

# IR PUMPED THIRD-HARMONIC GENERATION AND SUM-FREQUENCY

## GENERATION IN DIATOMIC MOLECULES

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It is well known that the efficient lasers we have, approximately 20 percent for CO<sub>2</sub> around 10.6  $\mu$  and 60 percent for CO around 5  $\mu$ , have inherent disadvantages for certain types of power transmission. First, since beam divergence scales as  $\lambda/D$ , we are confronted with either limited range or excessively large optics (e.g., 30-m diameter collection mirror at geostationary orbit for Earth-to-space transmission of 10.6- $\mu$  wavelength) for reasonable transmission efficiency. Secondly, the use of solid state converters is limited to 2 $\mu$  and, for maximum efficiency, wavelengths below 1  $\mu$  are desirable. Even if the laser-driven engine is used for conversion, the need for high temperature strength and transmission of the beam entrance window dictates the use of sapphire which has a long wavelength cutoff at about 5.5  $\mu$ . Thus the CO<sub>2</sub> laser wavelength would certainly need up-conversion.

For these reasons, we began a study recently to assess the possibility and potential efficiency of using nonlinear up-conversion techniques for the high efficiency type lasers (CO, CO<sub>2</sub> and chemical). This paper is a preliminary report on what we believe are some encouraging results. Although the conversion efficiencies are not extremely high, it should be borne in mind that this may be improved as we examine other candidate molecular gases. Also, especially for ground-based laser type missions, one might be more tolerant of overall laser and up-converter efficiency, especially if it reduces the need for many large onboard collection optics systems by area factors of nine, say, or if this overall efficiency exceeds that of the best direct (no up-converter) laser operating at the same wavelength.

Efficient up-conversion of visible laser radiation by third-harmonic and sum-frequency techniques, using metallic vapors with added atomic vapor for phase-matching, has recently been an active and successful area of research (refs. 1 through 4). Very high conversion efficiencies (ref. 5) are attributable to the use of resonance enhancements, particularly a resonance at twice the pump frequency (refs. 4 and 5). In principle, such conversion processes should also be possible for longer wavelength laser radiation. However, the smaller pump photon energy necessitates the use of molecular media for conversion if resonance enhancement is to be used. Molecular systems present certain difficulties: their levels are complex and transition probabilities often unknown. Also, the oscillator strengths among vibrational levels in the ground electronic state of a molecule are either zero or much smaller than those among electronic states of an atom, thus limiting the magnitude of nonlinear interactions. However, as we will show here, this potential problem in the up-conversion process can be eliminated by making use of virtual vibronic (vibration-electronic) transitions which, being primarily electronic transitions have much larger matrix elements and efficient conversion *can* be achieved with molecular systems.

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The energy diagram of a typical molecule is shown in figure 1. Both the ground and excited electronic states are split into rotation-vibrational levels with each denoted by electronic, vibrational, and rotational quantum numbers (e, v, and J). The incident infrared laser frequencies are  $\omega_1$  and  $\omega_2$  and the converted (or generated) frequency is  $\omega_3$ . For many molecules, the rotation-vibrational levels in the ground electronic state are well separated in comparison with their linewidths; thus only one pair of such levels, with energy separation  $\hbar\omega_0$ , may be assumed to satisfy the condition of two photon resonance, namely,  $\omega_0 \simeq 2\omega_1$ . Only this pair of levels, denoted by  $|g\rangle$  and  $|a\rangle$  in figure 1, will make a significant contribution to the nonlinear interaction in question.

Because there is no resonance requirement of the rotation-vibrational levels in the excited electronic state, all those levels which are electric-dipole-allowed will participate in the nonlinear process. The energy of all these levels in the excited electronic state may be approximated by their average value  $\hbar\Omega$  because  $\Omega \gg \omega_2$  and  $\omega_3$ . We therefore lump all these excited vibronic levels into a single upper state  $|b\rangle$ , and the molecule depicted in figure 1 may be represented by a three-level system with energies  $\hbar\Omega$  for  $|b\rangle$ ,  $\hbar\omega_0$  for  $|a\rangle$ , and zero for  $|g\rangle$ .

The basic difference between the molecular system considered here and the atomic system considered by previous investigators (refs. 1 through 5) is that  $\Omega$  is much greater than  $\omega_3$ . Hence, the only possible resonance enhancement effect which may be used is the two-photon resonance namely,  $\omega_0 = 2\omega_1$ . Because there is no resonance enhancement at  $\omega_3$  the system considered here would have relatively lower conversion efficiency but, as will be seen, much wider bandwidth than those considered by Harris and Bloom (ref. 6). The simplified expression for the relevant third-order susceptibility for the three level system depicted in figure 1 can be found by standard methods (ref. 7) to be

$$\chi^{(3)}(\omega_3 = 2\omega_1 + \omega_2) = \frac{1}{4\hbar^3} \frac{\mu_{gb} \mu_{ba} \mu_{ab} \mu_{bg}}{(\omega_0 - 2\omega_1) + i(\delta\omega_0/2)} \frac{2\Omega - \omega_3 + \omega_2}{(\Omega - \omega_1)(\Omega + \omega_2)(\Omega - \omega_3)} \quad (1)$$

where  $\mu_{ab}$  is the electronic dipole matrix element between  $|a\rangle$  and  $|b\rangle$ ,  $\delta\omega_0$  is the linewidth of level  $|a\rangle$ , and all frequencies are expressed in circular measure. Since  $\Omega \gg \omega_1$ ,  $\omega_2$ , and  $\omega_3$ , the susceptibility of equation (1) is insensitive to  $\omega_2$  (and  $\omega_3$ ), and the conversion efficiencies for third harmonic and sum-frequency generation would be comparable. We therefore consider the third harmonic generation only. By setting  $\omega_2 = \omega_1$  and  $\omega_3 = 3\omega_1$ , the expression needed for  $|\chi^{(3)}(3\omega_1)|^2$  may be easily obtained from equation (1).

The general expression for the ratio of third harmonic output to pump input, or conversion efficiency, can be written as (refs. 7 through 9)

$$\epsilon = \alpha \eta^4 N^2 \left| \chi^{(3)}(3\omega_1) \right|^2 \quad (2)$$

where the wave impedance is  $\eta = \sqrt{\mu/\epsilon}$ ,  $N$  is the effective molecular concentration (to be explained later), and the value of  $\alpha$  is dependent upon whether the pump beam is unfocussed (plane wave) or is a focussed Gaussian beam in the medium. For the former case, the cross-sectional areas for both the fundamental and third harmonic are the same and hence  $\epsilon_1 = I(\omega_3)/I(\omega_1)$ , the intensity ratio, and  $\alpha = \alpha_1 = 9\omega_1^2 I^2(\omega_1) F^2 L^2$ . The coherence factor is  $F = \sin(\Delta k L/2)/(\Delta k L/2)$ ,

$\Delta k = 6\pi(n_3 - n_1)/\lambda_1$ , where  $(n_3 - n_1)$  is the refractive index difference for  $\omega_3$  and  $\omega_1$ , and  $L$  is the interaction length. For the focussed Gaussian case, the effective cross section of the fundamental is three times that of the third harmonic because the pertinent induced nonlinear polarization is cubic in the electric field (refs. 7 through 9). Then the conversion efficiency, written in terms of powers,  $\epsilon_p = P(\omega_3)/P(\omega_1)$  is found using  $\alpha = \alpha_p = (3/4) (\omega_1/\lambda_1)^2 P^2(\omega_1) |F'|^2$ , where  $F'$  is the phase mismatch integral  $I(\Delta k, \xi, \zeta)$  given by Ward and New (ref. 9).

In order to evaluate these efficiencies for a given molecular gas, the matrix elements of individual rotation-vibrational levels between different electric states must be known to calculate  $|\chi^{(3)}(3\omega_1)|^2$ . These transition probabilities have been reported (ref. 10) for the  $B^1\Sigma_u^+ - X^1\Sigma_g^+$  band system of molecular hydrogen. A slight complication arises because of the difference in statistical weight of para ( $J = 1$ ) and ortho ( $J = 0$ ) states: at 300°K the ground state population density of the  $J = 1$  level is 65 percent while that of  $J = 0$  is only 13 percent of the total molecular density  $N_0$ . For this reason, we calculate the para-hydrogen conversion, that is, setting  $|g\rangle = |X^1\Sigma_g^+, 0, 1\rangle$ ,  $|a\rangle = |X^1\Sigma_g^+, 1, 1\rangle$ ,  $N = 0.65 N_0$ . To evaluate the product of the four matrix elements in equation (1), a sum over all the rotation-vibrational levels in the excited state must be made. Standard application of the Born-Oppenheimer approximation  $|e, v, J\rangle = |e, v\rangle |J\rangle$ , the rotation sum-rule, and algebraic simplification gives the desired matrix product

$$M = (2J_a + 1) \left[ \sum_{v'} \langle e'', v_g | \mu | e', v' \rangle \langle e', v' | \mu | e'', v_a \rangle \right]^2 \quad (3)$$

where, for the case considered here,  $J_a = 1$ ,  $v_g = 0$ , and  $v_a = 1$ . With the reported band oscillator strengths  $f_{v',v''}$  for  $B^1\Sigma_u^+ - X^1\Sigma_g^+$  of  $H_2$  (table 4 of ref. 10), the linearly polarized dipole matrix elements of equation (3) may be calculated through the relationship,  $f_{v',v''} = 2\Omega m |\langle e'', v'' | \mu | e', v' \rangle|^2 / \hbar e^2$ , where  $m$  is the mass and  $e$  the charge of the electron. Using the averaged value of the electronic state energy,  $\Omega = 103710 \text{ cm}^{-1}$ , we finally obtain  $M = 1.14 \times 10^{-117} \text{ (C-m)}^4$ .

The value of the linewidth,  $\delta\omega_0$  to use in equation (1) is complicated to a certain extent by a pressure dependent quadrupole interaction in hydrogen which produces collision-narrowing (refs. 11 and 12). The full width at 300°K is calculated to be narrowed to less than  $16 \times 10^{-3} \text{ cm}^{-1}$  for pressures between 1-4 atm with a minimum of  $12 \times 10^{-3} \text{ cm}^{-1}$  at 2 atm. For simplicity, we will ignore this factor in calculated efficiency and use the Doppler full width of  $36.5 \times 10^{-3} \text{ cm}^{-1}$ , together with an assumed pump frequency of  $\omega_1 = \omega_0/2 = 2077.6 \text{ cm}^{-1}$  (at resonance) to obtain  $|\chi^{(3)}(3\omega_1)|^2 = 1.52 \times 10^{-115} \text{ m}^5 \text{V}^{-2}$ .

The conversion efficiencies may now be calculated. Without using special provisions for phase matching, the maximum interaction length is just the coherence length  $L_c = \lambda_1/6(n_3 - n_1)$ . Using the standard equation (ref. 13) to calculate the index difference in hydrogen at 300°K, one obtains  $L_c = 240 \text{ cm}$  at 1 atm and  $L_c = 60 \text{ cm}$  at 4 atm. For the pressure range of 1-4 atm,  $NL_c = 3.83 \times 10^{25} \text{ m}^{-2}$ , approximately pressure independent. Since the intensity conversion efficiency  $\epsilon_I \propto (NL_c)^2$ , no enhancement is obtained by increasing the pressure. On the other hand, the power conversion efficiency for the focussed Gaussian beam  $\epsilon_p \propto N^2$ , and there is a definite advantage in using higher pressures. Of course, both cases must be more closely examined to include the pressure narrowing effect, which cannot be done in this brief note. Using  $F = 2/\pi$  and  $L = L_c$ , the calculated  $\epsilon_I$  is 10 percent for  $I(\omega_1) = 19.9 \text{ MW/cm}^2$  and 30 percent for  $I(\omega_1) = 34 \text{ MW/cm}^2$ . For the focussed case, we choose the confocal parameter  $b$  to be three times the interaction length, that is,  $(b/L) = 3$  and use the maximum  $|F'|^2$  which, according to Miles and Harris (ref. 8), is about 0.5.

The calculated  $\epsilon_p$  is then 10 percent for  $P(\omega_1) = 1.80$  MW at 4 atm. Should the pressure narrowing be included, only 780 kW is necessary to achieve the same efficiency. It should be noted that, for the pressures and laser pulses of interest here, competing processes, such as two-photon absorption (ref. 6) and gas breakdown (ref. 14) occur at intensities around  $10^3$  MW/cm<sup>2</sup> and therefore should not present a problem.

It has been pointed out by Harris (ref. 15) that the microscopic processes for third harmonic generation with two-photon resonance enhancement and stimulated Stokes-Raman scattering are similar, and that the calculated third harmonic conversion efficiency may be checked independently by existing Raman gain data. We have derived the relationship between the intensity (plane wave) conversion efficiency,  $\epsilon_I$ , with  $L = L_c$ , and the normalized stimulated Raman gain coefficient  $g$  as

$$\epsilon_I = \left[ \frac{3\omega_1}{\pi\omega_s} \left| \frac{\chi^{(3)}(3\omega_1)}{\chi_R''(\omega_s)} \right| L_c I(\omega_1) g \right]^2 \quad (4)$$

where  $\omega_s = \omega_0 - \omega_0$  is the Stokes frequency stimulated by a laser at frequency  $\omega_0$ , and  $\chi_R''(\omega_s)$  is the associated Raman tensor. Using the measured gain (ref. 16) for H<sub>2</sub> at 300°K and 1 atm,  $L_c = 240$  cm, and the calculated ratio  $|\chi^{(3)}/\chi_R''| = 1.107$ , we find from equation (4) the pump intensity necessary for 10 percent conversion efficiency to be 39.2 MW/cm<sup>2</sup>, a value in favorable agreement with the value of 19.9 MW/cm<sup>2</sup> calculated above.

The question of phase-matching is of interest. If the conversion medium is positively dispersive, like H<sub>2</sub>, this can be accomplished by adding the appropriate mole fraction of a selected negatively dispersive diatomic molecule. If heteronuclear molecules are selected as the interaction medium, and the  $v = 2$  level is used for the two-photon level  $|a\rangle$ , the medium could have negative dispersion if the pump frequency  $\omega_1$  is smaller than, but very close to, the  $v = 1$  level. For such a negatively dispersive conversion medium, phase matching can be achieved by adding positively dispersive diatomic molecules to the system. However, since neither oscillator strengths nor refractive indices at infrared frequencies are known for most molecules, phase-matching may have to be determined by experiment rather than *a-priori* quantitative calculation.

In summary, we have suggested a mechanism with which efficient third-harmonic and sum-frequency generation, pumped by infrared lasers, should be practically achievable. We have outlined the method for calculating the third-harmonic conversion efficiencies for unfocussed and focussed Gaussian pump beams. A single relation for estimating the intensity conversion efficiency, when the appropriate Stokes-Raman gain coefficient is known, has been given. Our major reason for using H<sub>2</sub> as our model molecular converter was the availability of the oscillator strengths needed for the calculation. However, the required resonance pump radiation at  $\omega_1 = 2077.6$  cm<sup>-1</sup> for hydrogen molecules, falls between the strong lines of the CO and chemical lasers, the nearest line being a  $v' = 2 \rightarrow v'' = 1$ ,  $J' = 9 \rightarrow J'' = 10$  transition in CO at 2077.1 cm<sup>-1</sup>. Other molecular systems, which have either Rydberg transitions (ref. 17) or smaller  $\Omega$ , should yield similar conversion efficiencies. The purpose of this paper was to demonstrate that indeed efficient conversion in molecules is possible and to motivate thereby the further study of other common molecules such as HCl, N<sub>2</sub>, CO, and CN, which would undoubtedly result in suitable systems for experimentation. For example, both CO and CH<sub>3</sub>F molecules (ref. 18) would be candidates for up-converting CO<sub>2</sub> laser radiation. Other possibilities, rather than such chance laser-molecule wavelength matches, are available, however. With the recent advance in the development of high pressure infrared lasers, it should be possible to tune the laser to achieve resonance. It must be noted, however, that if the

laser linewidth is larger than  $\delta\omega_0$ , the required power to achieve a given conversion efficiency is proportionately increased. Alternately, the molecule can be brought to resonance with a nearby laser line by Stark tuning with an external electric field (ref. 18).

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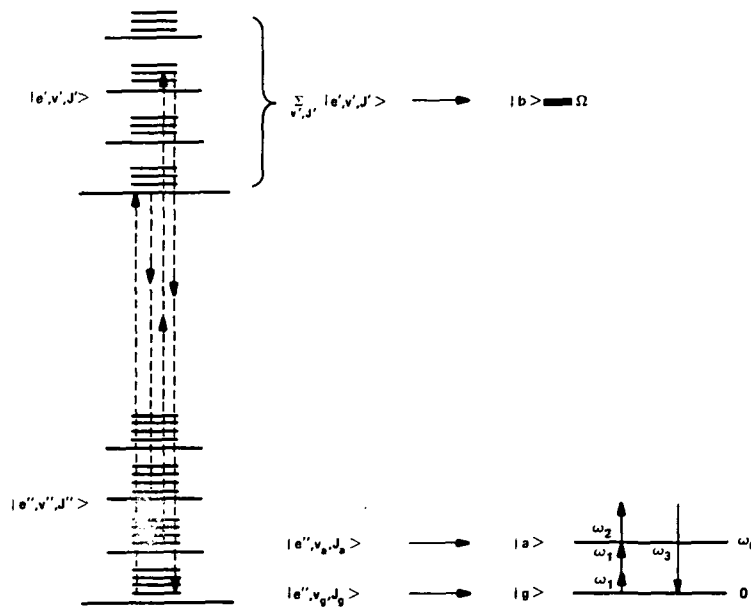


Figure 1.— Energy levels of a typical diatomic molecule. Each electronic state is split into a series of rotation-vibrational levels, with short horizontal lines indicating rotation sublevels. One possible path of virtual vibronic transitions contributing to the product of four matrix elements in equation (1) is shown by the four vertical dashed lines. For the up-conversion process of interest, the molecule may be represented by a three-level system with the upper-state  $|b\rangle$  forming a band containing all sub-levels in the excited electronic state. For the interaction considered (using the  $\text{B}^1\Sigma_u^+ - \text{X}^1\Sigma_g^+$  band system of  $\text{H}_2$ ),  $|e', v', J'\rangle = |\text{B}^1\Sigma_u^+, v', J'\rangle$ ,  $|a\rangle = |e'', v_a, J_a\rangle = |\text{X}^1\Sigma_g^+, 1, 1\rangle$  and  $|g\rangle = |e'', v_g, J_g\rangle = |\text{X}^1\Sigma_g^+, 0, 1\rangle$ .

## DISCUSSION

**Ernest Brock, Los Alamos Scientific Laboratory** – With respect to the dispersion in the infrared in the hydrogen molecule, there has been a recent report in JETP Letters, September-October, where some Soviet scientists use a Raman pumping technique to pump hydrogen from  $v = 1$  to  $v = 2$ , ground state. They observed a fringe shift which they were able to interpret as an index change. Their experimental data is supported by a German calculation, which they reference.

**Joe She:** Thank you for calling it to our attention.

**Dick Miles, Princeton University** – You might consider focusing as a means of phase matching.

**Joe She:** Yes, for other molecules this may work, but you need an actively dispersive medium which is not the case for hydrogen.