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Resonance-enhanced coherent anti-Stokes Raman scattering in $\text{C}_2$

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Abstract. — We have obtained resonance-enhanced Coherent Anti-Stokes Raman Scattering (CARS) spectra of the $\text{C}_2$ radical formed in a microwave discharge and in an acetylene welding torch. Electronic resonance enhancement was obtained in the Swan system. In order to prepare this work, Swan band emission spectra of $\text{C}_2$ had been recorded and assigned using Fourier-transform spectroscopy; this enabled us to determine the optimal conditions for the CARS spectroscopy and to assign the CARS spectra unambiguously. Numerical simulations were performed, with due account for the effects of upper vibrational state populations and for Doppler broadening; the agreement with experimental spectra is fair. We deduce from the spectra $\text{C}_2$ densities of about $5 \times 10^{11}$ cm$^{-3}$ in the discharge and $10^{13}$ cm$^{-3}$ in the flame. The detection sensitivity is of the order of $10^{10}$ cm$^{-3}$ for our system.

1. Introduction. — Coherent Anti-Stokes Raman Scattering (CARS) is an attractive technique for combustion diagnostics [1-5]. Its detectivity, however, is limited by the existence of a non-vibrationally resonant background of electronic nature which can preclude the detection of trace species, i.e. species with concentrations below 1 % by volume. Hence the interest in using the electronic resonance enhancement of the CARS susceptibility, from which gains of $10^4$ to $10^8$ should follow for the detectivity. Resonance CARS has been studied [6, 7] and then observed, first in liquids, then in gases [8-13]. In gases, resonance-enhanced CARS is extremely difficult to observe. Several factors are responsible for this difficulty [14]. The main difficulty is one-photon saturation which prevents us from applying large power densities to the sample. As a consequence, one is tempted to raise the gas density in order to have a larger susceptibility, hence a larger source polarization and a stronger signal. But a limit is soon reached where the one-photon absorption attenuates the pump beams as well as the signal, yielding distorted lineshapes from which the proper line contours cannot be extracted. If one uses a shorter cell, a background signal is generated in the windows, swamping the weaker lines or distorting them. This last problem may be circumvented by using a cross-beam arrangement [15, 16], which adds somewhat to the experimental complexity.

In addition, resonance CARS spectra in gases are difficult to interpret properly since precise spectroscopic data are unavailable for the many molecules and radicals which are of interest in reactive media or plasmas. This difficulty is aggravated by the need to use two or three monochromatic and stable pulsed lasers which must be tuned precisely. When trying to detect trace species using resonance CARS, the problem is posed in slightly different terms since one is not trying to perform an analysis of spectral properties of molecules, but to generate as large a signal as possible. Furthermore it can be shown that high power lasers tuned at a few linewidths away from the one-photon resonances will actually generate more signal [14]; frequency stability then is less critical.

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These reasons largely explain why so few papers in this field have appeared so far. The only species studied or seen by resonance CARS are I₂ [10, 17, 18], C₂ [12, 19] and NO₂ [11, 13], yet only I₂ spectra had been thoroughly understood. This work gives an account of a C₂ study undertaken to precisely demonstrate the mechanism of electronic enhancement in the Swan system within the framework of the multiple resonance theory [10, 14]. In view of the absence of spectral data of sufficient quality on C₂, we had to first obtain emission spectra of the Swan system using a high resolution Fourier-transform spectrometer [20]. To record the CARS spectra, two low power flash-pumped lasers were used which were tuned into a spectral region so as to satisfy the condition of near-triple resonance. Thanks to that consideration, some strong lines were found. Using the frequency combination which gave maximum signal, we were also able to detect C₂ in an oxyacetylene flame.

2. Spectroscopy of C₂. — For the present work, resonance enhancement was sought from the Swan electronic transition \( a^3Π_u \rightarrow a^3Π_g \), which lies in the visible. In order to precisely interpret the CARS spectral content, the positions of the emission lines had to be known to an accuracy of better than 0.01 cm\(^{-1}\). Since the information is not available from earlier work [21-23], the recording of high resolution spectra by means of Fourier-transform spectroscopy was undertaken in collaboration with CNRS. That study has provided us with accurate C₂ emission frequencies, together with an appropriate set of spectroscopic constants, including those for the \( \Lambda \)-type doubling [24, 25].

One-photon spectroscopy of C₂. — The Swan system is spread all over the visible, with a maximum in the green at 516.5 nm [26, 27]. A stable emission source was developed for this work, based on a microwave discharge in helium mixed with acetylene and traces of O₂.

Several vibrational bands were recorded with the Fourier-transform spectrometer of Aimé-Cotton Laboratory between 420 and 600 nm. Part of the green sequence \(( \Delta v = 0 \) ) is displayed in figure 1 under a spectral resolution of 0.07 cm\(^{-1}\). It shows the characteristic triplet splitting of each line and the staggering of the triplet components caused by the absence of one \( \Lambda \) doublet component resulting from the nuclear spin statistics pertaining to the zero nuclear spin of carbon. An improved set of spectroscopic constants was derived from the positions of these lines and of those seen in the rest of the spectrum; these will be published elsewhere [20].

Resonance-enhanced CARS. — Resonance CARS studies in C₂ are made delicate by numerous difficulties experienced in preparing samples of sufficient concentration or in avoiding saturation of the one-photon and Raman transitions in resonance with the fields. Since the objective is also to find conditions appropriate for optimal detection sensitivity, our analysis was to concentrate on the transitions associated with the lower vibrational states \(( v < 3 \) ) and with rotational quantum numbers containing a sufficient fraction of the total population \(( J < 40 \) ). The discussion will centre first on the main spectral features which are contributed by the lower rovibrational levels \(| a \rangle \). Then some attention will be given to the upper rovibrational levels \(| b \rangle \), which give corrective contributions of great significance.

2.1 Analysis of lower level \(| a \rangle \) contribution. — The rules used in the interpretation of resonance CARS spectra have been discussed some time

Fig. 1. — Emission spectrum of C₂ in a microwave discharge; 0-0 band of the \( a^3Π_u \rightarrow a^3Π_g \) Swan system; instrumental resolution of inset spectrum: 0.07 cm\(^{-1}\).
ago [10, 14, 28]. In the following, we use the notations of these references. We recall that there are in general three types of lines associated with double resonances pertaining to the initial state \(|a\rangle\) of the CARS energy level diagram, as depicted in figure 2. Two of these are found when the pump frequency at \(\omega_1\) is in resonance with a one-photon frequency \(\omega_{\text{ph}}\); the third one being obtained for \(\omega_1 = \omega_{n'\Lambda}\). It is possible to visualize the susceptibility in three dimensions as a function of parameters \(\omega_1 - \omega_2\) and \(\omega_1\); \(\omega_1 - \omega_2\) is the usual variable versus which CARS spectra are displayed, and \(\omega_1\) is the field frequency usually held fixed in resonance CARS. Figure 3 illustrates a typical case: the modulus of the susceptibility contribution from \(\rho_{aa}\) has been calculated assuming \(\omega_{n'n} < \omega_{ba}\) and taking the same value \(\gamma\) for the three damping constants. The relief is composed of three straight "ridges" each of which corresponds to a minimum in one of the susceptibility denominators. The projections of the crests of these ridges are close to straight lines having the following equations:

\[
\begin{align*}
\omega_1 &= \omega_{na} \\
\omega_1 - \omega_2 &= \omega_{ba} \\
\omega_1 &= \omega_{n'a} - (\omega_1 - \omega_2)
\end{align*}
\]

These straight lines are shown in figure 4.

**Fig. 2.** — Energy level diagrams representing the states contributing to resonance-enhanced CARS in a diatomic molecule: (a) \(\omega_{na}\) enhanced fundamental (\(\Delta \nu = 1\)) vibrational transition; (b) double electronic resonance with \(\omega_1 = \omega_{na}\) and \(\omega_2 = \omega_{n'a}\); (c) \(\omega_{n'a}\) enhanced vibrational transition. \(\omega_1, \omega_2, \omega_3\) are the familiar CARS frequencies [14].

**Fig. 3.** — Three-dimensional plot of modulus of susceptibility proportional to \(\rho_{aa}\) es. \(\omega_1 - \omega_2\) and \(\omega_1\). The conditions chosen for the frequencies are similar to those prevailing for the main lines of \(C_2\) studied below; i.e. \(\omega_{n'n} \approx \omega_{ba} - 0.8 \text{ cm}^{-1}, \gamma \approx 0.08 \text{ cm}^{-1}\), no Doppler broadening.

**Fig. 4.** — Straight lines corresponding to the nulls in the denominators of the susceptibility. The intercepts correspond to the double resonances.

Well below electronic resonances \((\omega_1 \ll \omega_{na}\)\), only the "ridge" corresponding to the vibrational resonance given by equation (1b) is seen in the spectra. If \(\omega_1\) is made large enough \((\omega_1 > \omega_{n'a}/2)\), \(\omega_3\) can reach resonance with the lowest level \(|n\rangle\) of the excited electronic state for \(\omega_2 = 0\), so that the anti-Stokes resonance \(\omega_3 = \omega_{n'b}\) appears at the high frequency end of the CARS spectrum (i.e. at \(\omega_1 - \omega_2 = \omega_{n'a}/2\)). As \(\omega_1\) increases, this line is downshifted, eventually crossing the vibrational line when \(\omega_1 = \omega_{n'b}\), where it gives rise to the so-called anti-Stokes-enhanced Raman line. The other two double resonances are found on \(\omega_1 = \omega_{na}\) at:

\[
\omega_1 - \omega_2 = \omega_{ba},
\]

and

\[
\omega_1 - \omega_2 = \omega_{n'a} - \omega_1 = \omega_{n'n}.
\]

Triple resonances, i.e. lines obtained when the three equations (1) are simultaneously fulfilled, are for-
tuous, yet extremely interesting for the potential gain in detection sensitivity they afford. The three peaks of figure 3 then merge into a single and stronger maximum. Triple resonances are highly improbable in light molecules or molecules like OH or hydrogen halides which have considerable line spacing. They are more likely to be found, however, in heavier species like I$_2$. A molecule of intermediate characteristics like C$_2$ fortunately offers a limited number of near-triple resonances. The condition for a triple resonance to exist is easily seen to be:

$$\omega_{n'a} = \omega_{ba}$$  \hspace{1cm} (2)

for the situation where excitation is done using two pump frequencies $\omega_1$ and $\omega_2$. Note that the use of three separately tunable sources would enable one to achieve triple resonance conditions without restrictions on any available molecular transition; these possibilities as well as other aspects of resonance CARS spectroscopy are developed in [14]. Equation (2) can be expanded as a function of the vibrational, rotational and spin quantum numbers $\nu$, $J$ and $\Omega$ respectively. For the specific case of a fundamental vibrational transition we have $\Delta \nu = 1$; in addition, the one-photon selection rules $\Delta J = \pm 1$ and $\Delta \Omega = 0$ must be respected [24]. The systematic search for near-triple resonances using equation (2) then gives the lines:

$$[Q,(1-0), R,(0-0), P,(1-0)] J$$

and

$$[S,(1-0), R,(0-0), R,(1-0)] J,$$

which are found in the spectrum at the positions:

$$\omega_1 - \omega_2 \approx 1611 \text{ cm}^{-1}$$

and

$$\omega_1 - \omega_2 \approx 1743 \text{ cm}^{-1},$$

respectively for three sets of quantum numbers and term indices $i$:

$$J = 18, \Omega = 0, \ i = 3,$$

$$J = 19, \Omega = 1, \ i = 2,$$

$$J = 20, \Omega = 2, \ i = 1.$$  
2.2 Analysis of upper rovibrational level $| b \rangle$ contributions. — The preceding discussion has been devoted to spectral contributions from the ground vibrational level population $\rho_{aa}$. We cannot, however, disregard the contributions of upper rovibrational level $| b \rangle$, since we are dealing with discharges and flames wherein high degrees of vibrational and electronic excitation will prevail. Furthermore, some of these contributions are known to be Doppler-free [29], which is likely to enhance their strengths relative to the ground state ones. Some attention was thus paid to the main three terms contributed by $| b \rangle$.

Several general remarks here have to be made with regard to their actual existence and to their spectral properties when Doppler broadening is negligible. As a matter of fact, the reality of those terms which contain resonances pertaining to unpopulated molecular states has been the object of a controversy [14, 30, 31]. Some terms of similar nature have been experimentally shown to exist in other forms of four-wave mixing by Bloembergen and coworkers using Na vapour [32-34]; the physical interpretation of the terms studied by these authors has also attracted attention recently [35].

The time-ordered diagrams for the $\rho_{ba}$ contributions in CARS are shown in figure 5 along with their resonance denominators, giving the full expression:

\begin{align}
\chi_b = \frac{N}{h^3} \rho_{bb} \mu_{ba} \mu_{ba} \mu_{ba} \mu_{ba} (\omega_{ba} + \omega_2 - i \gamma_{ba})^{-1} (\omega_{ba} - \omega_1 + \omega_2 - i \gamma_{ba})^{-1} \times \\
\times (\omega_{n'a} - \omega_3 - i \gamma_{n'a})^{-1} + (\omega_{n'b} - \omega_1 - i \gamma_{n'b})^{-1} (\omega_{n'a} - \omega_1 + \omega_2 - i \gamma_{n'a})^{-1} \\
\times (\omega_{n'a} - \omega_3 - i \gamma_{n'a})^{-1} + (\omega_{ba} + \omega_2 - i \gamma_{ba})^{-1} (\omega_{n'a} - \omega_1 + \omega_2 - i \gamma_{n'a})^{-1} (\omega_{n'a} - \omega_3 - i \gamma_{n'a})^{-1}. \hspace{1cm} (3)
\end{align}

Under certain conditions on damping, it can be shown (Ref. [14], Appendix 1) that these terms combine to give a single susceptibility term of the form:

$$\chi_b \propto \rho_{bb} [(\omega_{ba} + \omega_2 - i \gamma_{ba}) (\omega_{ba} - \omega_1 + \omega_2 - i \gamma_{ba}) (\omega_{n'b} - \omega_1 - i \gamma_{n'b})]^{-1}.$$

Fig. 5. — Diagrammatic representation of the major susceptibility contributions proportional to $\rho_{bb}$, and associated energy denominators.
Fig. 6. — Plots of modulus of susceptibility for three $\rho_{ab}$ contributions under same conditions as figure 3 and assuming the same value for $\rho_{ba}$ as for $\rho_{ab}$. Cases (a), (b), (c) correspond to figures 5a, b, c, respectively. The loci of the minima in the energy denominators are also shown in the projections. Those double-resonance lines which are Doppler-free are so marked (D.F.). The vertical scale is the same as in figure 3.
Several damping conditions can lead to this expression:

(i) if there are no collisions, with lifetime-broadened states;
(ii) if there are collisions and if the so-called damping approximation

\[ \gamma_{n'a} - \gamma_{n'b} - \gamma_{bn} = \gamma_{nm' - \gamma_{n'b} - \gamma_{bn} = 0} \]

is satisfied.

The expression given by equation (4) can also be derived using a simpler wavefunction (instead of density operator) representation of the molecular system. The wavefunction approach is not appropriate at resonance since the damping approximation is often invalid. Well below electronic resonance, however, the exact expression with the three terms of equation (3) and the approximate expression of equation (4) give the same result. This is because the last two terms (Figs. 5b and 5c) almost exactly cancel and because the main term of figure 5a tends to the expression of equation (4). At resonance, the terms of figures 5b and 5c (second and third term of Eq. (3)) are as important as that of figure 5a (first term of Eq. (3)). In our calculations, the exact equation (3) was always used.

The spectral contours and straight lines corresponding to the nulls in the denominators are shown in figure 6. The plots are presented under conditions similar to those of figure 3. Figure 6a is associated with figure 5a. Note that, in the limit of Doppler broadening, two of the lines are Doppler-free [29]; these lines are marked on the projection. None of the lines in figure 6b (corresponding to the figure 5b term) are Doppler-free, but there are also two in figure 6c. There are two lines (one in Fig. 6a, one in Fig. 6c) which are a factor of 2 stronger than all other lines because the resonances are so placed that the real parts of the denominators not at resonance are only half as large.

In figure 7, one can see the effect of adding the two terms having the \( \omega_{n'a} \) resonance: the \( \omega_{n'n} \) resonance is seen to rapidly decay when \( \omega_1 \) is tuned below \( \omega_{n'b} \) as noted earlier; this fact is consistent with the absence of upper electronic state vibrational resonances in conventional off resonance CARS spectra; the two Doppler-free lines of figure 6c interfere constructively with the two lines having \( \omega_1 = \omega_{n'b} \) in figure 6b, while the third lines of these figures, which are found for \( \omega_1 = \omega_{n'a} \), undergo near complete cancellation. Adding the contribution of figure 6a (term of Fig. 5a) further complicates the contours (Fig. 8).

The \( \rho_{bb} \) contributions naturally interfere with that of \( \rho_{aa} \). The corrections they introduce become appreciable (> 10%) when the vibrational temperature exceeds 1000 K in C\(_2\). In addition, the Doppler effect, if any, will reduce predominantly the amplitudes of the lines of electronic character (except those in \( \rho_{bb} \) which are Doppler-free).

A computer program was written in order to fit the experimental spectra. This program calculates the four major susceptibility contributions, one from \( \rho_{aa} \) and three from \( \rho_{bb} \) with due account for the Doppler effect. In the spectral window from 1611 to 1616 cm\(^{-1}\) which has been studied in detail, 24 values of \( J \) are taken into consideration, 3 of which (\( J = 18, 19 \) and 20 as explained in section 2.1 above) have major contributions. For each value of \( J \), only one set of states \( |a\rangle, |b\rangle, |n\rangle, |n'\rangle \) actually is close enough to the situation of very strong double or near triple-resonance and is accounted for. No convolution is done with the laser linewidth function; the width of the latter is comparable to or smaller than that of the CARS lines.

3. Instrumental details. — The CARS spectrometer is the one used for the work on \( I_2 \) [10, 14], with some minor modifications. This is a system with flash-pumped lasers giving a pulse duration of 500 ns. The entire optical set-up is mounted on a cast aluminium table of \( 0.5 \times 1.5 \) m. The elements of the two laser cavities are fixed on a ceramic glass slab of 80 cm length, which is sunk into this table, and insures proper mechanical and thermal stability. The two dye cells are attached to the glass bench and are enclosed in the same flashlamp head, so that synchronous pulses are emitted. Four water-cooled ablation flashlamps connected in parallel are used for the pumping, with a
discharge energy of 200-350 J, typically. The capacitor has a capacitance of 4.5 μF. The flashlamps are made of pure, fused silica, with 4.5 mm i.d. and 7.5 mm o.d. They are mounted so as to couple the largest possible fraction of the output into the dye cells. The latter have a small bore (3.5 mm) and a large o.d. (8 mm) to increase the apparent diameters of the dye flows (Fig. 9). Segments of tungsten wire of 25 mm length, wound in coils over a 3.5 mm diameter cylinder, were introduced in these dye cells at regular intervals leaving a useful aperture of 2.9 mm diameter. They reduce amplified spontaneous emission very effectively. The active length of the flashlamps and dye cells is 15 cm. A saturated copper sulfate water solution is circulated in the flashlamps for cooling; this solution is introduced at the same temperature as the dye solution. If the temperature difference exceeds 0.1 °C, the resulting density gradients in the dye solution keep the lasers from emitting in a single transverse mode and raise their thresholds. The temperature condition is fulfilled by maintaining the dye reservoirs in a temperature-controlled bath. The coolants, as well as both dye flows after passing through their pumps and Millipore filters, are passed through heat exchangers also placed in the bath. The copper sulfate serves two functions: by cutting short wavelength UV beyond 300 nm, it improves the dye service life; by cutting the red and IR beyond 700 nm, it also reduces thermal shocks in the dye flows and improves beam quality and reproducibility.

The lasers are fired at a rate of 6 shots per minute. Triggering initially was performed with an ignitron. A grounded-grid hydrogen thyratron was later introduced, giving a slightly shorter discharge pulse of 1.5 μs. Finally, a prepulse circuit was added, which resulted in a 10% reduction in energy necessary for lasing. The flashlamps are filled with 20 mbar of argon; the gas is flown and evacuated from both ends using a primary pump. Argon slightly improves lasing. If the pressure is brought below 2 mbar, flashtube failures quickly occur, because the discharge energy does not split evenly between them. The flashtube life is about $10^4$ shots; it is limited by a slow wall erosion which eventually leads to mechanical failure. The tungsten electrodes are mounted 4 mm away from the lamp axes and 3 mm away from the tube ends. This precaution taken in conjunction with argon gas flowing considerably reduces pollution by sputtering.

Two different techniques are used for tuning (Fig. 10). The « laser » at $\omega_1$ is limited in bandwidth and tuned by means of an interference filter and solid 0.1 mm and 1 mm thick silica etalons of 85%, reflectivity, whereas the « Stokes » beam at $\omega_2$ is tuned by a set of four prism expanders and one grating of 1 200 g/mm in Littrow mount blazed at 1 μm and tilted to second order. The grating rotation is entrained using a carbon fiber composite arm of 310 mm length and a differential screw. The tuning precision is 0.04 cm$^{-1}$.

Both oscillators produce beams 2 mm in diameter, with divergence less than 1.5 times the diffraction limit and peak power of 1-10 kW between 480 and 650 nm. The linewidth is typically 0.02 cm$^{-1}$ at $\omega_1$ and 0.07 cm$^{-1}$ at $\omega_2$. Both beams are horizontally polarized. Powers up to 100 kW can be generated with these lasers at some cost in spectral purity and divergence. The pulse duration is about 0.5 μs. In order to obtain these performances, it is necessary to use mixtures of ethanol and water by equal volumes as the dye solvent. COT is added as a triplet quencher and 1 mole % Triton X100 to prevent dimer formation.

Several dyes were tried in order to cover the required spectral ranges with good efficiency. Satisfactory results were obtained by mixing different dyes, one of which acted as a fluorescent wavelength shifter which increased the energy available to pump the lasing dye. Output energies in the range of 1 to 5 mJ are emitted at $\omega_1 = 19 494$ cm$^{-1}$ with a mixture of Coumarin 504 and Coumarin 450; Rhodamine 110 with LD 490 or Coumarin 480 gave comparable energies at $\omega_2$ in the vicinity of 17 880 cm$^{-1}$. Note that similar transfers have been reported for laser-pumped dyes by Cox and Matise [36].

![Fig. 9. Cross section of flashlamp head.](image-url)
The laser beams are combined by means of a dichroic mirror mounted on a stable support with 20 μrad. alignment sensitivity. In spite of the tungsten wire diaphragms, a copious amount of incoherent fluorescence is emitted on the anti-Stokes side by the laser dyes. This emission is suppressed by inserting 6 mm of GG 495 Schott glass at Brewster’s angle and a diaphragm on the common beam path (i.e. after their combination on the dichroic mirror). The beams are first focused into a reference cell filled with 50 bars of argon, then recollimated again. The anti-Stokes from that cell is split off by means of a dichroic flat and sent to a double monochromator for spectral filtering and detection. The pump is filtered again with a Schott GG 495 plate and is focused into the sample cell with a 30 cm focal length lens. This loose focusing minimizes one-photon saturation, which takes place at power densities as low as about $10^4$ W/cm$^2$ in the (0-0) band of C$_2$ (where the transition moment is close to 4 Debye). When recording the spectra, calibrated neutral density filters are used to attenuate the pump beams if the signal intensity exceeds $10^9$ photoelectrons per shot in order to avoid photomultiplier saturation. This procedure offers the advantage of avoiding or appreciably reducing one-photon and vibrational saturation so that the strong lines are properly rendered in their peak amplitudes, but it has the drawback of « crushing » the weaker features (laser-enhanced and double-electronic) if $\omega_1$ is in very close resonance with their $\omega_2$.

The anti-Stokes signals generated in the sample and in the reference are filtered using dichroics to reflect off the lasers followed by double monochromators with concave holographic gratings. The light transmitted by the latter is detected by photomultipliers employing 1 mm dia. optical fibers of 8 m length. This allows us to enclose the photomultipliers in a shielded box to reduce the impact of RF noise emitted by the laser discharge.

The spectra are run by tuning $\omega_1$ to the desired position, then scanning $\omega_2$. For each laser shot, the signal and reference anti-Stokes powers collected are ratioed and the square root of the ratio is taken; the results of 6 such consecutive measurements are averaged for each spectral element. Calibration of the tuning elements is done beforehand in two steps. A Jobin-Yvon monochromator of 0.6 nm/mm dispersion is first calibrated using argon-ion laser lines and the lines of a mercury lamp at 546.07, 576.96 and 579.07 nm. This allows a coarse calibration of the lasers to be performed by passing their beams through the monochromator. A finer calibration is done subsequently. A small fraction (5 %) of the $\omega_1$ laser beam is passed through an I$_2$ fluorescence cell and an excitation spectrum is recorded by scanning a few wavenumbers about the selected position; identification of the I$_2$ lines is done by comparing the spectrum with the Atlas of Gerstenkorn and Luc [37, 38]. This procedure allows the $\omega_1$ laser to be tuned with a precision of ± 0.05 cm$^{-1}$. It is only applicable to that laser because its linewidth is under 0.05 cm$^{-1}$. The fluorescence cell is filled with pure I$_2$ at room temperature with a pressure of 0.8 mbar; all the fluorescence is collected using a photomultiplier; the radiation is filtered by a coloured filter which absorbs light near the laser wavelength or shorter. As an example, figure 11 presents an excitation spectrum recorded around 19 495 cm$^{-1}$ together with the corresponding portion of the absorption spectrum of reference [37]. This scan was used to tune $\omega_1$ on the $R_2$ (0-0) 19 emission line of C$_2$ at 19 494.18 cm$^{-1}$. The I$_2$ excitation technique is not as readily applicable to the $\omega_2$ calibration since the latter source is broader (0.07 cm$^{-1}$) which complicates line identification. Instead, non-resonant CARS spectra of species with known vibration frequencies like CO$_2$ ($v_1$ at 1 388.2 cm$^{-1}$), O$_2$(Q(3) at 1 556.2 cm$^{-1}$), C$_2$H$_4$ ($v_2$ at 1 622.6 cm$^{-1}$) are scanned for a known value of $\omega_1$.

4. Results. — Two C$_2$ sources were investigated, namely a microwave discharge and a flame. The most intense spectra were obtained from the discharge and numerous studies were conducted using that source.

4.1 Discharge investigations. — A microwave generator of 2.45 GHz and 200 W was used for the excitation. The gas mixture was flown through a quartz glass tube of 8 mm i.d. placed in a resonant cavity coupled to the generator. Experimentally, the discharge was first ignited in pure He. The acetylene flow was then admitted and adjusted such that a bright green glow was emitted from the waveguide. The length of the active zone was about 20 mm. Trace amounts of oxygen

![Fig. 11. — Excitation spectrum of I$_2$ obtained by scanning \(\omega_1\) near 19 495 cm$^{-1}$ and absorption Fourier-transform spectrum of the same spectral region [37].](image-url)
were then added in order to prevent formation of solid carbon deposits on the tube walls, a partial pressure of about 0.5 mbar being adequate to keep the tube clean without disturbing the C\textsubscript{2} generation. However, a rapid quenching of the Swan emission is seen if the O\textsubscript{2} flow rate is increased. The total pressure was about 40 mbar with 3 \% acetylene.

Two experimental spectra are shown in figure 12 and figure 13, along with computer simulations, for two distinct values of \( \omega_{1} \) (19 493.80 cm\(^{-1}\) and 19 493.86 cm\(^{-1}\) respectively) and for the same discharge conditions. Note how a minute change in \( \omega_{1} \) drastically affects the spectral contours. The computer-generated profiles are obtained under the following assumptions:

(i) \( \gamma_{aa} = \gamma_{a'a} = \gamma_{ba} = 0.08 \text{ cm}^{-1} \); this value is used as a reasonable estimate since no reliable collisional linewidth measurement has been published so far in C\textsubscript{2} ;

(ii) the temperature (translational, rotational and vibrational) is taken to be 1000 K, from which both Doppler broadening (\( = 0.09 \text{ cm}^{-1} \)) full width at half maximum for the one-photon lines and 0.01 cm\(^{-1}\) for the Raman ones) and \( \rho_{ob}/\rho_{aa} = 0.1 \) naturally follow; the temperature is estimated with a fair degree of confidence from the rotational population distribution seen in the Fourier-transform spectra recorded under the same discharge conditions [20]. The latter spectra actually give somewhat higher vibrational temperatures (\( > 2000 \text{ K} \)) because of the strong non-equilibrium conditions created in the d \( ^{3}\Pi_{g} \) state by

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**Fig. 12.** — Resonance CARS spectrum of C\textsubscript{2} in a microwave discharge with computer simulation (see text for details). The positions of the various single resonances are marked in the theoretical plot with bars of unequal length to distinguish the \( J = 18, 19 \) and 20 contributions.

**Fig. 13.** — Same as figure 12 with a different value of \( \omega_{1} \). The theoretical spectra have the same scale and similarly for the experimental ones. The amplitude of the experimental spectrum is markedly weaker than that of the figure 12 spectrum. This is because the spectra were recorded on different days and results from the impossibility of adjusting the acetylene flow to the same level in independent runs. Tests conducted during the same run show that the peak amplitudes of the spectra behave according to the computer code predictions when \( \omega_{1} \) is varied.
the discharge, but it is reasonable to assume that the a \( ^2 \Pi_u \) state is close to a Boltzmann equilibrium. These assumptions are vindicated by the computer fits, for which the \( \rho_{bb}/\rho_{aa} \) ratio of 0.1 gives the best agreement;

(iii) we assume the CARS rotational line strength factor \( S(J) \) [28, 39] to be constant as a rough approximation, and the Franck-Condon factors to be the same for all transition moments since all the lines seen belong to one vibrational band.

The strongest feature of the spectra of figure 12 is the laser-enhanced Raman resonance contributed by the \( N = 19 \) triplet. The three triplet components \((Q_2(20), Q_2(19), Q_2(18))\) are almost superposed \( (\omega_{aa} = 1\,611.698; 1\,611.716; 1\,611.738 \, \text{cm}^{-1} \text{ respectively})\). The weaker line at the left in figure 12 is a double electronic line proportional to \( \rho_{aa} \) for \( J = 18 \); it also receives significant contributions from the upper vibrational state \((\text{Stokes-enhanced Raman in } \omega_{aa} \text{ and } \omega_{bb} \text{ proportional to } \rho_{aa} \text{ of } J = 20)\). In addition, two other weak Raman \( \rho_{bb} \) contributions in \( \omega_{aa} \) fill in the gap between the weaker line and the main one. The small shoulder on the left of the main line is the double electronic line in \( \rho_{aa} \) for \( J = 19 \). The smaller lines on the high frequency side are weakly laser-enhanced Raman lines contributed by eight consecutive triplets in \( N \), one of which is stronger (on the far right). The latter is composed of the triplet of anti-Stokes-enhanced Raman lines in \( \rho_{aa} \) with the form:

\[
[Q_1(1-0), r_1(0-0), P_1(1-0)] \, J
\]

with \((i = 3, J = 8), (i = 2, J = 9)\) and \((i = 1, J = 10)\), respectively. For such lines, the detuning between \( \omega_{aa} \) and the \( \omega_{bb} \) transitions \((19, 424.09 \, \text{cm}^{-1})\) is about 70 cm\(^{-1}\), but \( \omega_{aa} \) is in resonance with \( \omega_{bb} \). This is verified readily in figure 1, where \( \omega_{aa} \) is seen to lie in the head of the \((1-1)\) vibrational band close to the triplet \( P_6(10), P_6(9), P_6(8) \) at 19, 494.17, 19. 493.77 and 19. 493.19 cm\(^{-1}\) respectively. The spectral positions of the 3 CARS lines are respectively given by

\[
\omega_{ba} = 1\,616.518; 1\,616.548; 1\,616.562 \, \text{cm}^{-1}.
\]

The same general features are found in figure 13, with some minor differences which result from the double-electronic lines being shifted. The line on the left loses strength as its double-electronic component in \( \rho_{aa} \) is downshifted and the \( \omega_{bb} \) double resonance in \( \rho_{bb} \) is destroyed.

Some discrepancies can be seen between experimental and theoretical spectra. These discrepancies have several major causes:

- measurement error (CARS intensity measurement, detector noise of a few photo-electrons per shot, laser frequency calibration and jitter);
- saturation is present, although we reduce it as much as possible by attenuating the pump beams whenever the signal is strong enough to allow it; both one-photon and vibrational saturations reduce the amplitudes of some of the weaker lines for which \( \omega_{aa} \) is in close resonance with \( \omega_{bb} \); however, those weaker lines for which \( \omega_{aa} \) is several linewidths away from \( \omega_{bb} \) experience very little saturation; the latter fact may explain why the small triplets on the right of figure 13 are stronger in the experimental spectra than on the calculated ones;
- presence of a certain level of fluorescence noise which introduces in the spectra a flat background with an amplitude of about 1 in our vertical scale. This anti-Stokes fluorescence is generated by the \( \omega_{aa} \) beam only and depends on the value of \( \omega_{aa} \). In order to reduce it, careful aperturing of the CARS signal beam had to be done using 2 mm dia. diaphragms;
- the assumption of constant line strength factors is inaccurate and may cause errors of up to 20% ;
- uncertainty in the one-photon and Raman frequencies used.

The spectral contours calculated appear as extremely sensitive to the choice of \( \omega_{aa} \) and material frequencies entered in the calculations. For this reason, the value of \( \omega_{aa} \) taken in the computer simulations is always treated as an adjustable parameter. This parameter is allowed to vary within our current experimental uncertainty limits of ± 0.05 cm\(^{-1}\) with respect to the value selected for recording the spectrum.

Finally, it is possible to calculate a rough estimate of the \( C_2 \) density in the discharge. This calculation is based on our past results on \( I_2 \) obtained under similar pressure conditions, where a calibration was possible since the number density was precisely known [10, 14, 17]. For this, we use the following expression for the main susceptibility term:

\[
| x | \ll N \rho_{aa} \left| R_e \right|^4 S(J) \frac{\left< v_a \left| v_a \right> \left< v_a \right| v_a \right>}{\left< v_a \left| v_{aa} \right> \left< v_a \left| v_{aa} \right> \right> f(D)}
\]

where \( R_e \) is the electronic transition moment (which depends slightly on vibrational quantum \( v \) in \( C_2 \) [26]), \( \langle v_a | v_{aa} \rangle \) is the Franck-Condon factor of the transition between states \( a \) and \( n \), \( S(J) \) is the CARS rotational line strength factor [28, 39], and \( f(D) \) is the frequency-dependent part of the susceptibility.

For the temperatures at which the spectra were obtained \((318 \, \text{K} \text{ and } 2 \, \text{mbar} \text{ for } I_2 \text{ (see Fig. 51 of Ref. [14]) and } 1 \,000 \, \text{K} \text{ for } C_2)\), we easily calculate \( \rho_{aa} = 2.5 \times 10^{-3} \) for \( J = 67 \) and \( v = 1 \) in the X state of \( I_2 \) and \( \rho_{aa} = 3.4 \times 10^{-3} \) for \( J = 19 \) and \( v = 0 \) in the a \( ^3 \Pi_u \) state of \( C_2 \); note that this calculation assumes a Boltzmann equilibrium and that the \( v = 0 \), \( J = 0 \) level of the a \( ^3 \Pi_u \) state of \( C_2 \) is 1 536 cm\(^{-1}\) above the \( v = 0 \), \( J = 0 \) level of ground electronic state X \( ^3 \Sigma_g^+ \) [40]. The ratio of electronic-vibrational transition moments of \( I_2 \) and \( C_2 \) is \( 5 \times 10^{-6} \) [26, 41, 42]. The ratio of rotational line strength factors is calculated following reference [39], giving a value of 3.4 for the lines reported. Assuming all instrumental parameters to be equal, we thus arrive at a number density of \( 5 \times 10^{11} \, \text{cm}^{-3} \) for the \( C_2 \) in the discharge.
The detection sensitivity is about $10^{10}$ cm$^{-3}$ given our noise level and experimental conditions. Using higher power lasers, a detection sensitivity of $10^8$ cm$^{-3}$ should easily be demonstrated.

4.2 Flame. — An acetylene welding torch with 1 mm i.d. was used. The acetylene and oxygen flows (0.7 and 0.3 l/min. respectively) were adjusted so as to have a flame with a cone height of 2 mm, from which a very strong C$_2$ Swan band radiation is emitted. The flame was held vertical. The laser beams were focused horizontally at various heights above the burner outlet. The spectrum of figure 14 was obtained at a height of 0.3 mm and for $\omega_1 = 19\ 494.08$ cm$^{-1}$, for which large CARS signal intensities are expected based on the discharge results. The peak intensity of the C$_2$ spectrum in the flame. The collisional width (half width at half maximum) is taken as $\gamma = 0.25$ cm$^{-1}$ for all lines in the simulation.

Because of the larger linewidths, the structure of the spectrum is less evident than in the discharge. However, the computer fit, which is given for a temperature of 2 500 K, should be considered as satisfactory. Note that the $\rho_{bb}$ contributions are much larger in this spectrum because of the high temperatures. Saturation was not observed. Following a calculation similar to that for the discharge, we estimate that the C$_2$ density is of the order of $10^{13}$ cm$^{-3}$.

5. Conclusion. — A detailed analysis of resonance-enhanced CARS in C$_2$ has been carried out. Spectra of C$_2$ in a microwave discharge and in a flame were obtained, assigned and fitted. This effort has necessitated a long preparation with the recording of Fourier-transform emission spectra and with the writing of an elaborate computer program which allows for the effect of Doppler broadening. This work opens the field of trace species detection in reactive media, which was the goal originally assigned to resonance CARS. It has also confirmed the major role played by saturation in preventing us from obtaining the ultimate detection sensitivity. Optimum detection sensitivities will be obtained with three separately tunable lasers of high peak powers either used unfocused in a folded BOXCARS beam configuration or normally focused but with $\omega_1$ detuned slightly from the $\omega_{aa}$ transition from which enhancement is sought. A detection sensitivity of $10^{10}$ cm$^{-3}$ has been obtained for the C$_2$ radical using a CARS spectrometer which is far from offering those optimal conditions. With an optimized system, a gain of at least $10^2$ should be obtained. With such detectivities, most flame and discharge radicals will then become tractable, and significant progress in the understanding of flame chemistry may now be expected from these developments.

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References

[38] LUC, P., J. Mol. Spectrosc. 80 (1980) 41.
[42] YEE, K. K., Private communication to C. Bordé.