

The Absorption of Pulsed CO₂-Laser Radiation by Ethylene at Total Pressures from 25 to 3000 Torr

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Abstract. The absorption of pulsed CO₂-laser radiation by ethylene has been measured at total pressures from 25 to 3000 Torr, using the *P*(12) and *P*(14) lines in the 10.6 μm band, with incident fluences from 0.1 to 0.7 J/cm². Marked deviations from the Beer-Lambert absorption law were observed, with the effective absorption coefficient varying with pressure, fluence, absorption path-length and the addition of non-absorbing gas. Pressure broadening of the rotational lines of the ethylene absorption spectrum was shown to be the major cause of these deviations, together with lesser effects which can be attributed to the rise in temperature of the absorbing gas during the laser pulse.

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Many measurements have been reported of the absorption of infrared radiation from pulsed CO₂ lasers by polyatomic gases, mostly at low pressures (<1 Torr) at which multiphoton absorption occurs under conditions approaching collision-free. Relatively few quantitative studies have been done at higher pressures. Steel and his co-workers measured absorption in NH₃ from 5 to 244 Torr, and in several other gases at pressures up to 50 Torr [1–3], while Blazejowski and Lampe made measurements in PH₃ [4] and SiH₄ [5] at pressures from 10 to 150 Torr. Both these groups found deviations from a simple Beer-Lambert law and fitted their data to empirical equations with several parameters. It is clear that the energy absorbed in such high-pressure systems is a complex function of pressure and fluence, and may vary greatly from gas to gas, depending critically on the characteristics of the absorption spectrum and its overlap with the laser emission lines. The energy absorbed is crucial in determining the chemical reactions that will be induced by infrared laser radiation, and an understanding of the absorption process is essential to an understanding of the chemistry. In conjunction with some recent infrared photochemical studies [6], we have examined some of the factors affecting absorption of pulsed CO₂-laser radiation by ethylene at pressures

from 25 to 3000 Torr; the present paper reports these measurements.

Experimental Methods

A pulsed, line-tuneable CO₂ TEA laser, Lumonics Model 203, was operated at 0.5 Hz, using a gas mixture lean in N₂ to give a relatively short pulse (Fig. 1). The

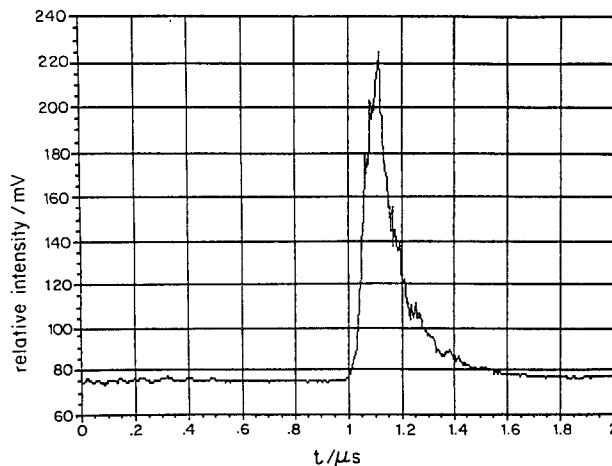


Fig. 1. Time profile of laser pulse; average of 10 pulses measured with a photon-drag detector

output beam was stopped down to a diameter of 0.98 cm, and the optics were carefully adjusted to give a uniform burn pattern on exposed Polaroid film. The absorption cell was a brass annulus with inside and outside diameters of 2 and 5 cm respectively, with NaCl laser-quality windows fixed to each end by Apiezon W wax. Two cells were used, 0.051 and 0.52 cm long. The energy transmitted by the cell was measured by a disc calorimeter (Scientech Model 36-0001) for each pulse, while the incident energy was measured by means of a beam splitter and a pyroelectric detector, carefully calibrated against the calorimeter for the empty cell, with appropriate window corrections, to give accurate values of E_0/E_t , (where E_0 and E_t are the incident and transmitted pulse energies) and thence the absorbance, A , defined in this system as $A = \log(E_0/E_t)$.

The absorption cell was attached to a conventional vacuum line for evacuation and filling. Pressure was measured by a Wallace and Tiernan bourdon gauge. Ethylene was Matheson Research Grade, thoroughly degassed under vacuum but not otherwise purified. Infrared absorbing impurities were negligible, and the sample in the cell was changed frequently so that decomposition was not appreciable.

Results and Discussion

Measurements were made at two laser wavelengths, the $P(12)$ and $P(14)$ lines in the $10.6 \mu\text{m}$ band, with frequencies of 951.19 and 949.48 cm^{-1} , respectively, lying in the central Q -branch of the ν_7 band of the ethylene spectrum (Fig. 2). In Fig. 3 are shown typical plots of absorbance, A , vs. C_2H_4 concentration for the $P(14)$ line at 3 incident fluences, measured in the long (0.52 cm) cell. While the upward curvature indicates a deviation from Beer's law, it is still useful to define an

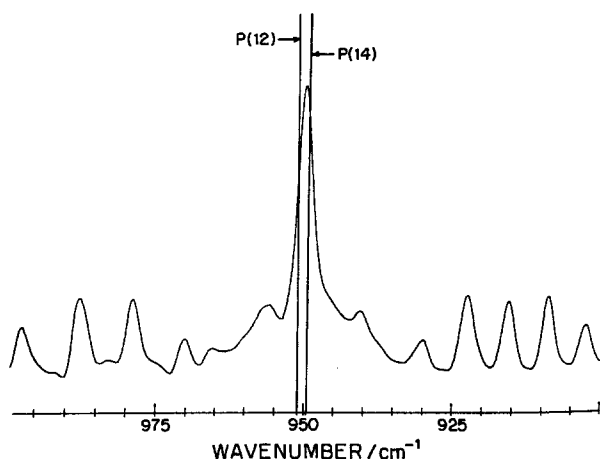


Fig. 2. Low-resolution absorption spectrum of ν_7 band of ethylene showing position of laser lines. Vertical scale is absorbance

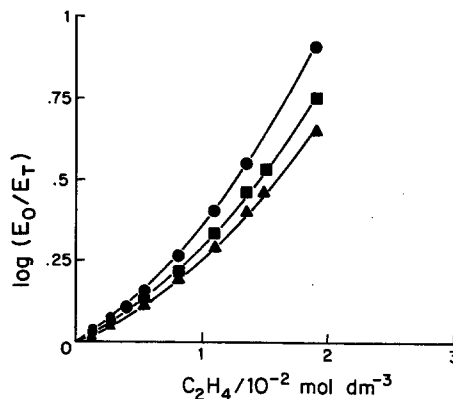


Fig. 3. Absorbance vs. ethylene concentration for the $P(14)$ line. \bullet : $F = 0.10 \text{ J/cm}^2$; \blacksquare : $F = 0.36 \text{ J/cm}^2$; \blacktriangle : $F = 0.69 \text{ J/cm}^2$

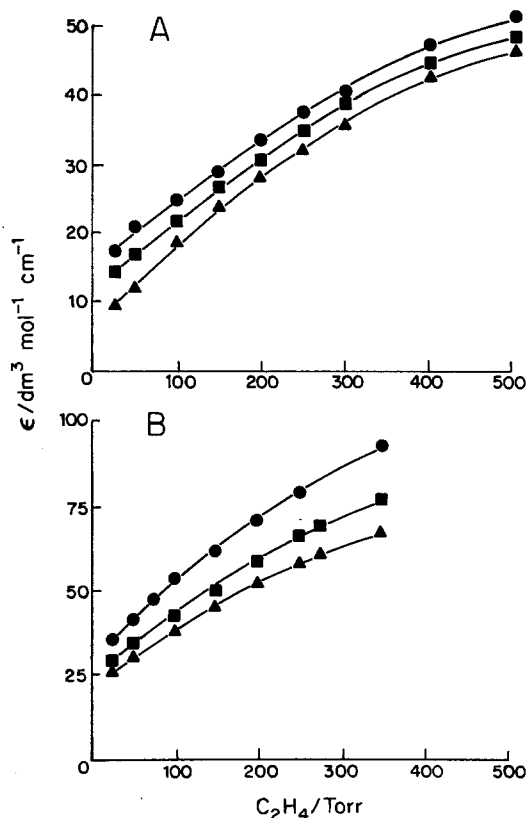


Fig. 4A, B. Molar decadic absorption coefficient vs. ethylene pressure, measured in long cell (0.52 cm). A $P(12)$ line; \bullet : $F = 0.18 \text{ J/cm}^2$; \blacksquare : $F = 0.30 \text{ J/cm}^2$; \blacktriangle : $F = 0.65 \text{ J/cm}^2$. B $P(14)$ line; \bullet : $F = 0.10 \text{ J/cm}^2$; \blacksquare : $F = 0.36 \text{ J/cm}^2$; \blacktriangle : $F = 0.69 \text{ J/cm}^2$

effective absorption coefficient, $\epsilon = A.l.c$, in the usual way (where l : path-length and c : concentration) for each experimental measurement. Plots of ϵ calculated in this way against C_2H_4 pressure are shown in Figs. 4 and 5 for the $P(12)$ and $P(14)$ lines for two ranges of pressure, with data for the higher pressures obtained in the short (0.051 cm) cell. The absorption coefficient ϵ shows a strong pressure dependence in all these

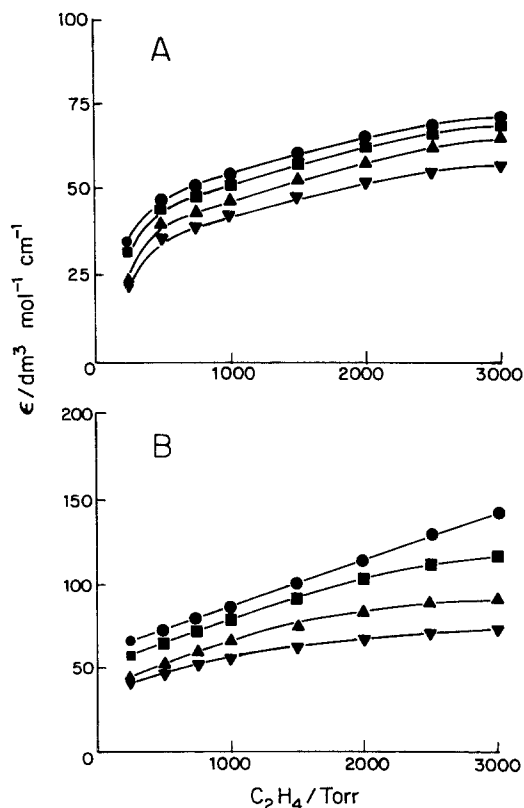


Fig. 5A, B. Molar decadic absorption coefficient vs. ethylene pressure, measured in short cell (0.051 cm). **A** $P(12)$ line; \bullet : 0.20 J/cm²; \blacksquare : 0.29 J/cm²; \blacktriangle : 0.37 J/cm²; \blacktriangle : 0.52 J/cm². **B** $P(14)$ line; \bullet : 0.18 J/cm²; \blacksquare : 0.25 J/cm²; \blacktriangle : 0.38 J/cm²; \blacktriangle : 0.53 J/cm²

measurements. It also depends on fluence, and, less obviously, is lower in the short cell than in the long one under similar conditions of pressure and fluence.

To explore further the pressure dependence, absorption was measured in a series of experiments in which a non-absorbing gas, ethane, was added. In Fig. 6 are shown values of ϵ vs. C_2H_4 pressure for pure C_2H_4 and for 3 different ethane-ethylene mixtures, all measured in the long cell at a single fluence for each line. The marked dependence on added ethane confirms that ϵ is pressure dependent; plots against total pressure (Fig. 7) show that ethane is somewhat more effective than ethylene in enhancing the absorption, especially with the $P(14)$ line.

At the relatively low fluences and high pressures employed, it seems unlikely that depletion of rotational levels resonant with the laser radiation (hole-burning) was of much importance, since extensive rotational relaxation by collision would be expected

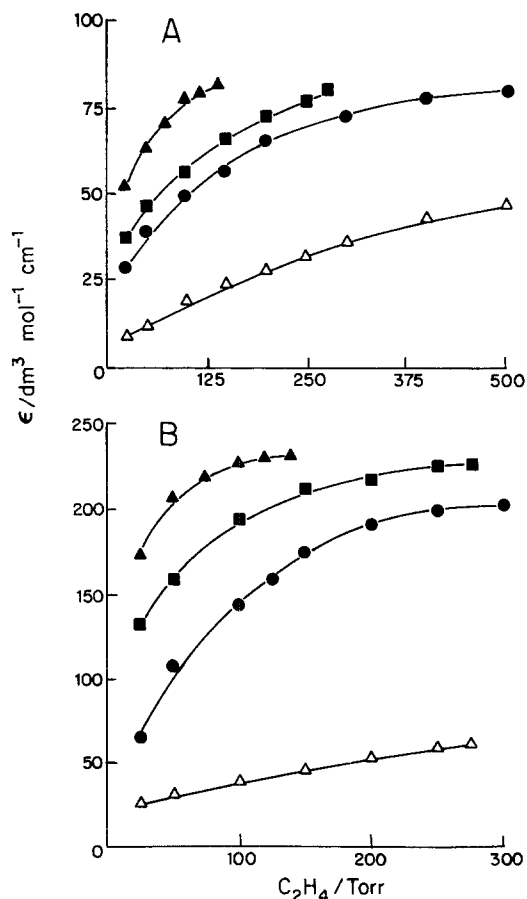


Fig. 6A, B. Molar decadic absorption coefficient vs. ethylene pressure in pure ethylene and in ethylene-ethane mixtures, in long cell (0.52 cm). **A** $P(12)$ line, incident fluence = 0.65 J/cm²; Δ : pure ethylene; \bullet : ethane/ethylene = 5.2; \blacksquare : ethane/ethylene = 10.3; \blacktriangle : ethane/ethylene = 20.8. **B** $P(14)$ line, incident fluence = 0.69 J/cm²; Δ : pure ethylene; \bullet : ethane/ethylene = 5.2; \blacksquare : ethane/ethylene = 10.3; \blacktriangle : ethane/ethylene = 20.8

during the pulse; the strong dependence of absorption on pressure cannot therefore be attributed to enhanced collisional relaxation. The most probable cause of the pressure dependence would appear to be instead the pressure broadening of the sharp features of the ethylene spectrum. To examine this, measurements were made with a Bomem FTIR spectrometer with a resolution of 0.05 cm⁻¹; the absorption spectrum of C_2H_4 near the $P(12)$ and $P(14)$ lines at 4 different total pressures is shown in Fig. 8. While individual rotational lines are not resolved, pressure broadening is evident, and with the laser lines lying on the shoulders of strong features rather than coincident with them, absorption will tend to be enhanced by the broadening. To explore further these effects, we have plotted in Fig. 9 calculated profiles for the rotational lines of ethylene close to the $P(14)$ laser line. Absorption line positions and relative intensities are taken from the very high-resolution measurements of Herlemont,

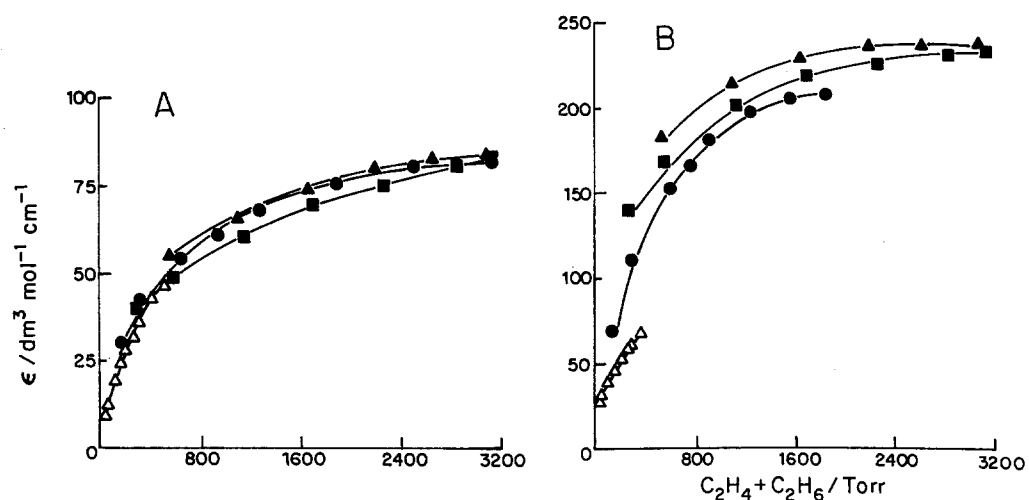


Fig. 7A, B. Molar decadic absorption coefficient vs. total pressure in pure ethylene and in ethylene-ethane mixtures, data from Fig. 6; legend as in Fig. 6

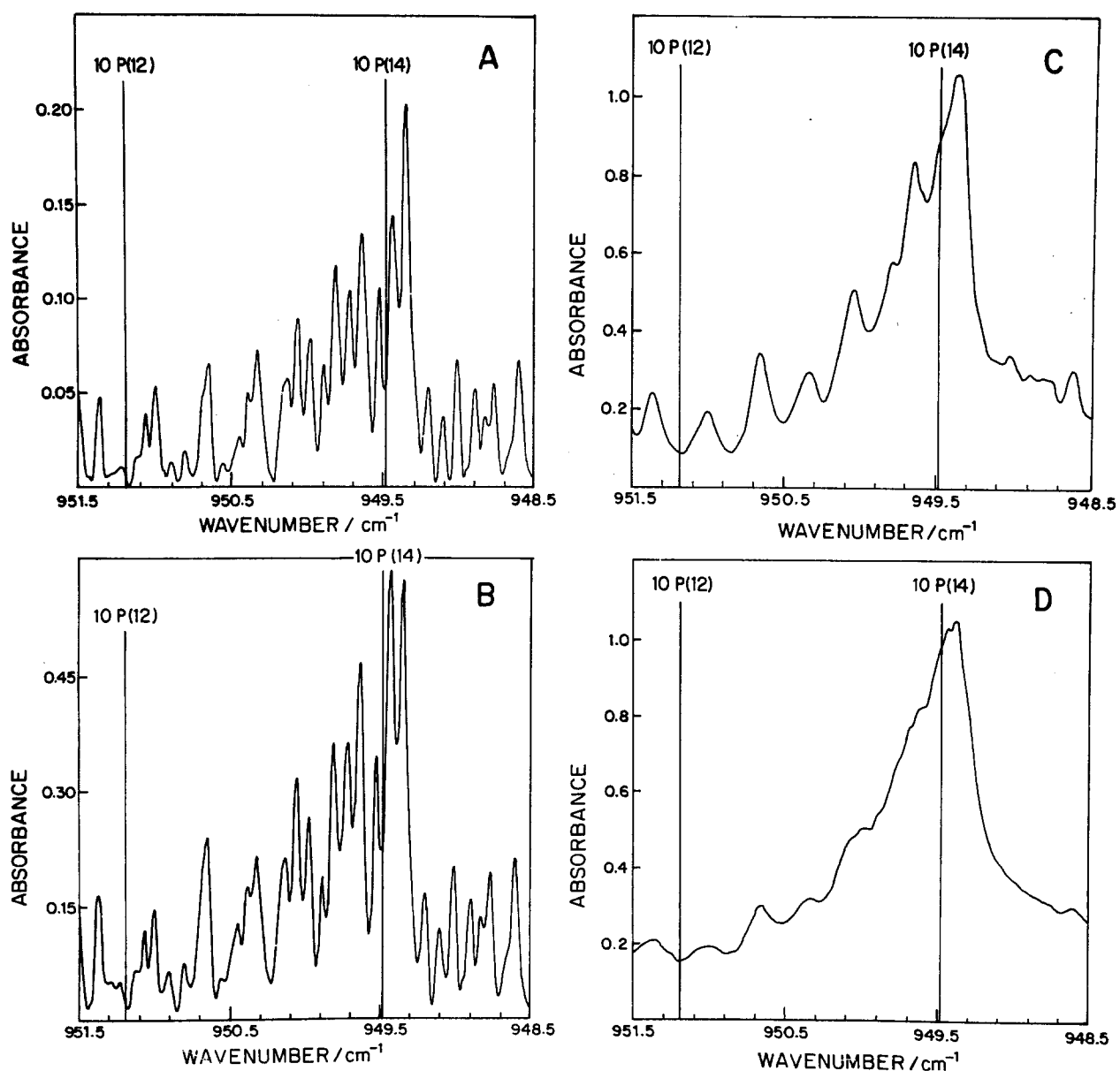


Fig. 8A-D. High-resolution FTIR absorption spectrum of ethylene; [A pure ethylene, (1 Torr); B pure ethylene, (5 Torr); C ethylene (5 Torr)+ethane (375 Torr); D ethylene (5 Torr)+ethane (755 Torr)]

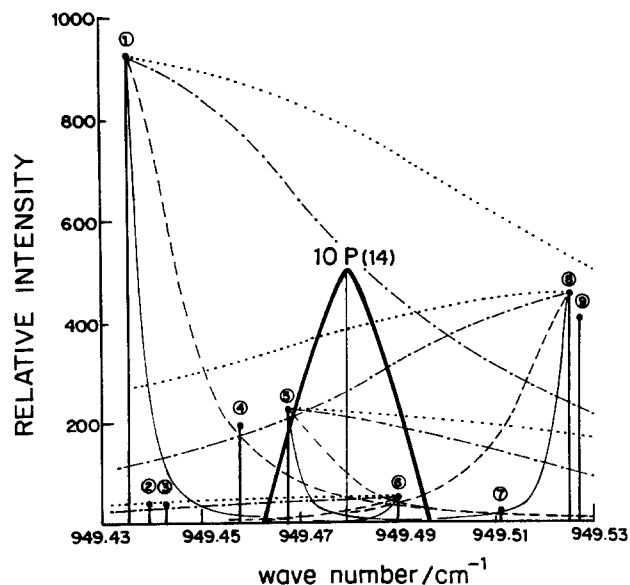


Fig. 9. Calculated profiles for ethylene absorption lines within $\pm 0.05 \text{ cm}^{-1}$ of the $P(14)$ laser emission line, for several pressures of ethylene. See text for details. — = 25 Torr; --- 100 Torr; - · - · 500 Torr; · · · · 1000 Torr. Each absorption line profile has been normalized to the same maximum intensity at all pressures; for true assessment of overlap, intensities should be scaled down by factors proportional to pressure. For clarity profiles have been drawn for only 4 of the 9 lines shown. At higher pressures, other lines further from resonance (not shown) will contribute to absorption

Lambeau et al. [7] while Lorentzian profiles were calculated from the pressure-dependent linewidth of $2.1 \times 10^{-4} \text{ cm}^{-1} \text{ Torr}^{-1}$ reported for ethylene by Tejwani and Yeung [8]. Also shown is a somewhat arbitrary profile for the laser line, based on reported gain profiles and making some allowance for narrowing by the tuning grating. The profiles shown in Fig. 9, while approximate, illustrate the way in which pressure broadening of the single rotational lines of the ethylene spectrum can be expected to enhance the overlap with the laser lines and hence the absorption. It appears that most of the pressure dependence of ϵ can probably be accounted for by line broadening, although a quantitative treatment of these effects would be difficult.

There still remain several lesser deviations from a simple absorption law that require explanation: 1) At constant pressure, ϵ in pure ethylene showed an inverse dependence on fluence, and was larger in the long cell (Fig. 4) than in the short one (Fig. 5); 2) At the same total pressure and otherwise similar conditions, values of ϵ were substantially higher in ethylene-ethane mixtures than in pure ethylene (Fig. 7); 3) These effects were more pronounced with the more highly absorbed $P(14)$ line than with the $P(12)$.

All these observations can be explained if ϵ is assumed to decrease with increasing temperature. Ethylene is substantially heated by the laser pulse, and

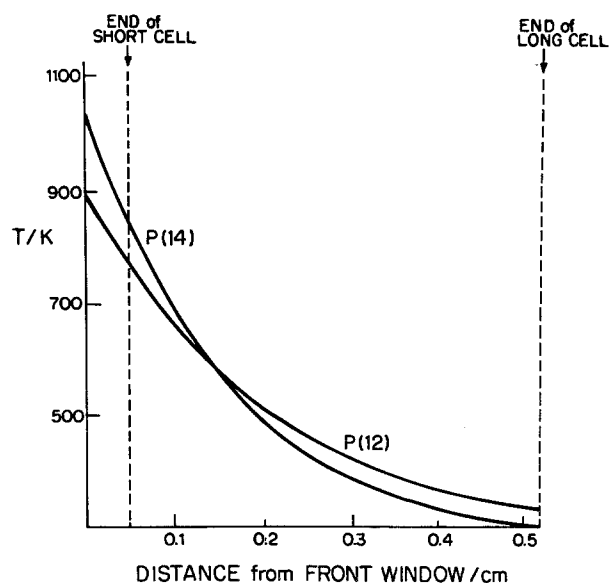


Fig. 10. Calculated temperature profiles in absorption cells for an ethylene pressure of 1000 Torr and incident fluence of 0.3 J/cm^2

the extent of this heating will depend in an obvious way on fluence, the difference in ϵ between the two laser lines, and the presence of ethane diluent. Dependence on the length of the cell arises from the greater attenuation of the laser beam in traversing the longer cell and the consequent smaller average temperature rise (see Fig. 10, above). In assessing the effect of temperature, it is reasonable to assume that at the high pressures and relatively low fluences employed, extensive collisional equilibration of rotational and vibrational energy occurred during the pulse. Measurements of vibrational-to-translational energy transfer in ethylene [9] suggest that at pressures below 1000 Torr, the translational temperature probably lagged somewhat behind the vibrational-rotational temperature; this should, however, have little effect on our subsequent arguments. Figure 10 shows typical temperature profiles in the absorption cell at the end of the laser pulse, calculated from heat-capacity data and our measured values of ϵ , assuming complete thermalization of the absorbed energy, and no energy loss. The temperature during each pulse would rise from 300 K to the values shown, and the effective temperature of the absorbing gas would be a rather complex average over the duration of the pulse and the length of the cell.

Under these conditions of approximate thermalization of the absorbed energy, the most probable cause of a decrease in ϵ with increasing temperature would appear to be the simple thermal population of excited vibrational states of ethylene, and the consequent depopulation of the vibrational ground state. Approximate Boltzmann calculations of relative vibrational state populations are shown in Table 1 for three

Table 1. Approximate thermal equilibrium populations of vibrational states of ethylene

Vibrational state	Energy/cm ⁻¹ above ground state	300 K		650 K		1000 K	
		Boltzmann factor	Fraction of molecules in state	Boltzmann factor	Fraction of molecules in state	Boltzmann factor	Fraction of molecules in state
ground	0	1.0	0.950	1.0	0.588	1.0	0.380
$v_{10}=1$	825.9	0.019	0.018	0.161	0.095	0.305	0.116
$v_8=1$	940.1	0.011	0.010	0.125	0.073	0.258	0.098
$v_7=1$	948.8	0.010	0.007	0.122	0.072	0.255	0.097
$v_4=1$	1026.4	0.007	0.003	0.103	0.060	0.228	0.086
$v_6=1$	1222.0	0.003	0.002	0.067	0.039	0.172	0.065
$v_3=1$	1345.5	0.002	0.001	0.051	0.030	0.144	0.055
$v_{12}=1$	1443.5	0.001	0.0	0.041	0.024	0.125	0.047
$v_2=1$	1625.4	0.0	0.0	0.027	0.016	0.096	0.036

In calculating the fraction of molecules in each state, molecules containing more than one quantum of vibrational excitation were ignored. The four C-H stretching modes have been omitted from the table since they accounted for a total of less than 2% of the population at 1000 K.

temperatures. In calculating these data, molecules having more than one quantum of vibrational excitation were neglected; the errors thereby introduced are small at these temperatures.

The effect of this thermal vibrational excitation is twofold. The first and most direct effect comes from the population of $v_7=1$, the upper level of the absorbing transition. Stimulated emission from this level will detract from the net absorption; the concentration term in Beer's law must be replaced by $c_0 - c_1$, where c_0 and c_1 are concentrations of molecules with $v_7=0$ and 1; the apparent value of ϵ will be reduced by a factor $(c_0 - c_1)/c_0$, which from Table 1 has a value of 0.745 at 1000 K.

The second effect on the absorption comes from the depletion of the vibrational ground state, and is less easy to assess. Thermal excitation of any of the vibrational modes leaves the ethylene molecule still capable of absorbing in the v_7 mode, but with a small shift in frequency. The change is probably largest for excitation of v_7 itself, for which the shift is simply the anharmonicity of the v_7 vibration. For excitation of other modes, the shift is generally not accurately known, but is probably less than 1 cm^{-1} ; it is probably still sufficient to shift the absorption away from the multiple close resonances with the laser lines which are responsible for their strong absorption (Fig. 9). If as an extreme limiting case these shifts reduced the absorption to zero, then the depopulation of the ground vibrational state would be directly reflected in the reduction of ϵ . From Table 1, for example, the fraction of molecules remaining in the vibrational ground state at 1000 K is 0.38, and a maximum reduction of ϵ by this factor could be expected; in fact, it is probably much less.

A quantitative assessment of changes in ϵ due to these thermal effects would not be easy, not only because of uncertainties in the result of depopulating the ground state, but also because of the variation of radiation flux during the pulse and along the axis of the cell. The effects observed, however, appear to be in qualitative agreement with those expected from the thermal population of excited vibrational states. Alternative explanations are not attractive. Non-equilibrium depopulation of absorbing levels ("hole-burning") would not appear to be important at the pressures and fluences employed. Radial expansion of the heated gas, with consequent decrease in the density in the absorbing gas, and related thermal lensing effects, are too slow to have affected the absorption measurements [6, 10].

Finally, the relatively low levels of excitation reached in the present work should be noted. For example, for the $P(14)$ line, $\langle N \rangle$, the average number of photons absorbed per molecule in a single pulse, had a maximum value of ~ 6 at the front window for a typical incident fluence of 0.3 J/cm^2 at 3000 Torr. This decreased to a value of ~ 1 at 25 Torr, reflecting the pressure dependence of ϵ , and decreased with attenuation along the cell. Given the rapidity of inter- and intra-molecular energy transfer at high pressures, most of the absorption will have been from low levels of v_7 . The characteristics of the absorption of laser radiation under these conditions are very different from those in the low-pressure multiphoton unimolecular decomposition regime in which individual molecules are pumped to much higher levels, requiring much higher fluences. The absorption process is nonetheless complex, as the present measurements have shown, with major complications arising from pressure broadening

and minor ones associated with the effects of heating. We have made no attempt to fit the experimental data to an empirical equation describing the dependences on pressure and fluence as has been done in other systems [1–5], but have tried instead to understand these dependences in terms of spectroscopic parameters of the absorbing molecule and the laser emission. These are highly specific to a particular system, and it seems doubtful whether any general expression can be found which would be widely applicable in describing or predicting absorption behaviour of molecular gases.

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