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Anharmonic Coherent Raman Scattering in H_2

J. Lukasik and J. Ducuing
Laboratoire d'Optique Quantique, Centre National de la Recherche Scientifique, Université de Paris XI, 91 Orsay, France
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The direct observation of anharmonic effect in coherently driven molecular vibrations is reported for low-pressure H_2. Under intense excitation of the gas by light waves of frequencies ω and ω', both electrical and mechanical anharmonicities contribute to a coherent polarizability modulation at $2(\omega-\omega')$. The corresponding anharmonic scattering dominates, at low pressure, the usually observed harmonic double scattering. We discuss application of the effect to the determination of the second-order polarizability derivative.

Two light waves with frequencies ω and ω' can coherently drive a molecular vibration at $\omega-\omega'$. This has been recognized[1,2] as an essential step in stimulated Raman scattering, where the laser and Stokes waves provide the driving light fields. The coherent vibration is reflected in a coherent modulation of the polarizability $\delta\alpha(t,\vec{r})=\delta\alpha(\omega-\omega',\vec{r})e^{i(\omega-\omega')t}+\text{c.c.}$ and the appearance of an index grating which can scatter inelastically incoming light waves, thus giving rise to the observed anti-Stokes spectrum. For intense excitations one expects the onset of nonlinear effects through the mechanical and electrical anharmonicities of the molecule creating Fourier components of the polarizability at harmonics of $\omega-\omega'$. In this paper we report what we believe to be the first observation of these effects.

Consider an exciting light field with Fourier components at ω and ω',

$$E(\vec{r},t)=E(\omega,\vec{r})e^{-i\omega t}+E(\omega',\vec{r})e^{-i\omega' t}+\text{c.c.},$$

interacting with a gas of N diatomic molecules per unit volume. The difference frequency $\omega-\omega'$ is close to the fundamental vibrational frequency ω_{10}. For ω and ω' far below the electronic transition frequencies, the interaction Hamiltonian can be written[3] as $H_I=-\frac{1}{2}\alpha_m(q)E^2$, where q is the internuclear distance and α_m the molecular polarizability operator. For the sake of simplicity, α is treated here as a scalar, and vibration-rotation interaction is neglected. The expectation value of α is given by $\langle\alpha_m\rangle=\operatorname{Tr}\alpha_m\rho$, where the molecular density operator in the presence of the light field can be obtained by standard perturbation theory as a series in powers of H_I, $\rho=\rho^{(0)}+\rho^{(1)}+\rho^{(2)}+\cdots$. The first-order term in $\langle\alpha_m\rangle$, averaged over the normalized distribution $g(\omega_{10})$ of vibrational frequencies, yields the Fourier component at $\omega-\omega'$ of the average polarizability,

$$\alpha(\omega-\omega',\vec{r})=(\alpha_{01}{}^2/\hbar)G(\omega-\omega')\times E(\omega,\vec{r})E^*(\omega',\vec{r}), \tag{1}$$

with

$$G(\omega-\omega')=\int d\omega_{10}\,g(\omega_{10})/(\omega-\omega'-\omega_{10}+i\Gamma_{10}),$$

where α_{ij} stands for the matrix element between vibrational (ground electronic) states i and j of the molecular polarizability operator α_m; and ω_{ij} and Γ_{ij} stand for, respectively, the angular frequency and the angular half-width of the $i \to j$ transition. Near-resonance terms only have been kept in this expression. Similarly, the second-order term contributes a Fourier component at the harmonic $2(\omega-\omega')$ of the driving difference frequency:

$$\alpha(2(\omega-\omega'),\vec{r}) = \frac{\alpha_{01}}{\hbar^2}\sum_n \alpha_{0n}\,\alpha_{n1}\{[2(\omega-\omega')-\omega_{n0}]^{-1}-[2(\omega-\omega')+\omega_{n1}]^{-1}\}G(\omega-\omega')E^2(\omega,\vec{r})E^{*2}(\omega',\vec{r}),$$

where the matrix elements of α have been taken as real. The contribution from $n=2$ will quite generally dominate the sum over intermediate states: For H_2, which has the strongest molecular anharmonicity, $2\omega_{10}-\omega_{20}=228\ \mathrm{cm}^{-1}\simeq 2\omega_{10}/40$. When only this contribution is retained, the harmonic polarizability reduces to

$$\alpha(2(\omega-\omega'),\vec{r}) = [\alpha_{02}\alpha_{21}\alpha_{10}/\hbar^2(2\omega_{10}-\omega_{20})]G(\omega-\omega')E^2(\omega,\vec{r})E^{*2}(\omega',\vec{r}). \quad (2)$$

This modulation can be detected through coherent inelastic scattering. The wave at ω creates a field at $\omega+2(\omega-\omega')$ through the nonlinear source polarization,[4]

$$\begin{aligned} P_{\mathrm{NLS}}(\omega+2(\omega-\omega')) &= N\alpha(2(\omega-\omega'),\vec{r})E(\omega,\vec{r}) \\ &= \chi^{(5)}(\omega,\omega,\omega,-\omega',-\omega')E^3(\omega,\vec{r})E^{*2}(\omega,\vec{r}). \end{aligned} \quad (3)$$

However, coherent radiation at $\omega+2(\omega-\omega')$ can also be produced through double coherent scattering associated with the polarizability modulation (1). Whereas the intensity of the anharmonic scattering is proportional to N^2, that of double scattering is seen to be proportional to N^4. Thus the latter effect dominates at high pressures and/or long scattering lengths. We have used these different dependences on density and scattering lengths to discriminate against double scattering and observe coherent anharmonic scattering in low-pressure normal H_2 with a focused geometry.

The experimental setup is shown on Fig. 1. A 40-MW, 20-nsec-long ruby laser pulse (ω) was focused into a high-pressure ($p\simeq 20$ atm) generator cell filled with a mixture of hydrogen and helium gases. The intense 10-MW Stokes radiation (ω'), produced by stimulated Raman scattering from the $Q(1)$ transition of the H_2 molecule, and the laser beam are, after filtering (F_1), refocused in a low-pressure excitation cell containing only H_2. The helium concentration in the generator cell was adjusted[5] so as to compensate for the pressure shift of the vibrational frequency. Thus the resonant condition $\omega-\omega'=\omega_{10}$ was ensured in the excitation cell. The coherent anti-Stokes scattering at frequency $3\omega-2\omega'=\omega+2\omega_{10}$ was isolated with appropriate filters (F_4) and detected by the 56 AVP (S11—14 stages) photomultiplier. The laser and Stokes radiations were detected by the C_2 and C_3 fast-response photodiodes. Along with the synchronization laser signal from C_1 and the detected signal C_4, they were transmitted to the photon counting and conversion

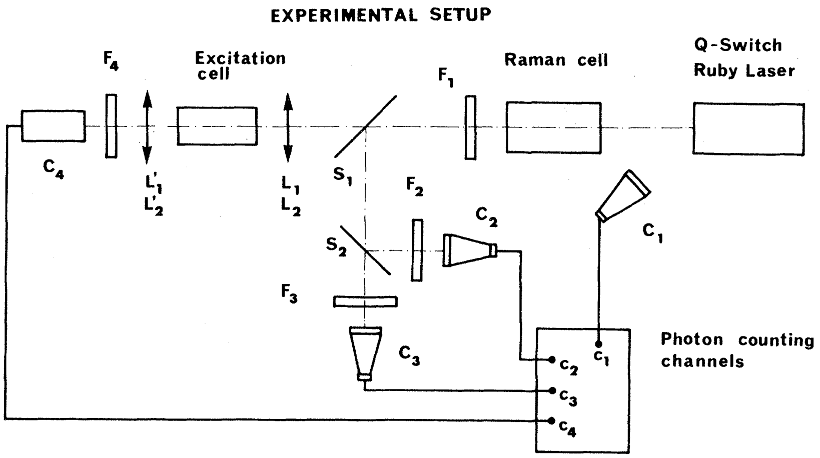

FIG. 1. Experimental setup (see text for details).

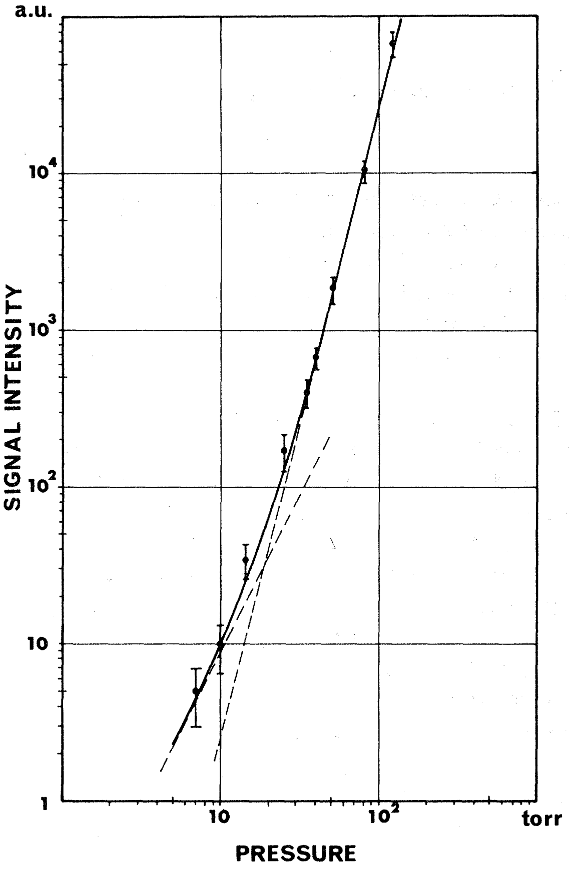

FIG. 2. $\omega + 2\omega_0$ signal intensity versus pressure in the excitation cell. Dashed lines, limiting p^2 and p^4 dependences.

channels. All the data were printed on a recording device. The number of photoelectron counts corresponding to photons at the frequency $\omega + 2\omega_{10}$ as a function of pressure in the excitation cell is displayed in Fig. 2. It is seen that at low pressures the p^4 dependence indicative of double scattering is replaced by a p^2 variation corresponding to anharmonic scattering. Each point represents the average number of counts for a series of about 100 laser shots. At the lowest pressures about 1 photoelectron was detected per 20 laser shots. The noise level was of the order of 1 photoelectron per 100 laser shots. For higher pressure values, calibrated neutral density filters kept the average number of counts per shot below 0.2, in order to ensure the linear response of the detection system. The signal intensity for $p > 50$ Torr followed a strict p^4 dependence.

The experiments were carried out with the excitation cell length $l_1 = 10$ cm and lenses L_1, L_2' of $f = 10$ cm and with $l_2 = 5$ cm and lenses L_2, L_2' of $f = 5$ cm. Figure 2 shows the results for $l_2 = 5$ cm. With $f = 10$ cm similar results were obtained, but as expected for a longer scattering length, anharmonic scattering dominated double scattering at lower pressures. The change of regime occurred at approximately half the pressure corresponding to $f = 5$ cm.

A discrimination ratio of the order of 10^{12} between the frequencies at $\omega + 2\omega_{10}$ and $\omega + \omega_{10}$ was achieved by adding to the interference filters in the F_4 system a liquid $[\mathrm{Cu(NH_3)_4}]^{++}$ filter. The transmission of the F_1 system for the $\omega + \omega_{10}$ and $\omega + 2\omega_{10}$ frequencies generated in the Raman cell was less than 10^{-16}. The polarization of the observed $\omega + 2\omega_{10}$ signals was found at all pressures to be the same as the polarization of the laser and Stokes light. It was checked that by placing the Schott OG-4 filter in front of the F_4 system, the previously observed signals disappeared. This filter rejects $\omega + 2\omega_{10}$ and transmits $\omega + \omega_{10}$ frequency.

The solid line in Fig. 2 represents a least-squares fit to the experimental data on the log-log scale. The fitted theoretical expression was taken as

$$I = Ap^2[(p/p_0)^2 + Bp/p_0 + 1].$$

The computer program yielded the values $p = 19$ Torr, $B = 7\times 10^{-4}$, showing that there was practically no contribution from the p^3 term. In this interaction between multimode laser beams and in the presence of chromatic aberrations, one does not expect a well-defined phase relationship between the fields E_a and E_d due, respectively, to anharmonic and double scattering. The detected intensity is proportional to the integral over the photocathode area, $\int_s d\sigma\, |E_a + E_d|^2$, which in this case reduces to $\int_s d\sigma\,(|E_a|^2 + |E_d|^2)$. This probably accounts for the absence of p^3 terms in the observed intensity dependence.

Both mechanical and electrical anharmonicities contribute to $\alpha(2(\omega - \omega'), \vec{r})$. Let us assume that the vibrational potential can be represented by

$$U(q) = \tfrac{1}{2}k_e q^2 + \beta q^3 + \gamma q^4$$

and the molecular polarizability by

$$\alpha_m = \alpha^0 + (\partial\alpha/\partial q)q + \tfrac{1}{2}(\partial^2\alpha/\partial q^2)q^2.$$

The matrix elements and energy denominator in (2) can be evaluated by standard perturbation theory. This gives

$$\alpha(2(\omega-\omega'),\vec{r})=\frac{(x\partial\alpha/\partial q)^2[4(x\,\partial\alpha/\partial q)\beta x^3/\hbar\Omega+x^2\,\partial^2\alpha/\partial q^2]}{60\beta^2x^6/\hbar\Omega-12\gamma x^4}\,G(\omega-\omega')E^2(\omega,\vec{r})E^{*2}(\omega',\vec{r})$$
$$=(\chi^{(5)}/N)E^2(\omega,\vec{r})E^{*2}(\omega',\vec{r}),\qquad(4)$$

where $x=(\hbar/2\mu\Omega)^{1/2}$, and μ and Ω are, respectively, the reduced mass and frequency of the corresponding harmonic oscillator. Equation (4) clearly separates the two contributions and shows that, β being negative, they will be quite generally of opposite sign. For the H_2 molecule, $\chi^{(5)}/N=\kappa^{(5)}$ can be calculated in the low-pressure case using a Morse potential fit, the values of $\partial\alpha/\partial q$ and $\partial^2\alpha/\partial q^2$ given by Ishiguro *et al.*,[6] and the Doppler width $\Delta\omega_D=3\times10^{-2}\,\text{cm}^{-1}$. We find $\alpha_{02}=4\times10^{-27}\,\text{cm}^3$ and, at resonance

$$i\kappa^{(5)}=\sqrt{2}\,\frac{\alpha_{01}{}^2\alpha_{02}}{\hbar^2(2\omega_{10}-\omega_{20})}\,\frac{2.96}{\Delta\omega_D}=-0.5\times10^{-45}\text{ esu},$$

to which the mechanical term in β contributes $i\kappa_{\text{mech}}{}^{(5)}=-1.85\times10^{-45}$ esu and the electrical term in $\partial^2\alpha/\partial q^2$, $i\kappa_{\text{el}}{}^{(5)}=+1.35\times10^{-45}$ esu. The harmonic coherent anti-Stokes scattering $\omega\to\omega+\omega_{10}$ can be described by a third-order susceptibility $\chi^{(3)}(\omega,\omega,-\omega')=N\kappa^{(3)}$, where at resonance $i\kappa^{(3)}=(\alpha_{01}{}^2/\hbar)2.96/\Delta\omega_D$. For a plane-wave interaction at the focus (only a rough approximation here), the ratio of the scattered power at $\omega+\omega_{10}$ to that at $\omega+2\omega_{10}$ is given by $[\kappa^{(3)}/\kappa^{(5)}EE']^2$. From the laser and Stokes powers and the diameter $d\simeq100\ \mu\text{m}$ of the focal zone, we estimate $E\simeq6\times10^4$ esu, $E'\simeq3\times10^4$ esu. Note that for the low pressures considered here, these values are more than 1 order of magnitude below breakdown threshold.[7] With the above value of α_{02} we find for the ratio of the scattered powers 1.6×10^7, in good agreement with the measured value of 10^7. Other things being equal, $\kappa^{(5)}$ increases for small mechanical anharmonicity. In this case there only remains the electrical contribution which is enhanced by the decrease of $2\omega_{10}-\omega_{20}$, i.e., a quasiresonance between $2(\omega-\omega')$ and ω_{20}. Thus it can be expected that in some heavy polarizable molecules the effect will be of purely electrical origin and larger than in H_2. In this situation the polarizability matrix elements can be calculated between harmonic-oscillator eigenstates: $\alpha_{02}=\frac{1}{2}\sqrt{2}(\alpha_{11}-\alpha_{00})$, and $\kappa^{(5)}$ is seen to be proportional to the difference in polarizabilities between ground and first excited vibrational states.

In its present state our experiment does not lend itself to a determination of $\kappa^{(5)}$. However, this would be possible with the use of single transverse-mode beams and achromatic optics. Furthermore, the method could be extended to other molecules by using a laser-pumped dye laser to provide the frequency ω'. Mechanical anharmonicities are accurately known from spectroscopic data, and $\partial\alpha/\partial q$ can be determined from Raman intensity measurements[8]: Experiments of the type presented here would allow the determination of $\partial^2\alpha/\partial q^2$ and $\alpha_{11}-\alpha_{00}$. In polyatomic molecules the interaction of vibrational modes through mechanical and electrical anharmonicities could also be studied.

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