Raman Spectroscopic Studies of Methane–Ethane Mixtures as a Function of Pressure

S. BRUNSGAARD HANSEN, R. W. BERG,* and E. H. STENBY

Department of Chemistry (S.B.H., R.W.B.) and Engineering Research Center, IVC-SEP, Department of Chemical Engineering (S.B.H., E.H.S.), Technical University of Denmark, DK-2800 Lyngby, Denmark

Raman spectra of methane and methane–ethane mixtures (100, 85, and 49 mole % CH_4) have been obtained as a function of pressure in the pressure range 0.1 to 15.3 MPa_A (MPa absolute). For these mixtures methane ν_1 (symmetric C–H stretching) band positions are given as a function of pressure; for pure methane they are in agreement with previous results. The new data on the methane ν_1 band position of ethane-containing mixtures clearly depend on the kind of molecules surrounding the vibrating methane molecule. The ν_1 band position decreases with increasing pressure; the stronger the dependency, the higher the content of ethane. The ethane ν_1 band position in the two mixtures showed the same kind of dependency. A qualitative explanation for this behavior is attempted, relating it to changes in van der Waals-type interactions on pressure.

Index Headings: **Raman spectroscopy; High pressure; Methane; Methane–ethane mixtures; van der Waals interaction.**

INTRODUCTION

Raman spectroscopic studies of methane-containing gases in previous studies[1–4] have shown peak position shifts as a function of pressure, indicating that the molecular vibrations in methane are influenced by its surroundings, i.e., composition and density. Recently we studied the Raman spectra of some natural gas samples.[5] Since ethane is the second most abundant component in natural gas, we found it of interest to investigate the influence of the presence of ethane on the vibrational levels of methane. Such a study has not been done previously and should be of use when analyzing methane gas mixtures.

In the following we report Raman spectra of pure methane and of two methane–ethane mixtures. The methane ν_1 band position is presented as a function of pressure and compared to the literature values known for pure methane. The ethane ν_1 band position as a function of pressure for the two mixtures is also presented. We have omitted measurements at pressures higher than 40 MPa_A (MPa absolute) because we selected pressure gauges limited to 40 MPa to obtain a high relative precision and because the overall purpose was to obtain information on the analysis of distributed natural gas and fluid inclusions in rocks (determination of total pressure or sample composition).

EXPERIMENTAL

High-Pressure Cells. Two different cells were used: a so-called tube cell and a so-called titanium cell. The tube cell has been developed for totally representative Raman measurements of natural gas. The design and construction of the cell are described in detail in Ref. 5. The titanium cell has a modified construction somewhat similar to the cells described in Refs. 6–8. The construction of the titanium cell used for the present experiments is described in detail in Ref. 9.

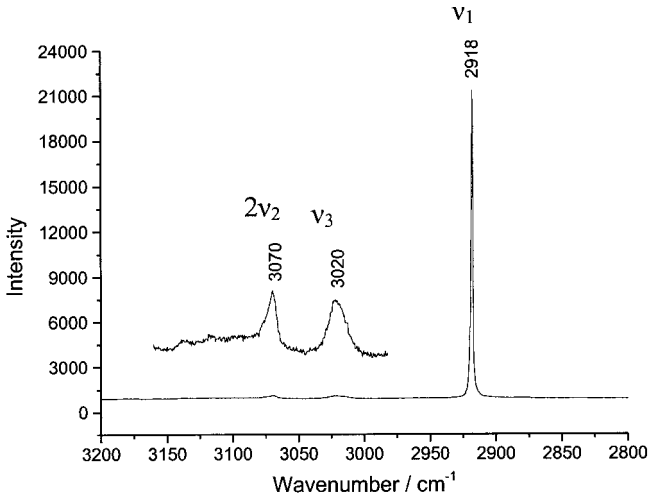

FIG. 1. The Raman spectrum (3200–2800 cm^{-1}) of methane obtained in the tube cell at 8.1 MPa_A. A fraction of the spectrum has been expanded by a factor of 15.

Gas Samples. Two gases from Hede Nielsen A/S were used: methane (99.995%) and ethane (99.95%). Two methane–ethane mixtures were prepared (mole fractions of CH_4, $X(CH_4)$ = 0.49 and 0.85 ± 0.01). A natural gas sample from the Nybro Gas Treatment Plant, Denmark, was also used.

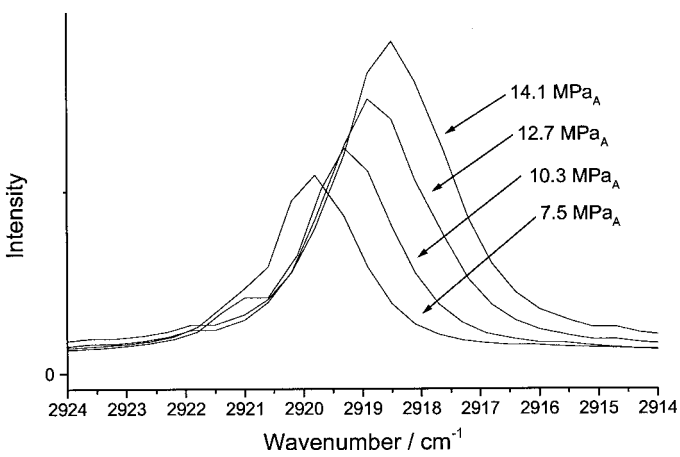

FIG. 2. The Raman spectra of methane in the ν_1 C–H symmetric stretching region obtained at four different pressures.

Received 26 June 2000; accepted 6 February 2001.
* Author to whom correspondence should be sent.

0003-7028/01/5506-0745$2.00/0

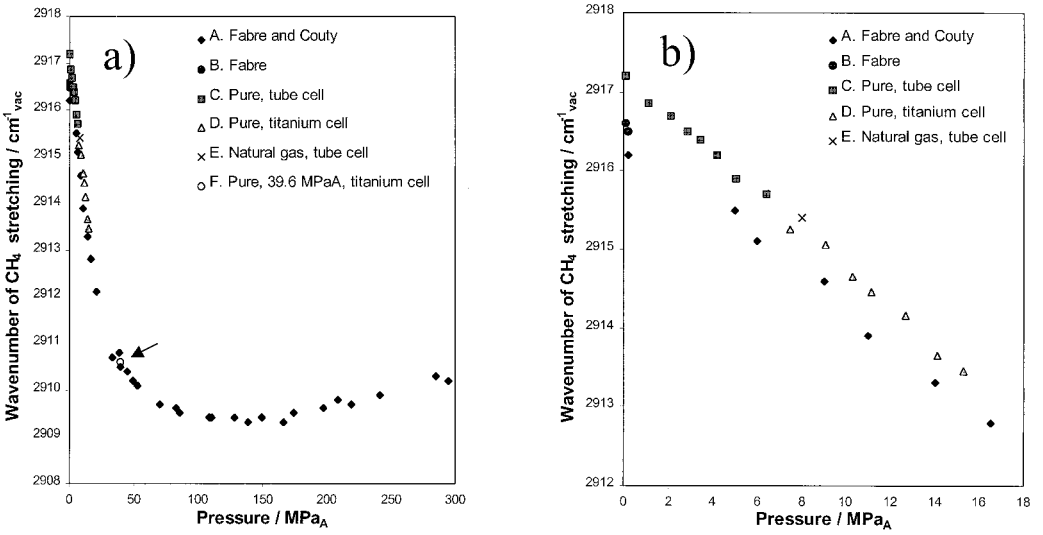

FIG. 3. The methane ν_1 band position as a function of pressure; **(a)** entire range and **(b)** expansion at lower range. (***A***) Ref. 1; (***B***) Ref. 12; (***C***) pure methane sample obtained in the tube cell; (***D***) pure methane sample measured in the titanium cell; (***E***) natural gas sample from the Nybro Gas Treatment Plant, 8.0 MPa_A, measured in the tube cell; and (***F***) pure methane, 39.6 MPa_A, measured in the titanium cell.

Raman Spectroscopy. Raman spectra of the gases were obtained with a DILOR-XY Raman spectrometer (Dilor, France). The collection geometry was (1) 180° for the titanium cell and (2) 90° for the tube cell. The excitation source was an Ar-ion laser (514.5319 nm_{air}, ~200 mW). All spectra were acquired by use of a spectrograph with a grating of 1800 grooves per mm. The scattered radiation was detected by a liquid nitrogen-cooled charge-coupled device (CCD) detector (1024 × 256 pixels). Rayleigh filtration was done with a holographic Super notch filter from Kaiser Optical Systems, Inc. (Ann Arbor, Michigan).

RESULTS AND DISCUSSION

The Raman spectrum (3200–2800 cm^{-1}) of pure methane at 8.1 MPa_A is presented in Fig. 1. The methane ν_1 band at ~2918 cm^{-1} is by far the most intense one in the spectrum. A part of the spectrum is shown in an expanded version, so that two other much weaker bands become obvious. The band at ~3020 cm^{-1} is the methane ν_3 (asymmetric C–H stretching), and the band at ~3070 cm^{-1} is the overtone of the methane ν_2 (C–H asymmetric bending).[5] Some of the rotational-vibrational transitions belonging to the ν_3 at ~3137 and ~3115 cm^{-1} are also observed.

In Fig. 2 Raman spectra of the methane ν_1 band obtained at four different pressures are presented. Three things are worth noting as the pressure is raised: the intensity increases, the wavenumber position decreases, and the bandwidth broadens. The first observation is due to a higher concentration of gas molecules with increasing pressure. The wavenumber shifts of the ν_1 band as a function of pressure are relatively small (within 1–2 cm^{-1}). Before discussing these shifts it is therefore important to verify the wavenumber calibration of the spectra. Calibration was done by obtaining the methane spectra simultaneously with the light from a neon lamp. Four neon lines in these spectra were compared to the same lines from the literature[10] occurring at the wavelengths λ_{vac}: 613.01462, 609.78503, 607.60198, and 603.16670 nm_{vac}. These values correspond to vacuum wavenumber shifts of 3116.9443, 3030.5471, 2971.6265, and 2850.6044 cm^{-1}, respectively, when using the Ar-ion laser (514.5319 nm_{air},[11] 514.67417 nm_{vac}[10]) as the exciting source. The averaged difference between the observed neon lines and the literature values was used to calibrate all band positions. In Fig. 3 the calibrated methane ν_1 band position as a function of pressure is presented. Series C and D (squares and triangles) indicate values obtained from methane in the tube cell and the titanium cell, respectively (data points are given in Table I). In Fig. 3 values from the literature[1] are also included, series A (calibration was done by use of an argon spectral line taken to occur at 2912.8 cm^{-1}). In Fig. 3a the entire pressure range is shown. In order to present some details at lower pressures, an expansion is given in Fig. 3b. Our values are in quite close agreement with the literature except for one value, the ν_1 band position at 2916.2 $cm^{-1}{}_{vac}$ for a pressure of ~2 bar (~0.2 MPa_A). Private communication with Prof. Philippe Marteau clarified that the first three values in the table of Ref. 1 were in error.[12] The values, corrected by D. Fabre,[12] are listed in Table II, and two values are included in Fig. 3 (series B). These corrected values are in closer agreement with our results. The slopes of regression lines are almost the same, but literature values are generally lower than ours (~0.5 cm^{-1}). A high-pressure measurement at 39.6 MPa_A is included in Fig. 3a (indicated with an arrow); as seen, this value is in close agreement with the literature.[1]

In Fig. 3a methane ν_1 value (2915.4 $cm^{-1}{}_{vac}$) for a natural gas sample at 8.0 MPa_A is also included. By comparing this value with the ν_1 values for pure methane, we see that the natural gas value is slightly higher (0.3 cm^{-1}). Similar ν_1 shifts, depending on the pressure, have been found for CH_4–N_2 mixtures,[2,3] CH_4–CO_2 mixtures,[3,4] and equimolar mixtures of CH_4 with H_2, Ar, and CO_2.[3] Since ethane is present in the next largest amount in natural (methane) gas, it was of interest to investigate the influence of the presence of ethane on the methane ν_1 band position.

TABLE I. Measured ν_1 wavenumber position for pure CH_4 and two methane/ethane mixtures as a function of total pressure.

	← ν_1 methane →			← ν_1 ethane →	
P_{total} (MPa_A)	CH_4 (cm^{-1}_{vac})	$X(CH_4)$: 0.85 (cm^{-1}_{vac})	$X(CH_4)$: 0.49% (cm^{-1}_{vac})	$X(C_2H_6)$: 0.15 (cm^{-1}_{vac})	$X(C_2H_6)$: 0.51 (cm^{-1}_{vac})
0.1	2917.2				
0.4			2916.8		
1.0		2916.8	2916.8		2898.5
1.1	2916.9				
2.0			2916.2		2898.4
2.1	2916.7				
2.4		2916.5		2898.8	
2.9	2916.5		2916.1		2898.2
3.4		2916.3		2898.7	
3.5	2916.4				
4.2	2916.2	2916.1		2898.4	
5.0			2915.3		2897.2
5.1	2915.9				
5.9			2915.2		2896.8
6.4	2915.7				
6.5		2915.4		2897.7	
7.0			2914.5		2896.2
7.5	2915.3				
8.0			2914.0		2895.6
9.0			2913.8		2895.0
9.1	2915.1				
10.3	2914.7				
10.4		2914.5		2896.5	
11.1	2914.5				
12.7	2914.2				
13.0		2913.8		2895.7	
14.1	2913.7				
15.3	2913.5				
39.6	2910.6				

The methane ν_1 band positions in two methane–ethane mixtures, with mole fractions $X(CH_4) = 0.85$ and $X(CH_4) = 0.49$, were measured and compared with the methane ν_1 band positions in pure methane. The results are presented in Fig. 4 (data points are given in Table I). Tendency lines have been calculated by regression to guide the eyes: one line connecting the points in series C and D (pure methane), one line connecting the points in series E, and finally, a line for series F. It is seen that the regression line for the mixture with high methane content [$X(CH_4) = 0.85$] lies lower than the line for pure methane, and the regression line combining the values for the equimolar mixture is even lower. This result means that the decreasing effect on the methane ν_1 band position with increasing pressure is enhanced when a higher fraction of ethane molecules surround the methane molecule. For a methane–nitrogen mixture [$X(CH_4) = 0.55$], Fabre and Oksengorn[2] have presented data indicating that the presence of nitrogen affects the slope of the methane ν_1 vibration vs. pressure, so that it becomes lower than for pure methane; i.e., the line lies higher.

A qualitative explanation for the red shifts of the vibrational frequencies on pressure is as follows: At high pressures, under which condition each methane molecule on average is closely surrounded by other methane mol-

TABLE II. Corrected methane ν_1 wavenumber positions as a function of pressure, given by S. Fabre.[12]

P (MPa)	ν_1 (cm^{-1})
$0.1 < P < 0.2$	2916.6
0.2	2916.5
<1.0	2916.4

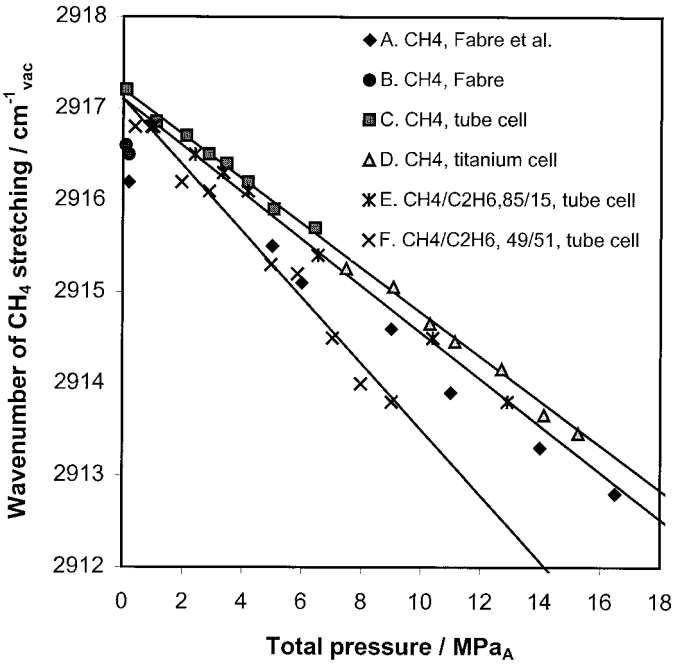

FIG. 4. The methane ν_1 band position as a function of total pressure. (***A***) Ref. 1, pure methane; (***B***) Ref. 12, pure methane; (***C***) pure methane sample obtained in the tube cell; (***D***) pure methane sample obtained in the titanium cell; (***E***) methane–ethane mixture, $X(CH_4) = 0.85$, $X(C_2H_6) = 0.15$, obtained in the tube cell; and (***F***) methane–ethane mixture, $X(CH_4) = 0.49$, $X(C_2H_6) = 0.51$, obtained in the tube cell.

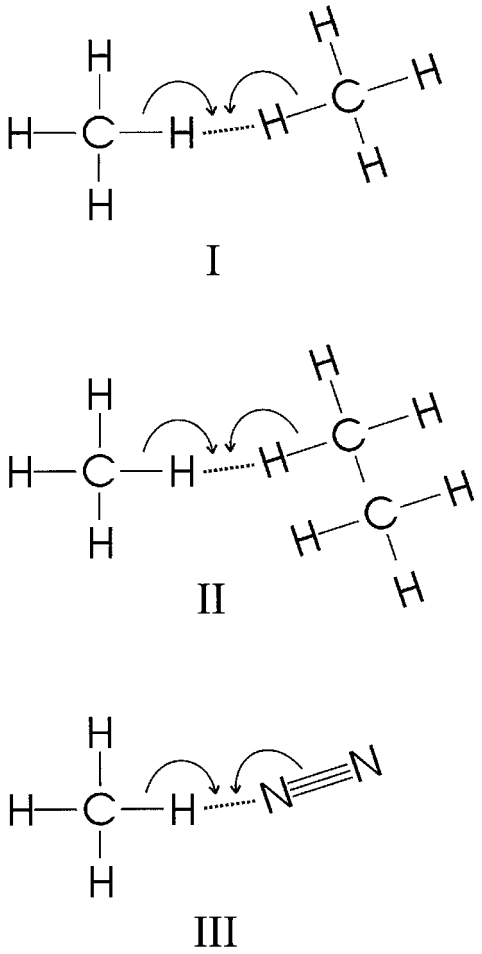

FIG. 5. Illustration of the qualitative explanation of the pressure dependence of vibrational band position shifts based on minute average charge redistributions evidenced by van der Waals interaction between molecules: **(I)** methane–methane, **(II)** methane–ethane, and **(III)** methane–nitrogen.

ecules, the van der Waals interaction is enhanced. At the same time, the ν_1 band wavenumber position has decreased, indicating that the C–H bond strength has also decreased. This result shows that some small amount of charge must have moved, as indicated in Fig. 5. The effect (minute average charge redistributions due to van der Waals interaction) is considered to be strong for methane interacting with methane, even stronger with ethane, and not so strong with nitrogen. According to this explanation the C–H bond strength weakening in methane should go up from methane interacting with N_2 to methane interacting with methane and to ethane interacting with methane. This pattern is reflected in the frequency of ν_1, which is lower for weaker C–H bonds. The nitrogen ν_1 band decreases with increasing pressure in pure nitrogen[2] and more for a methane-nitrogen mixture than for pure nitrogen. Similar interactions have been found previously for pure gases (H_2, CO, N_2) and mixtures (H_2-He, H_2-Ar).[13]

The same trend should be observed for the vibrations of ethane in the mixtures. In Fig. 6 the ethane ν_1 stretching wavenumber position ($\sim$2901 $cm^{-1}{}_{air}$) is plotted as a function of total pressure for the two methane–ethane mixtures, i.e., $X(C_2H_6)$ 0.15 and 0.51 (data points are given in Table I). In Fig. 6 tendency lines have not been

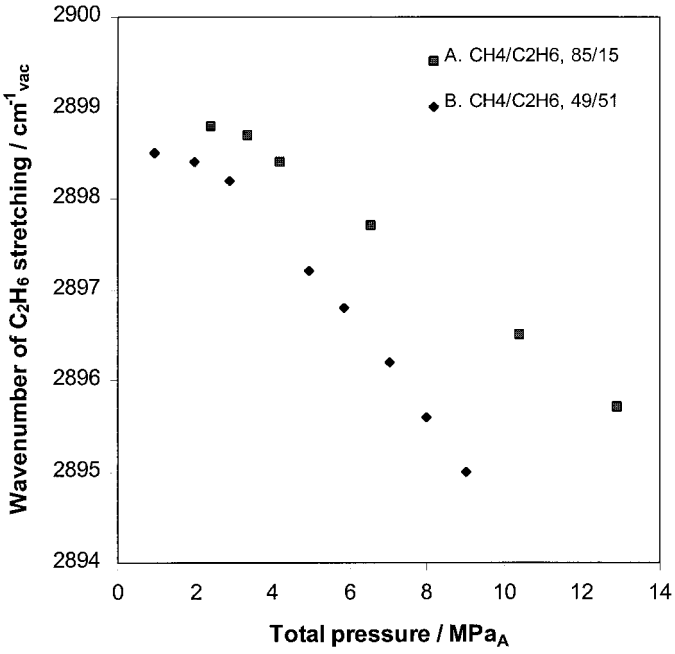

FIG. 6. The ethane ν_1 band position as a function of total pressure in methane–ethane mixtures. **(*A*)** $X(CH_4) = 0.85$, $X(C_2H_6) = 0.15$, and **(*B*)** $X(CH_4) = 0.49$, $X(C_2H_6) = 0.51$.

included because it appears that the points follow a non-linear curve. It is, however, clearly seen that the points for the high ethane mixture, $X(C_2H_6) = 0.51$, lie lower than the curve for the mixture with low ethane content, $X(C_2H_6) = 0.15$. This observation is in accordance with the charge redistribution explanation given above.

CONCLUSION

It has been shown that two high-pressure cells, available in our laboratory, give consistent results. The methane ν_1 band position as a function of pressure is shown in Fig. 3. Our values are in quite close agreement with (though a little higher than) the values of the literature,[1] and agreement was obtained with respect to the slope of tendency lines. New data for the methane ν_1 band position were obtained for two methane–ethane mixtures, $X(CH_4)$ 0.85 and 0.49. In comparison to pure methane, the decreasing effect on the methane ν_1 band position with increasing pressure is enhanced if the vibrating methane molecules are surrounded by ethane molecules. A qualitative explanation is given, relating these new observations to the electron density changes evidenced by van der Waals type interactions similar to what has been seen earlier in other gases. The position of the ethane ν_1 stretching band as a function of total pressure has also been measured, and the results are in accordance with the same explanation. Further studies of other methane mixtures would be useful to further verify the effect. More data are needed if, in particular, the total pressure in methane-containing mixtures is to be determined, e.g., for natural gas samples and inclusions in rocks.

ACKNOWLEDGMENTS

Professor Ph. Marteau, Université Paris Nord, developed the original piston cell in cooperation with the French ROP company and is thanked

for stimulating discussions and for the contact with D. Fabre. T. Lindgren and S. Dalsager, DONG A/S (the National Oil and Gas Company of Denmark), and S. I. Andersen, P. V. Andersen, T. T. Dang, and T. Langhoff, DTU (Technical University of Denmark) are thanked for cooperation, stimulating discussions, and technical support. DONG A/S developed the natural gas sample and contributed a Ph.D. grant, the rest of which came from the Danish Technical Research Council and the Nordic Energy Research Program.

1. D. Fabre and R. Couty, C. R. Acad. Sci. Paris **303,** série II, 1305 (1986).
2. D. Fabre and B. Oksengorn, Appl. Spectrosc. **46,** 468 (1992).
3. J. C. Seitz, J. D. Pasteris, and I.-M. Chou, Am. J. Sci. **293,** 297 (1993).
4. J. C. Seitz, J. D. Pasteris, and I.-M. Chou, Am. J. Sci. **296,** 577 (1996).
5. S. Brunsgaard Hansen, R. W. Berg, and E. H. Stenby, Appl. Spectrosc. **55,** 55 (2001).
6. Ph. Marteau, J. Obriot, and R. Tufeu, J. Supercrit. Fluids **8,** 20 (1995).
7. Ph. Marteau, P. Tobaly, V. Ruffier-Meray, and A. Barreau, Fluid Phase Equilibria **119,** 213 (1996).
8. Ph. Marteau, J. Obriot, A. Barreau, V. Ruffier-Meray, and E. Behar, Fluid Phase Equilibria **129,** 285 (1997).
9. S. Brunsgaard Hansen, Ph.D. thesis, ISBN 87-986985-6-7 (printed at Department of Chemistry, Technical University of Denmark, 2000).
10. H. Hamaguchi, Appl. Spectrosc. Rev. **24,** 137 (1988).
11. N. C. Craig and I. W. Levin, Appl. Spectrosc. **33,** 475 (1979).
12. Ph. Marteau and D. Fabre, Université Paris Nord, private communication (1999).
13. A. D. May, V. Degen, J. C. Stryland, and H. L. Welsh, Can. J. Phys. **39,** 1769 (1961); A. D. May, G. Varghese, J. C. Stryland, and H. L. Welsh, Can. J. Phys. **42,** 1058 (1964); and C. H. Wang and R. B. Wright, J. Chem. Phys. **59,** 1706 (1973).