

From: ATOMIC AND MOLECULAR PROCESSES WITH SHORT
INTENSE LASER PULSES
Edited by Andre D. Bandrauk
(Plenum Publishing Corporation, 1988)

THE INTERACTION OF INTENSE PICOSECOND INFRARED PULSES WITH ISOLATED MOLECULES

Eric Mazur

*Division of Applied Sciences and Department of Physics
Harvard University
Cambridge, MA 02138, USA*

Introduction

In the past decade there has been much interest in the dynamics of highly vibrationally excited and dissociating molecules. Selectivity at high levels of excitation may eventually lead to the realization of laser-controlled photochemistry, with broad applications in such diverse areas as laser-assisted chemical vapor deposition, isotope separation, and photosynthesis. Polyatomic molecules in the ground electronic state can reach levels of excitation up to the dissociation threshold by absorbing a large number of photons from a resonant high-power infrared laser. Despite the selectivity of infrared excitation at low energy, however, at high excitation the excitation energy is no longer confined to one 'mode'. It has been shown experimentally that for molecules excited close to or above the dissociation threshold equilibration of energy occurs, in agreement with theoretical predictions. There is no agreement, however, as to the validity of theoretical models that presuppose equipartitioning of energy in the region *below* the dissociation threshold. Recent spontaneous Raman spectroscopy experiments on infrared multiphoton excited molecules in our laboratory provide information on the intramolecular vibrational energy distributions of highly vibrationally excited molecules in this region. The experimental results show that an excess of energy can remain in the pumped mode up to levels of excitation close to the dissociation threshold. This paper provides a review of the results that were obtained in the past three years, part of which were published previously.

Background

In 1973 it was discovered that isolated molecules in the ground electronic state can be dissociated by a short, intense pulse from a CO₂ laser.¹ Since then the absorption of large numbers of monochromatic infrared photons by isolated molecules has been studied extensively.²⁻⁸ The early work in this field was motivated by the hope of driving chemical reactions in either a bond-specific or isotopically selective fashion by 'localized' deposition of energy in a small subset of modes.

In the past ten years many experimental techniques have been applied to study infrared multiphoton excitation. Photoacoustic measurements were applied to determine the energy absorbed by the molecules,⁹ and to study the excitation as a function of various pa-

parameters, such as pumping fluence, intensity, and wavelength, pressure, etc. Photoacoustic spectroscopy was also used at high intensities to study dissociation yields as a function of absorbed energy. More detailed information on infrared multiphoton dissociation, such as the species of the dissociation fragments, branching ratios of different dissociation channels, and the translational energy distribution of the fragments, was obtained by mass and time-of-flight spectrometry.¹⁰ Pump-and-probe experiments have also provided more detailed knowledge of the infrared multiphoton excitation and dissociation. For example, laser induced fluorescence^{11,12} was used to measure the vibrational energy distribution of the infrared multiphoton dissociation fragments. Infrared double-resonance experiments¹³⁻¹⁵ were done to determine the rotational relaxation rate and the population depletion of the vibrational ground state. Spontaneous and coherent anti-Stokes Raman scattering were used to probe the distribution of vibrational energy over the different modes of infrared multiphoton excited molecules.¹⁶⁻²⁴

The following qualitative picture has emerged from the experimental results. Basically, one can distinguish between three different regions in the molecular vibrational spectrum depending on the level of excitation. At low excitation the energy is essentially confined to the pumping mode, just as in ordinary one-photon spectroscopy: the first few photons absorbed by a 'cold' molecule produce transitions between separate discrete vibrational states located in the resonant mode (region I). At higher levels of excitation, the spacing between individual vibrational states becomes increasingly smaller due to molecular anharmonicities, and other nonresonant modes also acquire energy during the excitation (region II, often referred to as the 'quasicontinuum'). Molecular excitation in this region is thought to occur through stepwise incoherent transitions between homogeneously broadened states that are superpositions of various normal mode states. Once in region II, many polyatomic molecules easily absorb large numbers of infrared photons and reach the continuum above the dissociation threshold (region III). Clearly the excitation process is very different in each of these three regions, and experimental results often reflect a combination of the spectroscopies of different regions.

Most of the experiments carried out to date have centered around characterizing the gross features of infrared multiphoton excitation by relatively large molecules. The parameters that have been measured, such as average number of photons absorbed per molecule, dissociation rates and branching ratios, are the product of a number of mechanical and kinetic processes and, hence, are incapable of probing the detailed dynamics of the excitation process. It has been established, however, that the infrared multiphoton dissociation branching ratios and the energy distributions of the dissociation fragments are generally consistent with statistical theories, such as the RRKM theory. This means that when molecules are excited into region III, equilibration of the intramolecular vibrational energy distribution occurs, and dissociation takes place along a thermodynamically favored path, resulting in a loss of the initial 'selectivity'. Whether equilibration occurs for highly excited molecules *below* the dissociation threshold (region II) remains an open question.

Direct information on the intramolecular energy distribution in highly excited molecules was obtained experimentally with pump-probe type experiments, in particular by Raman probing. Raman spectroscopy was first employed by Bagratashvili and coworkers¹⁶ and later by our group¹⁹ as a tool for studying infrared multiple photon excitation. In the Raman experiments, the population in various vibrational modes is probed after excitation of the molecules into region II with an intense infrared pulse. Since the Raman signal intensities are a measure for the amount of energy in each mode,¹⁹ this type of experiment provides direct experimental information on the intramolecular energy distribution.

Intramolecular energy distributions

The experimental technique and apparatus have been described previously.^{20,21} Four different molecules, CF_2HCl , CF_2Cl_2 , SF_6 and CH_3CHF_2 , varying in size from five to eight

atoms, were studied with the present apparatus.^{20,22–24} An overview of experimental results is presented in Table I. All measurements were carried out at room temperature, with gas pressures ranging from 14 to 500 Pa and with infrared fluences up to $8 \times 10^4 \text{ J/m}^2$. The commercially obtained gases have a reported purity better than 99.99%.

The first molecule studied, SF_6 , has only one accessible Raman active mode, ν_1 , with a Raman shift of 775 cm^{-1} . Data were obtained for CO_2 -laser frequencies between the P(12) and the P(28) lines of the $10.6 \mu\text{m}$ branch, which are resonant with the triply degenerate infrared active ν_3 -mode (944 cm^{-1}). Two different infrared pulse durations were employed: 0.5 and 15 ns full-width at half-maximum pulses.

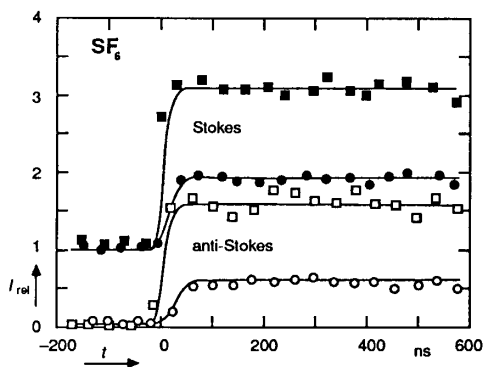


Fig. 1. Intensity of Stokes (closed symbols) and anti-Stokes (open symbols) signal as a function of the time delay between pump and probe pulses at a pressure of 67 Pa for SF_6 . Infrared excitation with 0.5 ns (squares) and 15 ns (circles) pulses at the $10.6 \mu\text{m}$ P(20) line. Average fluence: $0.8 \times 10^4 \text{ J/m}^2$. Data from Ref. 20.

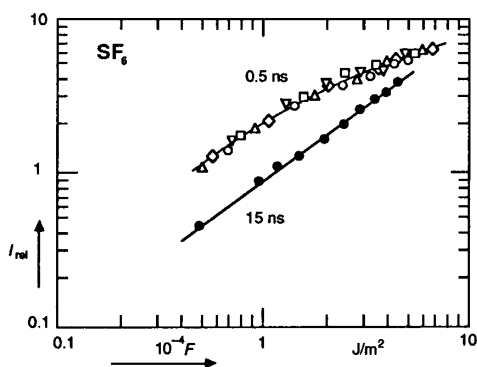


Fig. 2. Relative anti-Stokes signal of SF_6 as a function of the infrared pumping fluence for various pressures. Excitation at the $10.6 \mu\text{m}$ P(20) line with two pulse durations: 0.5 ns (open symbols) and 15 ns (closed symbols). Data from Ref. 20.

□ : 33 Pa; ○ : 67 Pa; ▲ : 133 Pa; ▼ : 200 Pa;
 ◆ : 267 Pa; ● : 133 Pa

Fig. 1 shows the increase in Stokes and anti-Stokes signals, measured at 356.7 and 338 nm respectively, as a function of the time delay between the pump and the probe pulse for two infrared pulse durations. The signals are normalized with the room temperature Stokes signal (for $t < 0$, room temperature equilibrium data are automatically obtained). At $t=0$ infrared excitation takes place and both Stokes and anti-Stokes signals increase. The rise time of the signals is determined by the 20 ns pulse duration of the second harmonic of the probe laser. However, although not resolved in these measurements, the increase in signal clearly occurs on a time-scale that is much shorter than the mean free time between collisions (about 200 ns at a pressure of 67 Pa). The pressure dependence of the signals further shows that the increase in signal is not due to collisions, but is truly a *collisionless* phenomenon.²⁰ Interestingly enough the signals remain constant, even on a time scale on which collisional vibrational energy relaxation occurs.²⁰ For longer delay times ($t > 2 \mu\text{s}$), diffusion of the excited molecules out of the probing region causes the signals to revert to their original values.²⁰

Table I. Spectroscopic data for the molecules studied in this paper. The vibrational data for SF₆ and CF₂Cl₂ are from literature. All data are in cm⁻¹, vs = very strong, s = strong, m = medium, and w = weak.

Molecule	CO ₂ line	Wavenumber	Mode	Activity	Remarks ^{20,22-24}
SF ₆ ²⁵	10.6 μm P(20)	944	v ₁ = 775	R (s)	changes after excitation
			v ₂ = 644	R (w)	not probed
			v ₃ = 965	IR	pumped
			v ₄ = 617	IR	
			v ₅ = 524	R (w)	not probed
			v ₆ = 363	inactive	
CF ₂ Cl ₂ ^{26,27}	10.6 μm P(32)	933	v ₁ = 1101	IR(s)	
			v ₁ = 1098	R (m)	changes after excitation
			v ₂ = 667	IR (s)	
			v ₂ = 667.2	R (s)	changes after excitation
			v ₃ = 457.5	R (s)	not probed
			v ₄ = 261.5	R (s)	not probed
			v ₅ = 322	R (w)	not probed
			v ₆ = 1159	IR (s)	
			v ₆ = 1167	R (w)	not probed
			v ₇ = 446	IR (w)	not probed
v ₈ = 922	IR (vs)	pumped			
v ₈ = 923	R (w)	changes after excitation			
		v ₉ = 437	IR (w)		
		v ₉ = 433	R (m)	not probed	
CH ₃ CHF ₂	10.6 μm P(20)		870	R	changes after excitation
			944	IR	pumped
			1140	R	no change
			1460	R	no change
			2980	R	no change
CF ₂ HCl	9.4 μm R(32)		590	R	no change
			800	R	no change
			1086	IR	pumped
			1130	R	no change
			1330	R	no change
			3030	R	no change

The dependence of the anti-Stokes signal intensity on the infrared laser fluence (energy per unit area) is shown in Fig. 2 for different pressures and pulse durations. The data obtained for the two pulse durations show that at low fluence the signals depend on the exciting laser pulse intensity: a larger increase in Raman signal occurs at the shorter, higher intensity, pulses. At low excitation one needs a high intensity for *coherent* multiphoton excitation through the lower part of the vibrational ladder. At the higher fluences, once the

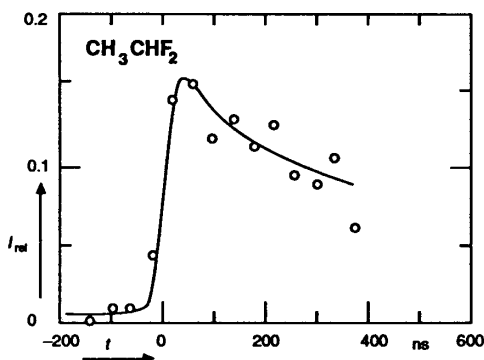


Fig. 3. Intensity of the anti-Stokes signals versus time delay between pump and probe pulse for CH_3CHF_2 at 660 Pa. Infrared excitation: $10.6 \mu\text{m}$ P(20) line, 0.5 ns pulse with average fluence $1.5 \times 10^4 \text{ J/m}^2$. Data from Ref. 22.

molecules are highly excited, the curves for the 0.5 and 15 ns pulse durations approach each other, and the dependence of the signal intensity on laser pulse intensity vanishes in agreement with the behavior observed in photoacoustic measurements.⁹

The observed collisionless changes in Raman signals provide clear and direct evidence that some of the nonresonant modes do indeed participate in the excitation process. The main purpose of this research is to obtain information on the role of nonresonant modes in the multiphoton excitation of polyatomic molecules. Since the intensity of the signals is proportional to the average energy in the mode, E_R , one can determine E_R from the ratio of the anti-Stokes intensity to the thermal room temperature value of the Stokes signal, I_{rel} . Unfortunately SF_6 has only one accessible Raman active mode, so that it is not possible to compare the values of E_R for different Raman active modes. This limits us therefore to a comparison of energy in the ν_1 mode with the average total energy absorbed per molecule, $\langle E \rangle$, known from photoacoustic measurements. If one assumes an equilibrium distribution of the excitation energy $\langle E \rangle$, the amount of energy in the ν_1 mode agrees remarkably well with the value for E_R that one obtains from the Raman measurements,^{19,20} suggesting that for SF_6 the intramolecular energy distribution indeed equilibrates. The absence of a decay of the Raman signals in Fig. 1 further supports this suggestion. Even though the initially nonequilibrium *intermolecular* distribution of energy equilibrates,¹⁸ E_R remains constant once intramolecular equilibrium is achieved. In the absence of intramolecular equilibrium, one would expect E_R , and consequently the signal intensities, to change on a much shorter time scale because of a rearrangement of energy over the various vibrational modes.

The asymmetric CF_2HCl molecule has five accessible Raman active modes of widely different energy ($600\text{--}3000 \text{ cm}^{-1}$). The peak absorption of this molecule coincides with the $9.4 \mu\text{m}$ R(32) CO_2 laser line at 1086 cm^{-1} . Even at the maximum fluence at this line ($2 \times 10^4 \text{ J/m}^2$), none of the five Raman lines show a detectable change in intensity.²² Photoacoustic studies²³ of the infrared multiphoton excitation of this molecule have shown that at such a fluence the molecules absorb about ten infrared photons ($10,000 \text{ cm}^{-1}$). The absence of anti-Stokes scattering from low lying levels, such as the Raman active mode at 587 cm^{-1} , suggests that not all modes participate in the excitation process, and that the energy distribution for this molecule does not equilibrate without collisions.

The asymmetric isomer CH_3CHF_2 has four accessible Raman modes. Data were obtained for 0.5 ns long pulses at the P(20) line of the $10.6 \mu\text{m}$ branch, which is resonant with the infrared active C—F stretch mode at 942 cm^{-1} . Only one of the Raman active modes, at 870 cm^{-1} , shows an increase in signal after excitation.²² Fig. 3 shows the time-

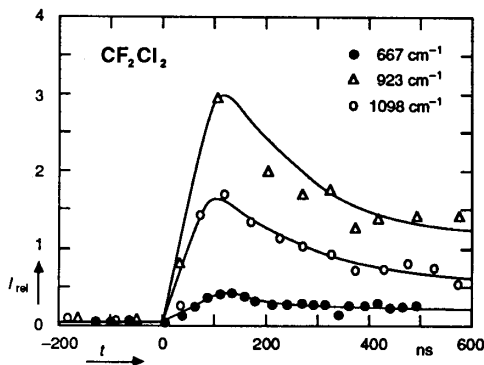


Fig. 4. Intensity of the anti-Stokes signals as a function of the time delay between pump and probe pulse for CF_2Cl_2 at 400 Pa. Infrared excitation: $10.6 \mu\text{m}$ P(32) line, 15 ns pulse with average fluence $1.8 \times 10^4 \text{ J/m}^2$. Data from Ref. 23.

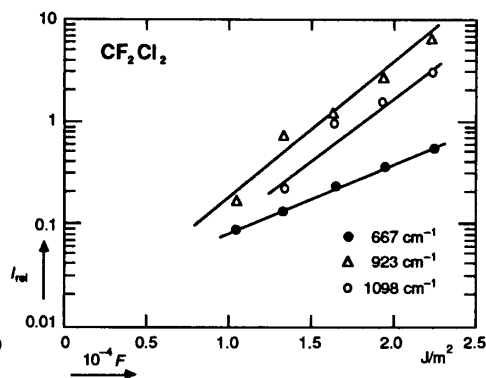


Fig. 5. Semilogarithmic plot of the fluence dependence of the anti-Stokes signals of CF_2Cl_2 at 400 Pa. The dependence is exponential for all three modes. Excitation with 15 ns pulses at the $10.6 \mu\text{m}$ P(32) line. Data from Ref. 23.

dependence of this signal at a pressure of 660 Pa and a fluence of $1.5 \times 10^4 \text{ J/m}^2$. Again a short collisionless increase in signal occurs, but in contrast to SF_6 the signal now decays on a time scale of the order of collisional relaxation times. This, combined with the fact that no other Raman active mode exhibits any change, leads to the conclusion that for this particular molecule too, the excitation energy does not equilibrate.

The most complete set of data was obtained for CF_2Cl_2 .^{23,24} This five atom molecule has four accessible Raman active modes, three of which (at 667, 923, and 1098 cm^{-1} respectively) were measured after infrared multiphoton excitation. The C—Cl stretch mode at 923 cm^{-1} is both infrared and Raman active and can be pumped with the P(32) line of the $10.6 \mu\text{m}$ branch of the CO_2 laser. This allows one to directly observe the energy in the pump mode and compare it with the energy in other modes. The measurements presented here were all carried out at a gas pressure of 400 Pa.

Fig. 4 shows the time-dependence of the anti-Stokes signals, each normalized with its corresponding room temperature Stokes signals. The signals rise in 20 ns and show a clear decay, especially for the two highly excited modes (923 cm^{-1} and 1098 cm^{-1}). This decay is most likely attributed to collisional transfer of energy to other, initially 'cold' vibrational modes. The fluence dependence of the anti-Stokes signals of CF_2Cl_2 is nearly exponential (Fig. 5): above $1 \times 10^4 \text{ J/m}^2$, the signals double roughly every $0.3 \times 10^4 \text{ J/m}^2$ increment. Since CF_2Cl_2 is smaller than SF_6 , fewer vibrational modes are available and one expects a stronger bottleneck effect in CF_2Cl_2 . The observed slow rise of the signals at low fluence, which is in sharp contrast with the linear fluence dependence of SF_6 (*cf.* Figs. 2 and 5), indeed suggests that this is the case. Measurements of the Raman signal with shorter infrared pulses would provide a better understanding of the role of intensity effects.

Since more than one Raman active mode was measured for this molecule, one can directly compare the intensities from the various modes. In equilibrium, the intensities of the normalized signals are given by a Maxwell-Boltzmann distribution. The results in Figs. 4, and 5, however, show that the signal intensities after infrared multiphoton excitation cannot be described by such a distribution. Especially the normalized intensity of the pumped vibrational mode at 923 cm^{-1} is considerably higher than the corresponding intensities of the other two modes: at all fluences most of the energy remains in the pumped mode. In addition, as is clear from Fig. 5 the rate of increase is different for the three modes. It appears that there is a stronger coupling of the pump mode with the 1098 cm^{-1} mode than with the less energetic 667 cm^{-1} mode, notably at the high fluence end. Note also that

although the intensities of the anti-Stokes signals increase significantly between 1.5 and $2.4 \times 10^4 \text{ J/m}^2$, the intensity *ratio* does not change much. This rules out the possibility that the observed nonequilibrium distribution is a result of averaging a 'hot' equilibrium ensemble and a 'cold' bottlenecked ensemble, since the ratio would change as the fraction of molecules in the hot ensemble becomes larger with increasing fluence. Adding up the energy content of the three modes for CF_2Cl_2 calculated from the signal intensities in Fig. 5, it follows that a complete equilibration of energy does not occur below $10,000 \text{ cm}^{-1}$ of excitation. Preliminary measurements show that after pumping the 1098 cm^{-1} mode an excess of energy is found in both the 923 and the 1089 cm^{-1} cm mode.

Conclusion

This paper presents an overview of the results of measurements on various collisionless infrared multiphoton excited molecules ranging in size from 5 to 8 atoms. The amount of energy in various modes of these molecules is determined from the spontaneous Raman scattering signals from each of these modes. Most of these molecules have more than one Raman active mode and thus allow *direct* observation of the intramolecular distribution of vibrational energy among these modes after the infrared multiphoton excitation. The experiments unambiguously show: (1) that collisionless intramolecular transfer of energy to Raman active modes takes place within the 20 ns time resolution, and (2) that for highly excited molecules below the dissociation threshold the final distribution of energy—after excitation, before collisional relaxation—is *not necessarily in equilibrium*. For CF_2Cl_2 in particular it was found that the pumped mode contains an excess of energy up to *at least* $10,000 \text{ cm}^{-1}$ of excitation energy. This implies a certain degree of 'localization' of excitation energy in the pump mode up to fairly high levels of excitation. Although this is at variance with observations made in the Soviet Union, that claim complete equilibration at about $7,000 \text{ cm}^{-1}$, it agrees with recent theoretical studies of the intramolecular dynamics of model systems, that show that for some molecules equilibration occurs only for energies very close to the dissociation limit.²⁵ To the best of our knowledge this is the first direct experimental evidence that region II may indeed extend quite close to the dissociation threshold.

Acknowledgments

We are pleased to acknowledge financial support by the Army Research Office, the Joint Services Electronics Program and by the Hamamatsu Corporation.

References

- 1 N.R. Isenor, V. Merchant, R.S. Hallsworth and M.C. Richardson, *Can. J. Phys.* **51**, 1281 (1973)
- 2 V.N. Bagratashvili, V.S. Letokhov, A.A. Makarov, E.A. Ryabov, *Multiple Photon Infrared Laser Photophysics and Photochemistry* (Harwood Academic Publishers, New York, 1985)
- 3 N. Bloembergen and E. Yablonovitch, *Physics Today* **5**, 23 (1978)
- 4 C.D. Cantrell, S.M. Freund, J.L. Lyman, *Laser Handbook*, Vol. 3, Ed. M.L. Stitch (North-Holland, Amsterdam, 1979)
- 5 P.A. Schultz, Aa. S. Sudbø, D.J. Krajnovitch, H.S. Kwok, Y.R. Shen, and Y.T. Lee, *Ann. Rev. Phys. Chem.* **30**, 379 (1979)
- 6 V.S. Letokhov, *Physics Today* **11**, 34 (1980)
- 7 W. Fuss and K.L. Kompa, *Prog. Quant. Electr.* **7**, 117 (1981)

- 8 D.S. King, *Dynamics of the Excited State*, Ed. K.P. Lawley (Wiley, New York, 1982)
- 9 J.G. Black, P. Kolodner, M.J. Schultz, E. Yablonovitch, N. Bloembergen, *Phys. Rev. A* **19**, 704 (1979)
- 10 Y.T. Lee and Y.R. Shen, *Physics Today* **33**, 52 (1980)
- 11 J.D. Campbell, G. Hancock, J.B. Halpern, and K.H. Welge, *Chem. Phys. Lett.* **44**, 404 (1976)
- 12 D.S. King and J.C. Stephenson, *Chem. Phys. Lett.* **51**, 48 (1977)
- 13 D.S. Frankel and T.J. Manuccia, *Chem. Phys. Lett.* **54**, 451 (1978)
- 14 R.C. Sharp, E. Yablonovitch and N. Bloembergen, *J. Chem. Phys.* **74**, 5357 (1981)
- 15 P. Mukherjee and H.S. Kwok, *J. Chem. Phys.* **84**, 1285 (1986)
- 16 V.N. Bagratashvili, Yu.G. Vainer, V.S. Dolzhikov, S.F. Kol'yakov, A.A. Makarov, L.P. Malyavkin, E.A. Ryabov, E.G. Silkis, and V.D. Titov, *Appl. Phys.* **22**, 101 (1980)
- 17 V.N. Bagratashvili, Yu.G. Vainer, V.S. Dolzhikov, S.F. Kol'yakov, V.S. Letokhov, A.A. Makarov, L.P. Malyavkin, E.A. Ryabov, E.G. Sil'kis, and V.D. Titov, *Sov. Phys. JETP* **53**, 512 (1981)
- 18 V.N. Bagratashvili, Yu.G. Vainer, V.S. Dolzhikov, V.S. Letokhov, A.A. Makarov, L.P. Malyavkin, E.A. Ryabov, and E.G. Sil'kis, *Opt. Lett.* **6**, 148 (1981)
- 19 E. Mazur, I. Burak, and N. Bloembergen, *Chem. Phys. Lett.* **105**, 258 (1984)
- 20 Jyhpyng Wang, Kuei-Hsien Chen, and Eric Mazur, *Phys. Rev. A* **34**, 3892 (1986)
- 21 Eric Mazur, *Rev. Sci. Instrum.* **57**, 2507 (1986)
- 22 Eric Mazur, Kuei-Hsien Chen, Eric Mazur, *Proc. Int. Conf. on Lasers '86*, 359 (1986)
- 23 Jyhpyng Wang, Kuei-Hsien Chen and Eric Mazur, *Laser Chemistry*, in press
- 24 Kuei-Hsien Chen, Jyhpyng Wang and Eric Mazur, to be published
- 25 G. Herzberg, *Molecular spectra and molecular structure*, Vol. 2 (Van Nostrand Reinhold, New York, 1979)
- 26 Charles A. Bradley, Jr., *Phys. Rev.* **40**, 908 (1932)
- 27 T. Shimanouchi, *J. Phys. Chem. Ref. Data* **6**, 993 (1977)
- 28 B.G. Sumpter and D.L. Thompson, *J. Chem. Phys.* **86**, 2805 (1987)