($v_i$ is vibrational quantum number). For $l = 2$ (i.e. $\Delta$ states) or greater, the $l$-type splittings are extremely small to be measured and usually observed for relatively high rotational states [3, 4].

Carbonyl sulphide (OCS) is a linear triatomic molecule which has three fundamental vibrations $\nu_1, \nu_2,$ and $\nu_3$ located at 858, 520 and 2062 cm$^{-1}$, respectively in which $\nu_1$ and $\nu_3$ are the stretching vibrations and $\nu_2$ is the bending vibration which exhibits the $l$-type doubling. There has been considerable interests over the last several decades to measure the $l$-type doubling transitions in OCS because it is an important molecule of astrophysical interest [5] and also the second most abundant sulphur-containing species in the atmosphere of Venus [6]. The high-resolution spectroscopic detections of individual ro-vibrational transitions of OCS which could be attributed to the weaker hot bands with $l$-type doubling are important for the studies of terrestrial and planetary atmospheres [7]. Moreover, a good understanding of spectral line parameters such as $l$-type doubling constant and transition dipole moments, determined from experimental analysis would help us to analyze the astrophysical observations with absorption bands of minor constituents.

However, early studies were primarily focused on the microwave and infrared measurements of $l$-type doubling transitions in OCS for $l = 1$ vibrational state [8]. For instance, using a Spin–Flip Raman Laser, Buckley et al [9] reported the $l$-type doubling in the hot bands of OCS for $l = 1$ state near 1890 cm$^{-1}$. In another study, the existence of $l$-type doubling in OCS was also recorded using the molecular beam electric resonance spectroscopy in low J states of the ($0^2\Pi$) vibrational state of $^{16}$O$^{12}$C$^{32}$S [3, 10]. In view of the earlier studies [11, 12], however, high-resolution spectroscopic measurements of $l$-type doubling transitions in the weak hot bands for higher values of $l$ i.e. $l = 2$ or $\Delta$ vibrational state are very limited and to our knowledge, it has never been explored before to record the $l$-type splittings involving the parity doublet $e$ and $f$ sub-states arising from weak hot band transitions. But, the recent technological innovations [13, 14] of the mid-IR continuous-wave (cw) external-cavity quantum cascade lasers (EC-QCLs) with extremely narrow linewidth ($\sim 0.0001$ cm$^{-1}$) and mode-hop-free (MHF) tuning capability in a wide range of frequency when combined with highly-sensitive cavity-enhanced absorption techniques such as cavity ring-down spectroscopy (CRDS) [15] opens the possibility of exploiting this high-resolution spectroscopy to measure the $l$-type doubling transitions in weak hot bands for OCS. We note that the observation of such $l$-doublet splittings between $e$ and $f$ sub-levels of OCS in high J states has not previously been reported.

In the present study, we first report the observation of $l$-type doubling in R branch of $^{16}$O$^{12}$C$^{32}$S in ($14^2\Pi$) $\rightarrow$ ($0^2\Pi$) hot band ro-vibronic transitions using an EC-QCL based high-resolution cw-CRDS technique in the region of 1900–1904 cm$^{-1}$. Subsequently, the line strengths of the $e$ and $f$ sub-states for J = 22 to J = 29 rotational lines were measured by probing the respective absorption lines. Finally, the $l$-doublet splittings were utilized to determine the vibrational transition dipole moments, rotational constants, centrifugal distortion constants and $l$-type doubling constant for both $e$ and $f$ components in $\Delta$ vibrational state ($l = 2$) of OCS.

2. Experimental technique

As mentioned above, high-resolution measurements of $l$-doublet splittings of OCS were made using the cw-CRDS method coupled with an EC-QCL operating at $\lambda \approx 5.2$ $\mu$m (1923 cm$^{-1}$). The experimental arrangement of the cw-CRDS system has been described in detail previously [16–19] and therefore only salient features of the spectrometer are given here. In a classical cw-CRDS system, the decay rate of a laser light trapped in a high-finesse optical cavity is measured and the direct absorption of molecular spectral lines is recorded. The number density of a molecular species is calculated in an absolute scale from the knowledge of the molecular absorption cross-section without the need for secondary calibration standards. Additionally, as CRDS measurements are carried out in the time-domain thus it is insensitive to laser intensity fluctuations. The minimum detectable change in the absorption coefficient, $c_{\text{min}}$ is $4.72 \times 10^{-9}$ cm$^{-1}$ and the effective optical path length that is easily achieved is of the order of few kilometres in a small cavity volume. For the described high-resolution CRDS measurements, the probe was an EC-QCL with a fine MHF tuning range of 1847–1865 cm$^{-1}$, an output power of >80 mW over this range and a linewidth of $\sim 0.0001$ cm$^{-1}$. The resulting short-time noise equivalent absorption (NEA) coefficient, which is given by $\sqrt{2} c_{\text{min}} f^{-1/2}$ $a_{\text{osc}}$, where $a_{\text{osc}}$ is the data acquisition rate, was $\sim 7.16 \times 10^{-10}$ cm$^{-1}$ Hz$^{-1/2}$ for $a_{\text{osc}} = 90$ Hz and $c_{\text{min}}$ was determined to be $5 \times 10^{-9}$ cm$^{-1}$ based on the typical empty cavity ring-down time (RDT) of $\tau_0 = 5.64$ $\mu$s and standard deviation ($\sigma$) of 0.08% with averaging of 6 RDT determinations. A cavity length of 50 cm and cavity mirrors with reflectivity of 99.98% at 5.2 $\mu$m were used in the cw-CRDS system, corresponding to finesse (F) of $\sim 15$ 700. Additionally, the linewidth of the EC-QCL ($\Delta\nu(\text{QCL})$) was determined to be $\sim 18$ MHz (0.0006 cm$^{-1}$), matching the manufacturer specified value of 0.0003 cm$^{-1}$ with the EC-QCL. The linewidth of the TEM$_{00}$ cavity modes was also measured to be $\Delta\nu_{\text{Cavity}} = (\text{FSR/F}) = 19$ kHz, where the cavity’s free spectral range (FSR) was 300 MHz. However, the high-
resolution Doppler-limited cw-CRDS spectra involving rotationally resolved \( l \)-type splittings were acquired over the R branch of \((14^0) \leftarrow (02^0)\) hot band transition of OCS by fine tuning over \(\sim0.1\) cm\(^{-1}\) of the piezoelectric transducer (PZT) attached to the tunable diffraction grating of the EC-QCL system. A custom written Labview program was used to scan the laser to acquire the absorption lines of OCS and the wavenumbers were recorded in real-time, utilizing a wavelength meter (Bristol Instruments, 621B) with an accuracy of \(\pm0.001\) cm\(^{-1}\).

3. Results and discussion

The performance of the cw-CRDS system was initially assessed by injecting a certified calibration gas mixture of \(31\pm0.2\) ppm of OCS in \(N_2\) (Air Liquid, UK, 99.999\%) inside the optical cavity with a pressure of 5 Torr. Figure 1 shows an example of high-resolution spectrum of OCS, probing the R(24) rotational line of the \((14^0) \leftarrow (02^0)\) hot band transition at 1900.255 cm\(^{-1}\) with a line-strength of \(\sigma_{\text{line}} = 9.59 \times 10^{-23}\) cm\(^2\) molecule\(^{-1}\) cm\(^{-1}\) at 296 K [20], as given by the HITRAN database [21].

The spectrum was fitted with a Gaussian line-shape profile with FWHM of 0.003 06 cm\(^{-1}\) which corresponds to the expected Doppler broadening at the measured wavelength. The integrated area under the curve was utilized to measure the concentration of the sample inside the cavity and it was measured to be \([X_{\text{OCS}} = (5.1 \pm 0.2) \times 10^{12}\) molecules cm\(^{-2}\). As mentioned later, the same sample inside the cavity was used to determine the vibrational transition dipole moments for \(e\) and \(f\) sub-states of the \((14^0) \leftarrow (02^0)\) ro-vibrational transition for \(l = 2\) state. However, we first focused on the measurement of the \(l\)-type doubling constant of \((14^0)\) vibrational state. To accomplish this, we then probed 8 rotationally resolved \(l\)-type doublet transitions for OCS from \(J = 22\) to \(J = 29\). The examples of the rotationally resolved \(l\)-doublet splittings between \(e\) and \(f\) components of the corresponding rotational lines for \(\Delta\) vibrational state are depicted in figure 2.

It was observed that the splitting between the \(e\) and \(f\) sub-states increases with increasing \(J\) value and subsequently the \(l\)-type doubling constant was calculated. The variation of \((\Delta\nu/2f)\) with \((J + 1)\) is shown in figure 3 and the slope of the straight line provides the \(l\)-type doubling constant [22, 23]. In our present study, the \(l\)-type doubling constant for \((14^0)\) vibrational state was found to be \((2.41\pm0.3) \times 10^{-3}\) cm\(^{-1}\) which is \(\sim10\) times smaller than the value of the \(l\)-type doubling constant for \(l = 1\) state of OCS.

We next investigated the vibrational transition dipole moment and in order to do that, we first estimated the line strengths or line intensities of the individual ro-vibrational transition of the probed absorption lines. The integrated areas under the curves as depicted in figure 2 were then utilized to estimate the line strength of the individual ro-vibrational transition. The individual absolute line intensity, \(S_{fi}\) can be expressed as [20, 24]

\[
S_{fi} = \frac{8\pi^3}{3hc} \frac{T_0}{T} \frac{-\nu N_c S_c S_R \mu_v^2 F \exp\left(-\frac{E^\nu}{k_B T}\right)}{Z_R} \left[1 - \exp\left(-\frac{h\nu}{k_B T}\right)\right] \tag{1}
\]

where \(T\) is the temperature in Kelvins, \(T_0 = 273.15\) K, \(\nu\) is the wavenumber of the line centre at cm\(^{-1}\), \(E^\nu\) is the energy of the lower state and \(k_B\) is Boltzmann constant. For \(\Delta I = 0\), the HönL-London factor, \(S_R\) is given by \(S_R = \frac{m^2 - I^2}{|m|}\), where \(m = J^e + 1\) for R branch, \(\mu_v\) is the vibrational transition dipole moment and \(F\) is the Herman-Wallis factor, \(S_c\) is the vibrational intensity factor for the triatomic molecule; \(Z_c\) and \(Z_R\) are the vibrational and rotational partition functions, respectively. The product of the Herman-Wallis factor \((F)\) and the squared of vibrational transition dipole moment \((\mu_v^2)\) were determined via experimental \(S_{fi}\) values of the recorded spectra of OCS. Equation no (1) can now be re-written as follows:
A plot of right-hand side of equation (2) as a function of \( m \) yields a curve whose intercept at the origin is the transition dipole moment squared and the slope is proportional to the Herman-Wallis constant, \( \alpha \). [Please see the supporting information for details is available online at stacks.iop.org/JPCO/2/045014/mmedia.]
values of $B_v$ and $D_v$ for the lower state i.e. (02$^2\text{O}$) of the recoded transitions are shown in table 1 and the values were taken from the microwave data [5, 10].

In our present calculation, the vibrational partition function, $Z_v$ was found to be 1.1987 at 296 K [20, 24]. Using equations (4) and (5) of the supporting information, we obtained $S_v = 3$ for both e and f sub-states of the (14$^2\text{O}$) $\leftarrow$ (02$^2\text{O}$) hot band transition [24] and consequently, we determined the $S_v$ values for e and f components probing the $J = 22$ to $J = 29$ rotational lines of R branch. The observed line strengths of the probed rotational lines of the measured transitions are shown in table 2. The $S_v$ values shown here are in the order of $10^{-23}$ cm$^2$ mol$^{-1}$ cm$^{-1}$. All the $S_v$ values mentioned in table 2 from the HITRAN database have the uncertainties of $\geqslant 20\%$ [21].

Subsequently, $\mu_v^2F$ values have been evaluated for both e and f sub-states of (14$^2\text{O}$) vibrational state using equation (2). The plots of $\mu_v^2F$ versus m for e and f sub-states are shown in figures 4(a) and (b).

The values of vibrational dipole moments ($\mu_v$) and Herman–Wallis constants ($\alpha$) have been mentioned in table 3 for e and f sub-states of the (14$^2\text{O}$) $\leftarrow$ (02$^2\text{O}$) hot band transition. As expected, the difference between the
is plotted as a function of \( m' = J + 1 \) to measure the vibrational dipole moments for \( e \) and \( f \) sub-states of the \((14^20)\) vibrational state.

In summary, we have employed an EC-QCL based high-resolution cw-CRDS technique for the measurement of \( l \)-type doubling in the \((14^20)\) \(\leftrightarrow\) \((02^20)\) weak hot band transition of OCS for \( l = 2 \) state. We have measured the \( l \)-type doubling constant in R branch of the selected hot band transition for the higher values of \( J \) and subsequently performed with values of the lower energy state were taken from microwave data of OCS and the least square analysis was performed with values for \( e \) and \( f \) sub-states were found to be \( \sim 2-3 \) times smaller than the values of the hot band transitions for the \( l = 1 \) state of OCS [20]. However it is noteworthy to mention here that the observed \( \mu_e \) values are much higher (\( \sim 30 \) times) than the values of the isotopic hydrogen cyanide (H\(^{12}\)C\(^{14}\)N) for the same vibrational transition in \( l = 2 \) state [24].

Additionally, we have made an attempt to measure the rotational constant, centrifugal distortion constant and band centres of \( e \) and \( f \) sub-components of the \((14^20)\) vibrational level in \( l = 2 \) state by the least square analysis method. For that purpose, we have monitored the \( l \)-type doublet transition frequencies of \( e \) and \( f \) components of the probed rotational lines belonging to the \((14^20) \leftrightarrow (02^20)\) hot band transition. Consequently, the transition frequencies were fitted with the following equation no (3) [9]

\[
\nu = \nu_0 + B_{\nu} [J'(J' + 1) - I^2] - D_{\nu} [J'(J' + 1) - I^2] - B_{\nu'} [J''(J'' + 1) - I^2] + D_{\nu'} [J''(J'' + 1) - I^2]
\]

where, \( B_{\nu}, B_{\nu'} \) are the rotational constants at higher and lower energy states; \( D_{\nu}, D_{\nu'} \) are the centrifugal distortion constants at higher and lower energy states, and \( \nu_0 \) is the transition center of the selected hot band.

The values of \( B_{\nu} \) for \( e \) and \( f \) sub-states are 6102.558 MHz and 6102.560 MHz, respectively whereas, the \( D_{\nu} \) values for \( e \) and \( f \) sub-states were found to be 1.54 KHz and 1.35 KHz, respectively [25, 26]. All the \( B_{\nu} \) and \( D_{\nu} \) values of the lower energy state were taken from microwave data of OCS and the least square analysis was performed with \( \nu_0, B_{\nu}, D_{\nu} \) as variables. Table 3 lists the observed and calculated values of transition frequencies of \( J = 22 \) to \( J = 31 \) rotational lines of the \((14^20) \leftrightarrow (02^20)\) hot band transition in R branches of OCS in \( l = 2 \) state.

The \( B_{\nu} \) and \( B_{\nu'} \) values for the \((14^20)\) vibrational state were found to be 6159.9 \(\pm\) 19 MHz and 6091.5 \(\pm\) 17 MHz, respectively which are consistent with and of comparable accuracy to the microwave values of 6150 \(\pm\) 12 MHz and 6099 \(\pm\) 18 MHz [27]. Our centrifugal distortion constants, \( D_{\nu} = 2.6 \pm 0.9 \) kHz and \( D_{\nu'} = 1.8 \pm 0.84 \) kHz, are new values, and can be compared with estimates from the force field of 2.57 KHz and 1.89 KHz [25].

### 4. Conclusions

In summary, we have employed an EC-QCL based high-resolution cw-CRDS technique for the measurement of \( l \)-type doubling in the \((14^20) \leftrightarrow (02^20)\) weak hot band transition of OCS for \( l = 2 \) state. We have measured the \( l \)-type doubling constant in R branch of the selected hot band transition for the higher values of \( J \) and subsequently measured the vibrational dipole moments and Herman-Wallis constant for \( e \) and \( f \) sub-states of the \((14^20)\) vibrational state.

| \( \nu_0 /\) Debye | \( \alpha \) |
|------------------|------------|
| \((14^20) \leftrightarrow (02^20)\) \(e\) | \(2.18 \times 10^{-2}\) | 0.072 |
| \((14^20) \leftrightarrow (02^20)\) \(f\) | \(2.15 \times 10^{-2}\) | 0.074 |
determined several spectroscopic parameters such as vibrational transition dipole moments, rotational constants, centrifugal distortion constants for e and f sub-levels and l-type doubling constant in Δ vibrational state (l = 2) of OCS. As the l-doublet splittings in the weak hot band transition (14^2)0 ← (02^2)0 of OCS for l = 2 state were not recorded before, therefore our new experimental data involving several spectroscopic parameters will be useful for better fundamental understanding of linear triatomic molecular properties and hyperfine structures of their isotopologues.

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