

## DIODE LASER KINETIC MEASUREMENTS OF VIBRATIONAL ROTATIONAL AND TRANSLATIONAL TEMPERATURES OF CO IN CO<sub>2</sub> LASER-EXCITED SF<sub>6</sub>

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The time-resolved diode laser spectroscopic method was applied to the characterization of pulsed CO<sub>2</sub> laser-excited SF<sub>6</sub>. The transient signals of rotation–vibration lines of CO, which was added to the system as monitor gas, were observed and dynamic changes of vibrational, rotational and translational temperatures ( $T_V$ ,  $T_R$  and  $T_T$ ) of CO were obtained. The  $T_R$  and  $T_T$  of CO increased within 30  $\mu$ s after the CO<sub>2</sub> laser shot, while the  $T_V$  of CO increased gradually in the time range of 0–1 ms at 1 Torr of SF<sub>6</sub>. The rise rate of  $T_R$  was determined to be  $(1.0 \pm 0.1) \times 10^5 \text{ s}^{-1} \text{ Torr}^{-1}$  from measurements in various pressures of SF<sub>6</sub>, and the result was explained by V–T, R energy transfer in highly excited SF<sub>6</sub>. The temperature determined from energy absorption measurements was compared with the  $T_R$  of CO.

### 1. Introduction

Irradiation of polyatomic molecules with intense pulsed CO<sub>2</sub> laser can promote them to high vibrational states and deposit sufficient energy to cause molecular decomposition as the result of absorbing numerous infrared photons [1]. The past twenty years investigations have been directed toward many subjects relating to this phenomenon, for instance, the basic nature of the absorption process, energy distribution in the resulting excited molecules, energy transfer from the molecules, laser-induced chemical reactions, and application to isotope separation and selective destruction of impurities in a mixture.

Recent attention has been focused on the laser-induced chemical reactions. These can be conveniently classified as direct or indirect processes according to whether the reactant molecule possesses or does not possess a strong absorption band in the 9–11  $\mu$ m emission region of the CO<sub>2</sub> laser. In the latter case, a sensitizer is usually utilized. This is a compound which absorbs the infrared radiation strongly and does not itself undergo chemical change. This kind of reaction proceeds by collisional energy transfer from the laser-excited sensitizer to a reactant molecule. Both SF<sub>6</sub> and SiF<sub>4</sub> have been widely employed as sensitizers. Excitation by energy transfer will generate a ther-

malized system in equilibrium at a temperature defined by the energy absorbed and the heat capacity of the system. This relaxation process and temperature may greatly affect reaction rate and yield of the laser-sensitized reaction. Few measurements of time variation of the temperature, however, have been reported in the literature even though large time variation of temperature has been predicted by gas dynamics calculations [2–4].

Development of the high-resolution infrared diode laser spectrometer made it possible to observe rotation–vibration lines in the 3–30  $\mu$ m region and precisely obtain rotational and vibrational distributions for small molecules [5]. Here high resolution means that the resolution is limited not by instrument but by Doppler broadening of spectral lines. Information on translational energy is available from the measurement of the linewidth.

In this paper we describe the result of an investigation by time-resolved diode laser spectroscopy on the dynamic behavior of SF<sub>6</sub> gas induced by the irradiation with pulsed CO<sub>2</sub> laser. The rotation–vibration lines of SF<sub>6</sub> in the infrared region are so complicated that we cannot distinguish them and obtain clear information about each energy state. Therefore, a small amount of CO molecule was added as monitor gas and the time-resolved signals of rotation–vi-

bration lines of CO were observed, which provided clear rotation–vibration distributions and translational energy without a complicated procedure such as simulation.

## 2. Experimental

A detailed description of the apparatus has been presented previously [6]. In this study “temperature” measurements of mixtures of SF<sub>6</sub> and CO were carried out in static cells. A pulsed CO<sub>2</sub> laser (Lumonics TEA-820) and an infrared diode laser spectrometer (Spectra Physics LS-3) were used to excite SF<sub>6</sub> and to observe the time-resolved absorption spectrum of CO, respectively.

The CO<sub>2</sub> laser was operated on the P(20) line of the 10.6  $\mu\text{m}$  band at a repetition rate of 1–3 Hz. The spatial profile of the laser beam was measured with a pinhole and a pyroelectric detector (Lumonics 20D), and was found to be nearly trapezoid. Only the middle part with uniform intensity of 0.45 J cm<sup>-2</sup> was passed through an iris with diameter of 13 mm. A temporal profile of the CO<sub>2</sub> laser pulse observed with a photon drag detector (Hamamatsu B749) showed that it had an initial spike (150 ns) and a weak tail (2  $\mu\text{s}$ ). Samples consisted of 0.12–1.05 Torr of SF<sub>6</sub> (Takachiho Kagaku > 99.99%) and 0.01–1.0 Torr of CO (Takachiho Kagaku > 99.95%). Long and short cylindrical pyrex cells, 15 and 3 cm in length and 3 cm in diameter, were used depending on the SF<sub>6</sub> pressure to maintain optically thin conditions, and therefore a small fraction (<20%) of the pulse energy was absorbed by the sample gas.

A laser diode with semicontinuous coverage of the 2060–2190 cm<sup>-1</sup> region was mounted in the diode laser spectrometer. The diode laser beam probed only the uniformly irradiated spatial volumes of the cells. A monochromator with a focal length of 25 cm was placed in front of an HgCdTe detector to eliminate emission induced by the CO<sub>2</sub> laser radiation. The detector signal was amplified, digitized, accumulated and stored in a microcomputer (NEC PC-9801VX). This computer also controlled the wave number of the diode laser by varying laser current. The overall response time of this apparatus was about 1  $\mu\text{s}$ .

## 3. Results and discussion

### 3.1. Observation of CO in excited vibrational state

Fig. 1 shows a typical time-resolved spectrum of CO obtained following CO<sub>2</sub> laser excitation of the mixture containing 1.0 Torr of SF<sub>6</sub> and 1.0 Torr of CO. The two lines observed are the P<sub>1,0</sub>(4) transition of <sup>13</sup>C<sup>16</sup>O and the P<sub>2,1</sub>(9) transition of <sup>12</sup>C<sup>16</sup>O at 2081.169 and 2081.259 cm<sup>-1</sup>, respectively. Here subscripts 1, 0 and 2, 1 mean transitions of  $v=1 \leftarrow 0$  and  $2 \leftarrow 1$ . The down and upward signals mean decrease or increase in population of the lower state of the transition since differences between the signals before and after the CO<sub>2</sub> laser pulse are detected. Fig. 1 shows that the concentration of <sup>13</sup>C<sup>16</sup>O in the ground state decreases within 30  $\mu\text{s}$  while that of <sup>12</sup>C<sup>16</sup>O in the excited state increases gradually in the 10–1000  $\mu\text{s}$  region.

Similar measurements of the R<sub>2,1</sub>(5), P<sub>2,1</sub>(14) and

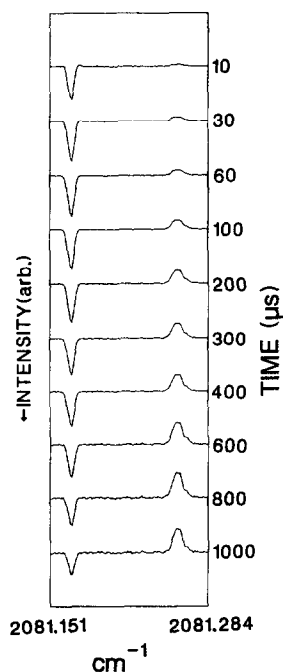


Fig. 1. A typical time-resolved spectrum of CO. The gaseous mixture containing 1.0 Torr of SF<sub>6</sub> and 1.0 Torr of CO was irradiated with the P(20) line of the 10.6  $\mu\text{m}$  band. Downward and upward signals can be assigned to the P<sub>1,0</sub>(4) transition of <sup>13</sup>C<sup>16</sup>O and the P<sub>2,1</sub>(9) transition of <sup>12</sup>C<sup>16</sup>O, respectively.

$R_{2,1}(16)$  transitions of  $^{12}\text{C}^{16}\text{O}$  were performed to determine the time variation of rotational distribution and temperature,  $T_R$ , of CO in the excited vibrational state. When the system has a Boltzmann distribution, the plot of  $\ln[A(J'', t)/(J'' + J' + 1)]$  versus  $BJ''(J'' + 1)/k$  should yield a straight line with a slope of  $-1/T_R$ . Here  $H''$ ,  $J'$ ,  $t$ ,  $A$ ,  $B$  and  $k$  represent the rotational quantum number of the lower state, that of the upper state, the time after the laser shot, absorption line intensity, rotational constant and Boltzmann constant, respectively. In the present investigation this plot actually gave straight lines, so that  $T_R$  was defined. The intercept of the plot provides the concentration of the lower state if the population of the upper state is negligible small. This condition was considered to be valid since the vibrational temperature was not very high as described below.

The lineshape is generally specified by Doppler broadening and pressure broadening. Under the present condition, the former predominantly contributes to the lineshape, and therefore one can obtain the translational energy by fitting observed line-shapes of CO ( $v=1$ ) to a Gaussian function which is the Doppler-broadened profile. The linewidth (hwhm),  $\delta$ , of the profile is given by

$$\delta = \nu_0 (2kT_T \ln 2/mc^2)^{1/2}, \quad (1)$$

where  $\nu_0$ ,  $T_T$ ,  $m$  and  $c$  mean the center wave number, translational temperature, mass, and speed of light, respectively. The  $T_T$  of CO was determined in this way.

The vibrational temperature,  $T_V$ , was estimated from the line intensities of  $P_{2,1}(9)$  of  $^{12}\text{C}^{16}\text{O}$  and  $P_{1,0}(4)$  of  $^{13}\text{C}^{16}\text{O}$  (fig. 1) by assuming that  $T_R$  of  $^{12}\text{C}^{16}\text{O}(v=1)$  was the same as that of  $^{13}\text{C}^{16}\text{O}(v=0)$ . Fig. 2 summarizes the time variation of  $T_R$ ,  $T_T$  and  $T_V$  determined for the mixture of CO<sub>2</sub> laser-excited SF<sub>6</sub> (1.0 Torr) and CO (1.0 Torr), which shows slow increase of  $T_V$  and rapid rises of  $T_R$  and  $T_T$ . The vibrational relaxation of CO in this system takes about 1 ms, while the rises of rotational and translational temperatures are completed within about 30  $\mu\text{s}$ .

### 3.2. Observation of CO in ground vibrational state

In the above experiments considerable amounts of CO and SF<sub>6</sub> were required to detect vibrationally excited CO and to monitor vibrational relaxation. On

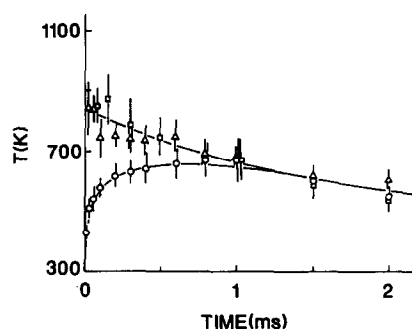


Fig. 2. Time variation of  $T_V$  ( $\circ$ ),  $T_R$  ( $\Delta$ ) and  $T_T$  ( $\square$ ) of CO obtained under the same experimental condition as that of fig. 1.

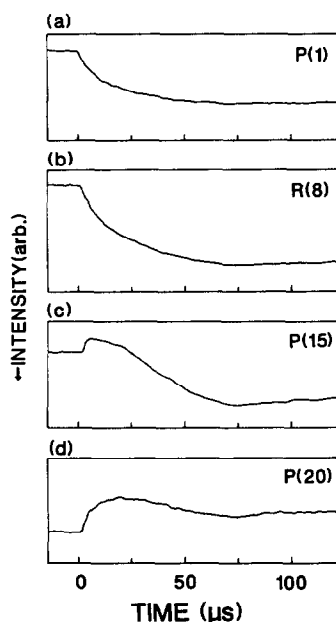


Fig. 3. Transient signals of (a)  $P(1)$ , (b)  $R(8)$ , (c)  $P(15)$  and (d)  $P(20)$  transitions of  $^{12}\text{C}^{16}\text{O}$  obtained in the presence of 0.28 Torr of SF<sub>6</sub> and 0.020 Torr of CO.

the other hand, smaller amounts of CO and SF<sub>6</sub> were necessary to observe the increase of  $T_R$ .

Fig. 3 shows transient signals of  $P_{1,0}(1)$ ,  $R_{1,0}(8)$ ,  $P_{1,0}(15)$  and  $P_{1,0}(20)$  transitions of  $^{12}\text{C}^{16}\text{O}$  obtained in a mixture containing 0.28 Torr of SF<sub>6</sub> and 0.020 Torr of CO. The operating wave number of the diode laser was fixed at each peak of the absorption lines. The signals of  $P_{1,0}(1)$  and  $R_{1,0}(8)$  both decrease with a rate of  $5 \times 10^4 \text{ s}^{-1}$  in the 0–70  $\mu\text{s}$  region, whereas behaviors of the others are quite complicated. Since

the Boltzmann plots of the data shown in fig. 3 gave straight lines at any times, time variation of  $T_R$  of CO( $\nu=0$ ) and CO concentration, [CO], were derived from the procedure mentioned in section 3.1. and displayed in fig. 4. The rise rate of  $T_R$  is very close to the decay rates of the  $P_{1,0}(1)$  and  $R_{1,9}(8)$  signals, and the decrease of [CO] with a decay rate of  $1.5 \times 10^4 \text{ s}^{-1}$  in the 0–70  $\mu\text{s}$  region can be attributed to expansion of the CO<sub>2</sub> laser-excited zone. Increase of [CO] observed after about 70  $\mu\text{s}$  may imply contraction of the zone by reflection of the expansion wave. In this manner, it has been shown that simultaneous changes of  $T_R$  and [CO] cause the anomalous behavior of  $P_{1,0}(15)$  and  $P_{1,0}(20)$  signals.

Similar measurements were carried out for various pressures of SF<sub>6</sub> (0.12–1.05 Torr) with fixed pressure of CO (0.02 Torr) in order to clarify the effect of SF<sub>6</sub> pressure on  $T_R$  and its time variation, and the following results were obtained.  $T_R$  rose rapidly with increasing SF<sub>6</sub> pressure, and a linear relationship between SF<sub>6</sub> pressure and decay rates of  $P_{1,0}(1)$  and  $R_{1,0}(8)$  signals was found, as shown in fig. 5. The slopes of the straight lines give a rise rate of  $(1.0 \pm 0.1) \times 10^5 \text{ s}^{-1} \text{ Torr}^{-1}$  for the  $T_R$  of CO( $\nu=0$ ) in CO<sub>2</sub> laser-excited SF<sub>6</sub>. From this figure the decay rate of  $(1.9 \pm 0.4) \times 10^4 \text{ s}^{-1}$  is obtained even at zero

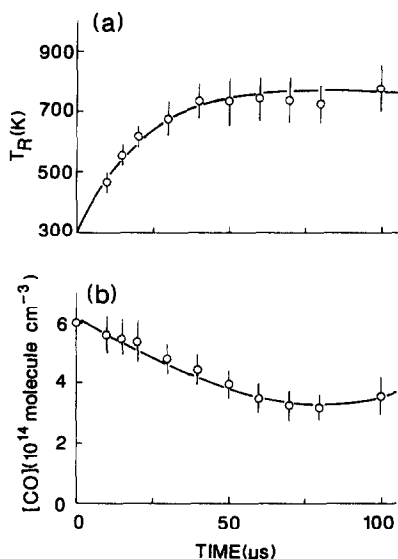


Fig. 4. Time variation of  $T_R$  and [CO] derived from the data shown in fig. 3 by using a Boltzmann plot.

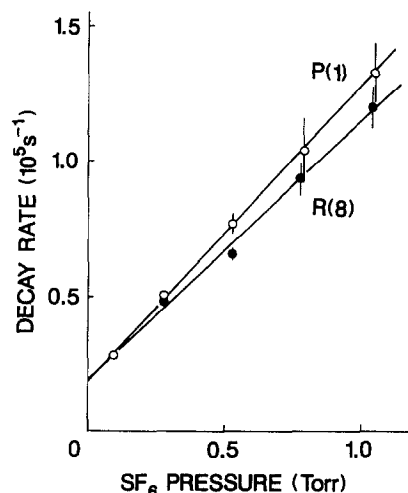


Fig. 5. Relaxation rates of P(1) (○) and R(8) (●) signals of the 1–0 band of <sup>12</sup>C<sup>16</sup>O against SF<sub>6</sub> pressure. The CO pressure is 0.02 Torr.

SF<sub>6</sub> pressure, which can be explained by the decrease of [CO] as mentioned above.

Collisional relaxation processes in CO<sub>2</sub> laser-excited SF<sub>6</sub> have been extensively studied, especially for the lower vibrational state of SF<sub>6</sub> [7–14]. Relaxation times of SF<sub>6</sub>( $\nu_3=1$ ) → SF<sub>6</sub>( $\nu_4$ ) and SF<sub>6</sub>( $\nu_3$ ) → SF<sub>6</sub>(T) processes were reported as 1.1 [11] and 120  $\mu\text{s}$  Torr [7], respectively. On the other hand, it was shown that the V–V process in highly excited SF<sub>6</sub> proceeded much more rapidly with a relaxation time of 13.5 ns Torr [12]. However, little is known about the rotational and the V–T, R process of SF<sub>6</sub> in highly excited vibrational states. The initial value of  $T_R$  (room temperature) and its slow increase (10  $\mu\text{s}$  Torr) obtained here suggest that the rotational distribution of SF<sub>6</sub> does not change very much immediately after the absorption of 17 infrared photons (present condition). For the R–R energy transfer in SF<sub>6</sub> a very fast relaxation time was reported between 36 and 43 ns Torr [13,15]. Since the R–R process between SF<sub>6</sub> and CO seems to occur as fast as that in SF<sub>6</sub>, rotational relaxation must be completed in the time region observed here. Consequently, the slow rise of  $T_R$  can be explained by V–T, R process in highly excited SF<sub>6</sub>. This may be supported by the much faster V–V process described above.

Fig. 6 summarizes the time variation of  $T_V$ ,  $T_R$  and  $T_T$  of SF<sub>6</sub> and CO in the presence of 1 Torr of SF<sub>6</sub>

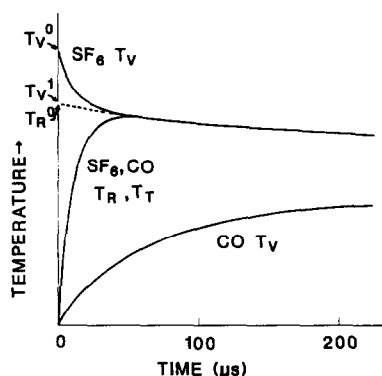


Fig. 6. Summary of time variation of vibrational, rotational and translational temperatures of SF<sub>6</sub> and CO at 1 Torr of SF<sub>6</sub>.  $T_V^0$  and  $T_V^1$  are vibrational temperatures calculated from statistical mechanical energy equation under the conditions of  $T_V \neq T_R = T_T = 300$  K and  $T_V = T_R = T_T$ , respectively, and  $T_R^0$  is the rotational temperature obtained from an extrapolation of  $T_R$  of CO to 0  $\mu$ s.

and a small amount of CO. The V-V process in highly excited SF<sub>6</sub> is completed with a relaxation time of 13.5 ns [12]. The vibrational energy of SF<sub>6</sub> is transferred to translation and rotation of SF<sub>6</sub> and CO (V-T, R process) with a relaxation time of 10  $\mu$ s, and finally thermalization among vibration, rotation and translation of SF<sub>6</sub> and CO is attained at about 1 ms.

### 3.3. Comparison of $T_R$ with temperature estimated from energy absorption measurements

The temperature of SF<sub>6</sub> can be also estimated from measurements of absorbed energy and heat capacity of the system. Table 1 compares the temperatures ob-

tained from the rotational distribution of CO and from this method. The vibrational temperature of SF<sub>6</sub> is computed from the statistical mechanical energy equations,

$$E_V = \sum \{ h\nu_i / [\exp(h\nu_i/kT_V) - 1] \}, \quad (2)$$

$$E_R = kT_R \quad (\text{for CO}),$$

$$= \frac{3}{2}kT_R \quad (\text{for SF}_6),$$

$$E_T = \frac{3}{2}kT_T, \quad (3)$$

where  $E_V$ ,  $E_R$  and  $E_T$  are vibrational, rotational and translational energies per molecule,  $h$  is the Planck constant and  $\nu_i$  is the vibrational frequency of the  $i$ th mode. In this table  $T_V^0$  and  $T_V^1$  mean vibrational temperatures calculated under the conditions  $T_V \neq T_R = T_T = 300$  K and  $T_V = T_R = T_T$ , respectively, and  $T_R^0$  indicates a value obtained from an exponential extrapolation of the experimental data of  $T_R$  to 0  $\mu$ s. These temperatures are shown in fig. 6. Table 1 indicates that the value of  $T_R^0$  is close to that of the thermalized temperature,  $T_V^1$ , and therefore the initial temperature in a thermalized system can be estimated from the simple energy absorption measurements.

## 4. Conclusion

The time-resolved diode laser spectroscopy was applied to the characterization of vibrational and rotational distributions and translational energy of CO in CO<sub>2</sub> laser-excited SF<sub>6</sub> in order to clarify the "temperature" of SF<sub>6</sub> and relaxation process. The rota-

Table 1

Comparison of vibrational temperatures estimated from the energy absorbed,  $T_V^0$  ( $\neq T_R = T_T = 300$  K) and  $T_V^1$  ( $= T_R = T_T$ ), with that obtained from the exponential extrapolation of  $T_R$  of CO ( $\nu=0$ ) to 0  $\mu$ s,  $T_R^0$

Pressure (Torr)		Temperature (K)		
SF <sub>6</sub>	CO	$T_V^0$	$T_V^1$	$T_R^0$
0.28	0.020	1170 $\pm$ 120	1010 $\pm$ 110	980 $\pm$ 80
0.53	0.020	1260 $\pm$ 130	1100 $\pm$ 110	1070 $\pm$ 150
0.78	0.020	1300 $\pm$ 130	1120 $\pm$ 120	1070 $\pm$ 120
1.05	0.020	1330 $\pm$ 140	1140 $\pm$ 120	1030 $\pm$ 130
1.0	1.0	1330 $\pm$ 140	990 $\pm$ 100	850 $\pm$ 100 <sup>a)</sup>

<sup>a)</sup> Obtained from  $T_R$  of CO in an excited vibrational state ( $\nu=1$ ).

tional temperature of CO increased with a rate of  $(1.0 \pm 0.1) \times 10^5 \text{ s}^{-1} \text{ Torr}^{-1}$  and then decreased in the several hundreds of microseconds region. The translational temperature of CO was close to the rotational one in the time region observed, while the vibrational one of CO increased slowly and V-T, R relaxation of CO was attained at about 1 ms. The increase of rotational temperature may be explained by R-R energy transfer from SF<sub>6</sub> to CO following V-T, R energy transfer in highly excited SF<sub>6</sub>, that is, the V-T, R process in highly excited SF<sub>6</sub> probably proceeds with a relaxation time of 10  $\mu\text{s}$  at 1 Torr of SF<sub>6</sub>. The initial temperature obtained from extrapolation of the rotational temperature of CO was in fair agreement with the value estimated from the energy absorption measurement.

## References

- [1] W.C. Danen and J.C. Jang, in: *Laser-Induced Chemical Processes*, ed. J.I. Steinfeld (Plenum Press, New York, 1981).
- [2] D.F. McMillen, K.E. Lewis, G.P. Smith and D.M. Golden, *J. Phys. Chem.* 86 (1982) 709.
- [3] H.-L. Dai, E. Spiccht and M.R. Berman, *J. Chem. Phys.* 77 (1982) 4494.
- [4] G.P. Smith, P.W. Fairchild, J.B. Jeffries and D.R. Crosly, *J. Phys. Chem.* 89 (1985) 1269.
- [5] E. Hirota and K. Kawaguchi, *Ann. Rev. Phys. Chem.* 36 (1985) 53.
- [6] K. Sugawara, T. Nakanaga, H. Takeo and C. Matsumura, *Chem. Phys. Letters* 130 (1986) 560; 134 (1987) 347; *J. Phys. Chem.* 93 (1989) 1894.
- [7] J.I. Steinfeld, I. Burak, D.G. Sutton and A.V. Nowak, *J. Chem. Phys.* 52 (1970) 5421.
- [8] O.R. Wood and S.E. Schwarz, *Appl. Phys. Letters* 16 (1970) 518.
- [9] I. Burak, P. Houston, D.G. Sutton and J.I. Steinfeld, *J. Chem. Phys.* 53 (1970) 3632.
- [10] R.D. Bates Jr., J.T. Knudtson, G.W. Flynn and A.M. Ronn, *Chem. Phys. Letters* 8 (1971) 103.
- [11] J.T. Knudtson and G.W. Flynn, *J. Chem. Phys.* 58 (1973) 1467.
- [12] H.S. Kwok and E. Yablonovitch, *Phys. Rev. Letters* 41 (1978) 745.
- [13] C.C. Jensen, T.G. Anderson, C. Reiser and J.I. Steinfeld, *J. Chem. Phys.* 71 (1979) 3648.
- [14] E. Mazur, I. Burak and N. Bloembergen, *Chem. Phys. Letters* 105 (1984) 258.
- [15] P.F. Moulton, D.M. Larsen, J.N. Walpole and A. Mooradian, *Opt. Letters* 1 (1977) 51.