HYPER-RAMAN SPECTRA OF METHANE, ETHANE AND ETHYLENE IN GAS PHASE

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We report here observations of laser-induced non-linear light scattering, both elastic and inelastic (hyper-Raman), from methane, ethane and ethylene. Observations on several other molecules, mainly substituted methanes and ethanes, will be reported elsewhere.

The several aspects of the theory of non-linear (three-quantum) light scattering have been treated by several authors [1-5]. We summarize here those aspects which are of aid in interpreting the results discussed below. Centrosymmetric molecules should exhibit no second harmonic
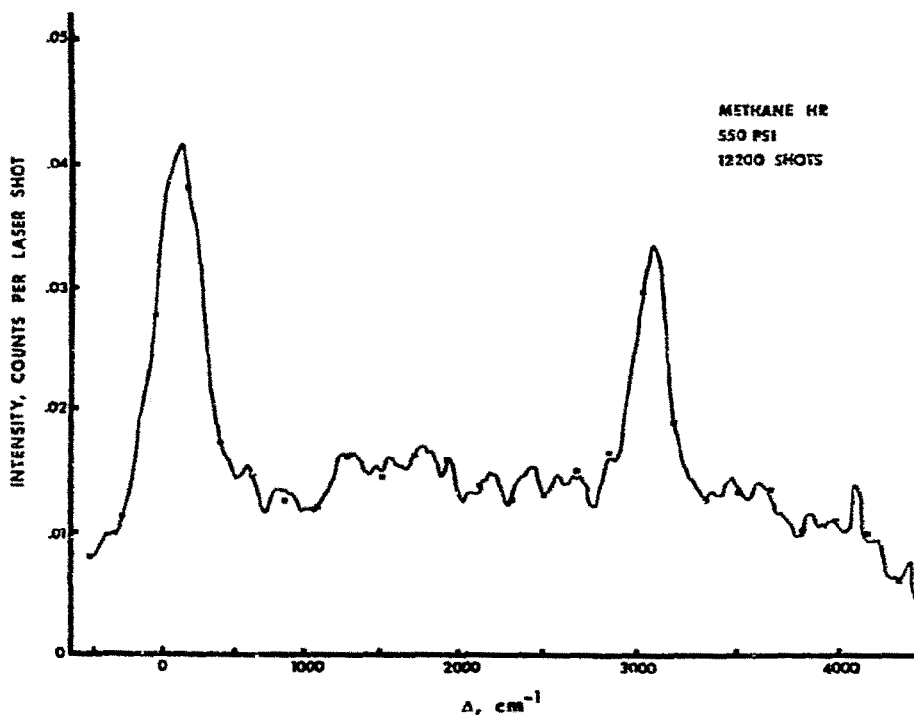

Fig. 1. The hyper-Raman spectrum of methane, under the conditions indicated. Horizontal scale is the hyper-Raman shift, $\Delta = 2\nu_{laser} - \nu_{scattered}$, and vertical scale is the number of counts accumulated divided by the number of laser shots.
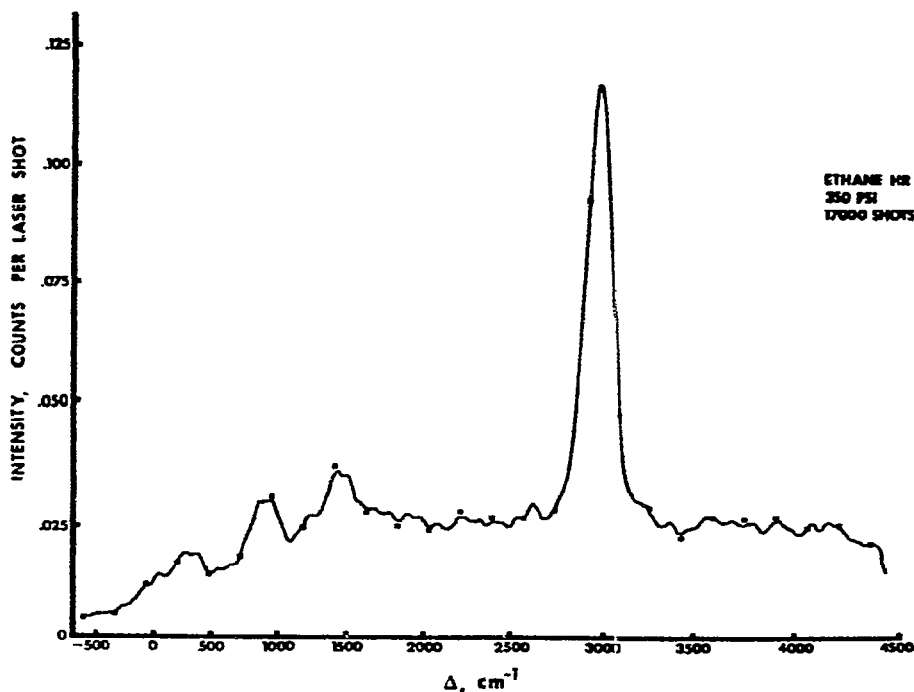
Fig. 2. The hyper-Raman spectrum of ethane; scales as in fig. 1.

(elastic) scattering [1]. Rotational transitions from $\Delta J = 0$ up to $\Delta J = 3$ are allowed in hyper-Raman [2]. The hyper-Raman allowed vibrational transitions may be separated into two classes, those which are also infrared allowed and those which are not. The two classes may be distinguished experimentally by their different polarization properties [3,5].

The present experimental arrangement differs from previous ones [1,2,5] in that an entire spectrum of the scattered light is collected and stored for each laser shot. This considerable economy in data-collecting time is achieved through the use of a multichannel photon counting detector comprised of an image intensifier-television camera-multichannel scaler. Details of the detection system will be published subsequently [6]. The ruby laser beam, of 2 MW peak power and 0.1 microsecond duration, was focused into the gas cell at f:10. The scattered light from the focal volume was collected at approximately f:1. We estimate roughly that the transmission efficiency of the entire system, including the quantum efficiency of the detector, is no greater than 5 per cent. Because of the uncertainty in this figure, relative scattering efficiencies of different molecules cannot be compared to better than a factor of two. No attempt to measure absolute intensities was made.

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The spectra shown below, covering some 5000 cm^{-1}, were stored in a 256 channel analyzer. The presentation shown is a computer fit to a three-point running average with every tenth raw datum point (channel) displayed. The system resolution is limited to that of the television camera tube, about 2 or 3 channels. The rotational envelope varies in width from 200 to 300 cm^{-1} and appears to be the limiting factor in determining band centers.

The spectrum of methane is shown in fig. 1. The two prominent lines, centered approximately at $\Delta = 100$ cm^{-1} and 3050 cm^{-1}($\Delta = 2\nu_{laser} -\nu_{scattered}$), represent 510 and 422 photoevents, respectively, from 12 260 laser shots. These two bands correspond to the non-linear "elastic" scattering and to the hyper-Raman shift due to the C-H stretching frequency $\nu_3(f_2)$. The infrared value for the latter is 3020 cm^{-1} [7]*. A much weaker peak, located roughly at 1300 cm^{-1}, may be matched with the known infrared band of 1306 cm^{-1} assigned as ν_4, also of f_2 symmetry. Note that the elastic peak is extremely weak, hardly stronger than the inelastic C-H stretching band. The shift of 100 cm^{-1} of this band to the Stokes side was predicted and observed earlier by

* All infrared values are from ref. [7].
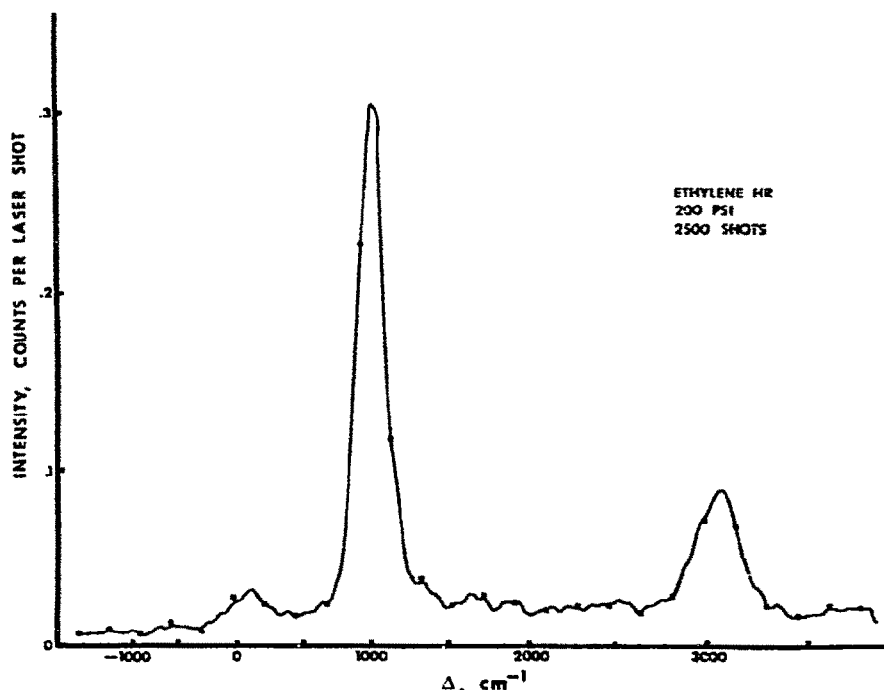
ETHYLENE HR
200 PSI
2500 SHOTS

Fig. 3. The hyper-Raman spectrum of ethylene; scales as in fig. 1.

Maker [5]. We note in passing that this band corresponds to a *pure rotational (hyper) Raman spectrum of a spherical top*.

Fig. 2 presents the hyper-Raman spectrum of ethane taken at 350 psi with 17 000 laser shots. The second harmonic line is totally absent. This is by far the strongest demonstration to date that centrosymmetric molecules do not produce elastic non-linear scattering [1], and at the same time firmly establishes D3d symmetry for ethane. The strong band located at Δ = 2950 cm^{-1} is identified as the overlap of ν_5 (a_{2u}) and $\nu_7(e_u)$ C-H stretching vibrations (infrared values of 2954 cm^{-1} and 2994 cm^{-1} respectively). The weaker band located at 1450 cm^{-1} may be the overlap of $\nu_6(a_{2u}$ and $\nu_8(e_u)$ CH$_3$ deformations, and that at 900 cm^{-1} to the whole molecule bending vibrations $\nu_9(e_u)$. The band at 300 cm^{-1} we can assign to the torsional vibration of symmetry a_{1u}, uniquely hyper-Raman allowed. This is apparently the first direct observation of this fundamental which does not invoke *a combination or difference frequency, or a perturbation to permit observation*. Agreement with the value of 289 cm^{-1} obtained by Weiss and Leroi [8] is reasonable.

Two spectra of ethylene under different polarization conditions are shown in figs. 3 and 4. The first of these was obtained from only 2480 laser shots and represents non-analyzed output scatter-

ing. The broad peak at 3040 cm^{-1} with shoulder toward lower energy is probably an overlap of $\nu_9(b_{2u})$ and $\nu_{11}(b_{3u})$ C-H stretching frequencies with infrared values of 3105 cm^{-1} and 2989 cm^{-1}. The very strong line at 980 cm^{-1} corresponds to the whole molecule bending mode $\nu_7(b_{1u})$, of infrared frequency 949 cm^{-1}. This strong band badly overlaps ν_{10} at 995 cm^{-1} and the predicted position of the torsional mode, $\nu_4(a_u)$, at about 825 cm^{-1} [7, p.326-328]. A weak unexpected second harmonic is seen at 80 cm^{-1}.

Because ethylene proved to have such high scattering power, an experiment with incident radiation circularly polarized and scattered light analyzed with polarization parallel to the scattering plane was performed. The resulting spectrum is shown in fig. 4. This particular observation yields a spectrum which arises from purely hyper-Raman allowed components, or, after Maker [5], a β [3] spectrum. Some caution on this point is advisable; the separation of the β [3] spectrum is not perfect because the finite collection angle permits some β [1] scattering to leak into the detection system. Thus a pure β[3] spectrum is not obtained. The most striking change is the nearly complete loss in intensity of the ν_7 (bending) vibration and the absence of the second harmonic band. This suggests that the two effects may not be independent, and that the unexpected second harmonic

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ETHYLENE PHR
CP IN, VERTICAL PROP
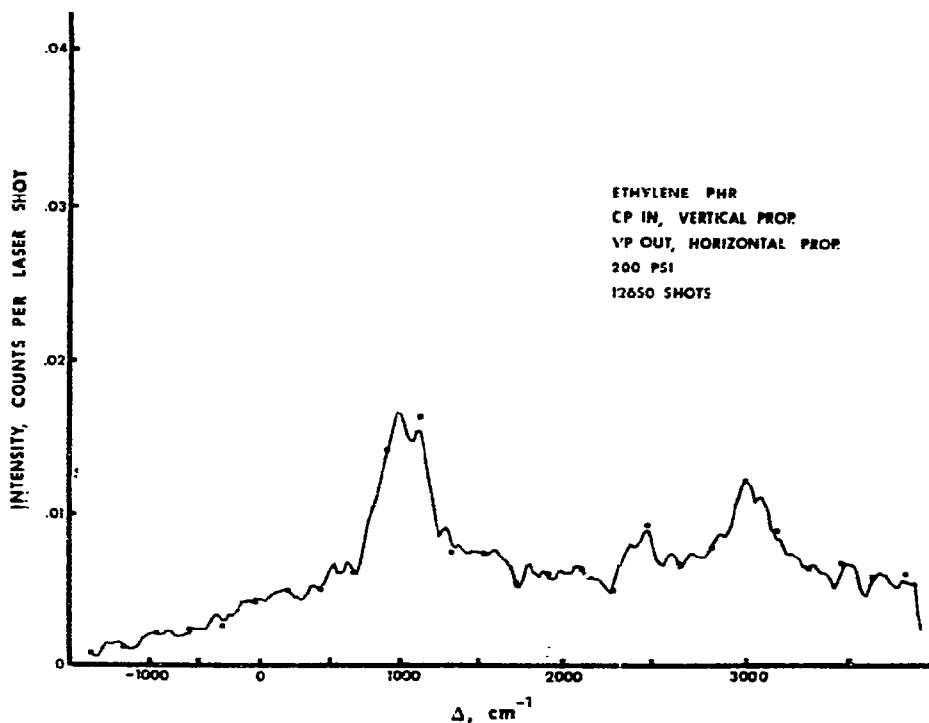VP OUT, HORIZONTAL PROP
200 PSI
12650 SHOTS

Fig. 4. The hyper-Raman spectrum of ethylene under polarization conditions listed in text; scales as in fig. 1.

may derive from the strong molecular bending vibration. We feel that the remaining intensity in the 950 cm^{-1} region represents overlapping of ν_4 and ν_{10}, but are reluctant to assign any numbers to band centers.

Attempts to find the f_{2u} infrared and Raman forbidden mode in octahedral SF_6 were unsuccessful, though 17 000 shots were taken. No bands were observed.

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