

Transient coherent anti-Stokes Raman scattering spectroscopy as a tool for measuring the diffusion coefficient and size of gas molecules

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Abstract. Formulas are derived for evaluating the diffusion coefficient and size of gas molecules from transient coherent anti-Stokes Raman scattering measurements. Numerical estimates are presented for hydrogen.

Keywords: coherent anti-Stokes Raman scattering, diffusion coefficient, molecular diameter.

1. Introduction

In 1981 S.A. Ahkmanov formulated the problem of theoretical analysis of transient coherent anti-Stokes Raman scattering (CARS) in gases. By that time, frequency-tunable picosecond lasers had already been created, and the first time-resolved CARS measurements had been carried out in hydrogen [1]. To interpret the data obtained, it was proposed to use the random frequency modulation model, well known in statistical radiophysics [2]. The idea was realised by D'yakov et al. [3], who managed to determine the collisional dephasing time and thermal velocity correlation time in molecular hydrogen. In subsequent years, time-resolved CARS measurements were made in a number of molecular and atomic gases [4–11], and related theoretical studies were performed [12–17]. The advent of femtosecond lasers led to the development of impulsive stimulated scattering spectroscopy [18], an effective approach for measuring not only the amplitude but also the phase of coherent molecular vibrations.

This paper presents formulas for evaluating the diffusion coefficient and size of gas molecules from transient CARS experiments.

2. Transient CARS in gases

Transient CARS spectroscopy involves impulsive laser excitation of Raman-active modes in molecules and anti-Stokes scattering of a laser pulse that probes the medium at probe delay τ . The energy of the scattered anti-Stokes pulse, W_a , is measured as a function of time delay τ . The data

carry information about molecular vibration dephasing processes in the medium [19, 20]. Such processes may be caused by the thermal motion of molecules (Doppler dephasing), molecular collisions (collisional dephasing), rotational splitting of vibrational levels (rotational dephasing) and other factors. The function $f(\tau) = W_a(\tau)$ is referred to as the impulse response function. In what follows, this function is calculated under the assumption that molecular vibration dephasing is caused only by the thermal motion of molecules in the gas.

2.1 Excitation of coherent molecular vibrations

Basic to Raman scattering is the dependence of the electronic polarisability, α , of a molecule on its internuclear distance. This dependence can be represented in the form $\alpha(q) = \alpha_0 + \alpha'q$, where q is the internuclear coordinate measured from the equilibrium position of the nuclei; $\alpha_0 = \alpha(q = 0)$; and α' is the derivative of the electronic polarisability with respect to the internuclear coordinate at the equilibrium position of the nuclei. A simplified procedure for estimating it was described previously [21]. The dipole moment of a molecule in an external electric field E is $p = \alpha E$. The potential energy of a molecule in an external electric field is the sum of the potential energies of its constituent ions: $\Pi = \sum_i \Pi_i$. The differential potential energy element for an ion in an external field is $d\Pi_i = -Eq_i dr_i$, where q_i is the charge on the ion and r_i is its radius vector. Therefore, $d\Pi = -Edp$, where $p = \sum_i q_i r_i$. Consequently, we have in the linear approximation $d\Pi = -\alpha EdE$ and $\Pi = -\alpha E^2/2$. The force $F = -\partial\Pi/\partial q$ exerted by the field on a molecular oscillator is then $F = \alpha'E^2/2$. With damping neglected, the equation of molecular vibrations can be written in the form $\ddot{q} + \omega_0^2 q = F/m$, where ω_0 is the natural frequency of molecular vibrations; m is the reduced mass of the oscillator; and the double dot denotes the second time derivative. The above formulas indicate that molecular vibrations in a medium can be resonantly excited via two-frequency laser pumping. To this end, the Raman resonance condition must be fulfilled: $\omega_1 - \omega_2 = \omega_0$, where ω_1 and ω_2 are the component pump frequencies. In transient CARS spectroscopy, such excitation is provided by picosecond laser pulses, which are focused into a cuvette filled with the gas.

A two-frequency pump pulse ensures impulsive excitation of molecular vibrations $q(t) = q_0 \cos[\omega_0(t - z_0/c)]$, where q_0 is the vibration amplitude; t is time; z_0 is the coordinate of the molecule along the direction of the laser beams at the instant in time when it is exposed to the excitation pulse; and c is the speed of light. Excited in this

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way, the medium is capable of effectively scattering laser radiation, which is employed to generate a scattered anti-Stokes pulse.

2.2 Probing of a moving vibrationally excited molecule

Molecular vibrations are probed by a laser pulse delayed with respect to the pump pulse by time τ . During this time, a vibrationally excited molecule diffuses a distance z along the axis of the laser beams as a result of thermal motion. The probe field acting on the molecule is $\mathbf{E}_p(t) = \mathbf{E}_{p0}(t) \cos\{\omega_p[t - (z_0 + z)/c]\}$, where ω_p is the probe frequency. In the alternating field of the probe wave, the dipole moment of a vibrating molecule has a component that oscillates at the anti-Stokes frequency, $\omega_a = \omega_p + \omega_0$, namely, $\mathbf{p}_a(t) = \mathbf{p}_{a0} \cos[\omega_a(t - z_0/c) + \omega_0\tau - \omega_p z/c]$ is the oscillation amplitude of the dipole moment. A dipole with an alternating dipole moment generates an anti-Stokes wave with a far-field electric vector given by [20]

$$\mathbf{E}_a(\mathbf{r}, t) = \frac{1}{c^2 r} \left[\mathbf{n}, \left[\mathbf{n}, \ddot{\mathbf{p}}_a \left(t - \frac{r}{c} \right) \right] \right],$$

where \mathbf{r} is the radius vector from the dipole to the observation point; $\mathbf{n} = \mathbf{r}/r$ is a unit vector along \mathbf{r} ; and r is the distance from the dipole to the observation point. Since the dipole moment oscillates at the anti-Stokes frequency, we have $\ddot{\mathbf{p}}_a(t) = -\omega_a^2 \mathbf{p}_a(t)$. If the receiver of the anti-Stokes radiation is located on the z axis, then $[\mathbf{n}, [\mathbf{n}, \mathbf{p}_a(t - r/c)]] = -\mathbf{p}_a(t - r/c)$ because the polarisation vector of the probe wave, $\mathbf{e}_p = \mathbf{E}_{p0}/E_{p0}$ is normal to the wave propagation direction (z axis) and, hence, the \mathbf{n} and \mathbf{p} vectors are mutually perpendicular. From the above relations, the anti-Stokes field has the form

$$\mathbf{E}_a(\mathbf{r}, t) = \frac{\omega_a^2}{c^2 r} \mathbf{p}_a \left(t - \frac{r}{c} \right)$$

or

$$\mathbf{E}_a(\mathbf{r}, t) = \mathbf{E}_{a0} \cos \left[\omega_a \left(t - \frac{r}{c} - \frac{z_0}{c} \right) + \omega_0\tau - \omega_p \frac{z}{c} \right],$$

where

$$\mathbf{E}_{a0} = \frac{\omega_a^2}{c^2 r} \mathbf{p}_{a0}$$

is the amplitude of the anti-Stokes wave. Let z_a be the z coordinate of the receiver of the anti-Stokes radiation. The distance between the probed molecule and the receiver is then $r = z_a - (z_0 + z)$, and the field of the anti-Stokes wave incident on it is given by

$$\mathbf{E}_a(z_a, t) = \mathbf{E}_{a0} \cos \left[\omega_a \left(t - \frac{z_a}{c} \right) + \omega_0\tau + \omega_0 \frac{z}{c} \right].$$

As seen from this formula, the anti-Stokes field is independent of the coordinate of the molecule at the instant in time when it is exposed to the two-frequency pump pulse, z_0 . At the same time, this field depends on the displacement z due to thermal motion during the time delay between the pump and probe pulses. Clearly, z is a random function of time. The above expression must be averaged over the thermal velocity distribution of the molecules.

2.3 Impulse response of the gas

Using Euler's formula and averaging the anti-Stokes field over the ensemble of gas molecules, we obtain

$$\mathbf{E}_a(z_a, t) = \frac{1}{2} \mathbf{E}_{a0} \exp \left\{ i \left[\omega_a \left(t - \frac{z_a}{c} \right) + \omega_0\tau \right] \right\} h(\tau) + \text{c.c.},$$

where $h(\tau) = \langle \exp[ik_0 z(\tau)] \rangle$ and $k_0 = \omega_0/c$ is the wave number of the molecular vibrations. The displacement z can be represented as the time integral of the Cartesian component of the thermal velocity of a gas molecule: $z(\tau) = \int_0^\tau v_z(\theta) d\theta$. The molecules have a Maxwellian velocity distribution, $w(v_z) = (\sigma_v \sqrt{2\pi})^{-1} \exp(-v_z^2/2\sigma_v^2)$, where $\sigma_v^2 = kT/m$ is the variance of the thermal velocity; m is the mass of the molecules; T is the absolute temperature of the gas; and k is the Boltzmann constant. At a constant temperature of the gas, the velocity of a gas molecule, $v_z(t)$, can be thought of as a Gaussian stationary random function of time with zero average and variance σ_v^2 . It is known from the theory of random processes [22] that if a process is Gaussian it remains so under any linear transformation, in particular under time integration. Therefore, the probability density distribution for the $z(t)$ coordinate of a molecule has the form $w(z, t) = [\sigma(t)\sqrt{2\pi}]^{-1} \exp(-z^2/2\sigma^2(t))$, where $\sigma^2(t) = \langle z^2(t) \rangle$ is the variance of the molecule displacement during time t . The average in question,

$$h(\tau) = \int_{-\infty}^{+\infty} \exp[ik_0 z(\tau)] w(z, \tau) dz = \exp \left[-\frac{1}{2} k_0^2 \langle z^2(\tau) \rangle \right]$$

is a real value. Consequently, the anti-Stokes field has the form $\mathbf{E}_a(z_a, t) = \mathbf{E}_{a0} h(\tau) \cos[(\omega_a(t - z_a/c) + \omega_0\tau)]$. Because the energy of the anti-Stokes pulse is proportional to the square of the field amplitude, we obtain for the impulse response function

$$f(\tau) = h^2(\tau) = \exp[-k_0^2 \langle z^2(\tau) \rangle]. \quad (1)$$

Therefore, to calculate the impulse response of the gas by Eqn (1), it remains to find the variance of the gas molecule displacement as a function of time. In addition, the function $\langle z^2(t) \rangle$ determines the diffusion coefficient of molecules in the gas.

3. Diffusion coefficient

The function $w(z, t)$ satisfies the one-dimensional diffusion equation

$$\frac{\partial w}{\partial t} = D \frac{\partial^2 w}{\partial z^2},$$

where

$$D = \frac{1}{2} \frac{d}{dt} \sigma^2(t) = \frac{1}{2} \frac{d}{dt} \langle z^2(t) \rangle$$

is the diffusion coefficient of molecules in the gas. Therefore, the diffusion coefficient can be defined as the time derivative of the variance of the molecule displacement. Using the relation $z(\tau) = \int_0^\tau v_z(\theta) d\theta$, the variance of the molecule displacement can be represented in the form

$$\langle z^2(t) \rangle = \int_0^t \int_0^t \langle v_z(\theta_1) v_z(\theta_2) \rangle d\theta_1 d\theta_2$$

or

$$\langle z^2(t) \rangle = \int_0^t \int_0^t B(\theta_1 - \theta_2) d\theta_1 d\theta_2,$$

where $B(\tau) = \langle v_z(t) v_z(t + \tau) \rangle$ is the thermal velocity correlation function for a molecule. Correlation functions are known to be even functions [22]. Therefore, $\langle z^2(t) \rangle$ can be transformed to the form (see, e.g., [23]) $\langle z^2(t) \rangle = 2 \int_0^t (t - \tau) \times B(\tau) d\tau$. Substituting this expression into the formula for the diffusion coefficient and then differentiating with respect to time, we obtain

$$D = \int_0^t B(\tau) d\tau. \quad (2)$$

Thus, the diffusion coefficient is expressed through the thermal velocity correlation function for a gas molecule. As shown previously [17], the thermal velocity correlation function for a gas molecule is an exponential function, $B(\tau) = B(0) \exp(-|\tau|/\tau_v)$, where $B(0) = \sigma_v^2$, and the thermal velocity correlation time is three times the mean free path time of the molecule: $\tau_v = 3\tau_c$. Therefore, the variance of the gas molecule displacement is given by

$$\langle z^2(t) \rangle = 2\sigma_v^2 \tau_c \left[\frac{t}{\tau} - 1 + \exp\left(-\frac{t}{\tau}\right) \right]$$

and the diffusion coefficient is

$$D = B(0)\tau_v \left[1 - \exp\left(-\frac{t}{\tau_v}\right) \right]$$

or

$$D = D_\infty \left[1 - \exp\left(-\frac{t}{\tau_v}\right) \right],$$

where $D_\infty = \sigma_v^2 \tau_v$ is the asymptotic value of the diffusion coefficient. The physical meaning of the variation of the diffusion coefficient on a time scale much shorter than the mean free path time of the molecule is that, on this time scale, its motion is uniform and rectilinear. The coordinate of the molecule is then a linear function of time, and the variance of its displacement is proportional to the square of time.

4. Numerical estimates

Using transient CARS spectroscopy, D'yakov et al. [3] determined the thermal velocity correlation time in molecular hydrogen. According to their results, $\tau_v = b/\rho$, where $b = 0.13 \times 10^{-9}$ s, $\rho = N/N_0$ is the density of the gas in Amagat units; N is the molecular concentration; and N_0 is the molecular concentration under normal conditions (Loschmidt constant). In molecular physics, the mean free path time of a gas molecule, τ_c , and its diameter, d , are related by $\tau_c^{-1} = N\sqrt{2}\langle v \rangle \pi d^2$ [24]. Here, $\sqrt{2}\langle v \rangle$ is the mean relative velocity of two gas molecules and $\langle v \rangle = (8kT/\pi m)^{1/2}$ is the mean magnitude of the molecular velocity. It follows from the formulas above that

$$d = (4\sqrt{\pi}N_0\sigma_v b/3)^{-1/2}. \quad (3)$$

This formula can be used to determine the molecular size. Let us estimate it for a hydrogen molecule with $\sigma_v = 1.1 \times 10^5$ cm s⁻¹ at room temperature. From Eqn (3), we obtain $d = 3.3 \times 10^{-8}$ cm. For comparison, the molecular diameter of hydrogen evaluated from thermal conductivity measurements is $d = 2.74 \times 10^{-8}$ cm [24]. The diffusion (self-diffusion) coefficient of hydrogen molecules under normal conditions is then $D_\infty = \sigma_v^2 \tau_v = 1.6$ cm² s⁻¹. For comparison, the self-diffusion coefficient of hydrogen was reported to be $D = 1.28$ cm² s⁻¹ [25].

5. Conclusions

Ultrashort laser pulses enable studies of fast processes, in particular, gas-phase diffusion when a nonequilibrium concentration is produced in a very small volume. One way of producing a local nonequilibrium concentration of particles is vibrational excitation of molecules by focused laser pulses. In the case of Raman transitions, such a possibility is offered by transient CARS. This method enables measurements of gas parameters such as the variance and correlation time of the thermal velocity of molecules. In this work, relations were derived between these parameters and the diffusion coefficient and size of gas molecules. Numerical estimates were made for molecular hydrogen.

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