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Time resolved high frequency spectrum of Br₂ molecules using pulsed photoacoustic technique



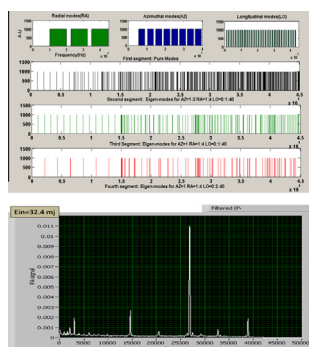
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HIGHLIGHTS

- A new time resolved PA spectroscopy of Br₂ molecules using a nanosecond pulses.
- To understand the coupling mechanism of optical energy into the acoustic energy.
- Clustering of acoustic frequencies in Br₂ molecules for the first time.
- Decay behavior of Br₂ molecules with respect to time.

GRAPHICAL ABSTRACT



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ABSTRACT

The paper reports the time resolved spectral distribution of higher order acoustic modes generated in Br₂ molecules using pulsed Photoacoustic (PA) technique. New time resolved vibrational spectrum of Br₂ molecules are recorded using a single 532 nm, pulses of 7 ns duration at 10 Hz repetition rate obtained from Q-switched Nd:YAG laser. Frank-Condon principle based assignments confirms the presence of 12 numbers of (v''-v') vibrational transitions covered by a single 532 + 2 nm pulse profile. Inclusions of higher order zeroth modes in Bassel's function expansion series shows the probability of overlapping of different types of acoustic modes in the designed PA cells. These modes appear in the form of clusters which occupies higher frequency range. The study of decay behavior of PA signal with respect to time confirms the photolysis of Br₂ at 532 nm wavelength. In addition, the shifting and clustering effect of cavity eigen modes in Br₂ molecules have been studied between 1 and 10 ms time scale. The estimated Q-factor of PA cell (l = 16 cm, R = 1.4 cm) is 145 ± 4 at 27 kHz frequency.

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Introduction

Bromine and iodine are very short lived halogen (VSL) produced by oceanic sources. They play very important role in gas phase photochemistry and heterogeneous reaction as aerosol. Bromine and iodine derivatives change the oxidation capacity of the troposphere and responsible for the depletion of Ozone layer. The long life time of Bromine compounds can also be transported to stratosphere.

Additionally, the use of Bromine in industry as a fire retardant, in water sanitation, insecticides, and an ant knocking agent for leaded gasoline is also another source of air pollution [1–8].

The photo acoustic effect was first reported by A. Bell (1880), [9]. Subsequently, this technique was modified by Tyndall and Rontgen to study this new phenomenon for atmospheric pollutants [10,11]. In Photoacoustic (PA) technique, the molecular samples absorb the photons which results in the excitation of molecular energy level, the excited state released its energy either by radiative process or by non-radiative process (collisional relaxation). As the radiative lifetime of vibrational level are longer than the time required for collisional deactivation. Therefore, the absorbed

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energy is completely released in the form of heat [12–22]. However, due to advancement of laser technology along with significant progress in the designing and sensitivity of microphones and data acquisition system the present form of photoacoustic spectroscopy becomes one of the most efficient and versatile tool to study the non-radiative relaxation transition in solid, liquid and gas samples [23–32].

The expansion of Bessel's function series in terms of higher order zeroth modes for a closed cylindrical cavity shows the formation of excited modes clusters in the higher frequency range. Therefore, judiciously designed acoustic cavity help us to amplify even some of the weakest modes. In addition, it also provides an ideal means for the coupling of the optical energy and elastic energy in the specially designed acoustic cavity which demonstrate the enhanced Raman scattering frequencies in Br₂ vapor.

The detailed absorption spectrum of Br₂ molecules based on Frank–Condon Factors and *r*-centroids for (B–X) transition have been reported by Coxon and other groups [33–40]. They have clearly demonstrated the presence of large numbers of transition lines associated with different energy levels of Br₂ molecules. It can easily be achieved by tuning the wavelength of incident light. Also, It is interesting to note that around 95% of the excited Br₂ molecules relax non-radiatively and 5% by fluorescence in the excitation range between 18,514 and 16945 cm⁻¹ [41].

Sharma et al have reported the photo acoustic spectroscopy of Br₂ molecule between 19,579 and 18,520 cm⁻¹ ranges. They found equal contribution to non-radiative decay of molecules from the B³π_{0u}⁺ and the ¹π_{1u} state in the same range of frequency [42,43].

The present report discuss the time resolved Photo acoustic spectra of Br₂ using a single nanoseconds pulse at 532 nm wavelength for the first time. We also demonstrated the spectral distribution of the acoustic modes at higher frequencies in different types of PA cells. The cell size and mode type are the main factors to control the distribution of higher orders acoustic modes. The assignment of allowed transition around 532 nm with their absorption intensities also presented in the paper. The second harmonic of Nd:YAG laser i.e. λ = 532 nm, 7 ns pulse width at repetition rate 10 Hz is employed to record the PA spectrum of Br₂ molecules in two different sized PA cells. The time resolved PA study also confirms the Photolysis of Br₂ at 532 nm.

Theory

This section is divided into four sub-sections. First three Sections (2.1–2.3) deal with theoretical aspects of Bessel's function, sound wave equation and excitation of Photoacoustic modes while subsection four (2.4) deals with distribution of clustering effects at higher frequency range.

Bessel functions of the first kind: J_m

Here, J_m(*x*), is a solutions of Bessel's differential equation which is given by

$$J_m(x) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n! \Gamma(1+m+n)} \left(\frac{x}{2}\right)^{2n+m} \quad (1)$$

where Γ(1 + *m* + *n*) is the gamma function and J'_{*m*} is the first order derivative of J_{*m*} which is given by:

$$J'_m(x) = \frac{xJ_m(x) - mJ_{m+1}}{x} \quad (2)$$

Similarly, higher order derivatives of J_{*m*}(*x*) can be used to calculate the extended values of α_{*m*} in the cylindrical cavity. The derivative of Bessel functions up to 7th order is shown in supplementary part. The calculated new values of α_{*m*} help us to understand the

position of different types of excited acoustic modes in the cavity. It also helps us to determine the common location or clustering of some of the excited modes at certain rang of frequencies.

Sound wave equation in the cylinder cavity

The inhomogeneous wave equation of the sound pressure in the lossless cylindrical resonator is well explained by different groups [10–25].

$$\frac{d^2 p(r, t)}{dt^2} - C^2 \nabla^2 p(r, t) = (\gamma - 1) \frac{dH(r, t)}{dt} \quad (3)$$

where *c*, γ and *H* are the sound velocity, the adiabatic coefficient of the gas and the heat density deposited in the gas by light absorption, respectively.

Because the sound velocity which is proportional to the gradient of *P*(*r*) vanishes at the cell wall, the *P*(*r*) must satisfy the boundary conditions of the vanishing gradient of *p*(*r*) normal to the wall. The solution of Eq. (1) is given by:

$$P(r, t) = C_0(t) + \sum_{n=0}^{\infty} C_n(t) P_n(r) \quad (4)$$

where C₀(*t*), C_{*n*}(*t*) are the eigen mode amplitude of corresponding sound wave, C_{*n*}(*t*) is given by the Fourier series as :

$$C_n(t) = \sum_{n,m} A_{n,m} e^{imw_0 t} \quad (5)$$

The dimensionless eigenmodes distribution of cylindrical resonator is the solution of the homogeneous wave equation and we can be expressed as:

$$P_n(r, t) = P_n(r) e^{iW_n t} \quad (6)$$

where W_{*n*} is the resonance frequency of the cavity resonator, P_{*n*}(*r*) is:

$$P_n(r) = P_{mnq}(r, \theta, z) = J_m(K_r r) \cos(K_z z) \begin{cases} \cos(m\theta) \\ \sin(m\theta) \end{cases} \quad (7)$$

And amplitude A_{*n*}:

$$A_n = \frac{iw_0(\gamma - 1)f_n}{w_n^2 - w_0^2 + (iw_0 \frac{w_n}{Q})} \quad (8)$$

where *f_n* is the overlap integral which describes the effect of overlapping between the pressure distribution of the *n*th acoustic resonance frequency and the propagating laser beam divided by the normalized value of the *n*th eigen mode as:

$$f_n = \frac{\int H(r) P_n(r) dv}{\int P_n^2(r) dv} \quad (9)$$

Acoustic modes

The frequency of acoustic resonant modes generated in the closed cylindrical cell is described by:

$$F_{mnq} = \frac{c}{2} \left(\left(\frac{\alpha_{mn}}{R} \right)^2 + \left(\frac{q}{L} \right)^2 \right)^{\frac{1}{2}} \quad (10)$$

where *c* is the sound velocity, α_{*m*} is the *n*th zero of the derivative of the *m*th Bessel function at *r* = *R*, where *R* and *L* represent the radius and the length of the cylindrical cavity, respectively. The normal acoustic spectrum lines are separated into longitudinal (*q*), radial (*n*) and azimuthal (*m*) modes, respectively. The solution of the inhomogeneous wave equation of sound pressure in the cylindrical resonator provides three types of eigen function in the cavity. The first

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