

Molecular Beam Opto-thermal Study of the Multiple-photon Infrared Excitation of $\text{CF}_3\text{Br}^\dagger$

D. BASSI‡, A. BOSCHETTI||, S. IANNOTTA||, M. SCOTONI‡ and
M. ZEN||

‡ *Dipartimento di Fisica dell'Università di Trento, 38050 Povo (TN), Italy*
|| *Istituto per la Ricerca Scientifica e Tecnologica in Trento, 38050 Povo*
(TN), Italy

(Received 13 April, 1984; in final form 6 June, 1984)

The multiple-photon excitation (MPE) of CF_3Br has been studied in strictly collisionless conditions by means of the molecular beam optothermal technique. The MPE spectrum shows strong structures which have been attributed to different orders of multiple-photon resonances. The experimental results have been compared with an available theoretical calculation based on the “heat-bath feed-back” model. The effect of the rotational population and of the vibrationally excited “hot bands” on the MPE yield is discussed.

1. INTRODUCTION

Several different experimental techniques have been developed in recent years for investigating the collisionless multiple-photon infrared excitation (MPE) of polyatomic molecules. The simplest experimental arrangement is based on a cell containing the sample gas. The absorption cross-section is obtained by the measurement of the laser transmission through the cell.¹

The sensitivity of such MPE cell measurements may be markedly increased by means of the Optoacoustic method.^{2,3} In this technique, a microphonic signal is produced by the sound waves generated in the cell by the V - T relaxation of the laser excited molecules. The Optoacoustic method has become very popular because of its simplicity and efficiency. Furthermore, such measurements are only

† Work supported, in part, by the Italian National Research Council (CNR-GNSM).

slightly affected by the instabilities of the laser pulse and therefore the experiments can be carried out even at small laser attenuations. The results of an Opto-Thermal experiment give the average number of photons absorbed by each molecule.

A more detailed diagnostic of the molecular population after the laser irradiation may be obtained by time resolved two laser experiments. Both infrared-infrared⁴⁻⁶ and infrared-Raman double resonance measurements⁷⁻⁹ have been reported in the literature. These studies have given information about the distribution of vibrational states and the relaxation phenomena.

Information about the multiple-photon excitation have been also obtained from fluorescence experiments. Both collision induced infrared fluorescence¹⁰ and reaction induced fluorescence^{11,12} have been successfully applied to MPE investigations.

The major problems encountered in cell experiments arise from the presence of collision induced relaxation phenomena.¹³

True collisionless conditions may be achieved only by choosing carefully the cell pressure and the laser pulse length¹⁴ in order to avoid any appreciable molecular relaxation during the laser pulse. In fact, experiments carried out with picosecond lasers have demonstrated the existence of relaxation processes with time constants of the order of few nanoseconds-torr.⁴ Therefore, cell experiments carried out at pressures around 1 torr and with conventional 100 ns pulsed lasers cannot be considered strictly collisionless.

The collision induced relaxation phenomena may be dramatically reduced by replacing the gas cell with an unskimmed free jet or with a supersonic molecular beam. In the first case the molecules may experience some residual collisions especially when the illuminated region is set very close to the source nozzle. The free jet method has become very popular for spectroscopic applications because of the recent development of simple and efficient pulsed molecular beam sources.¹⁵

Several spectroscopic methods have been used on free jets or molecular beams for investigating the multiple-photon excitation of polyatomic molecules. The laser induced fluorescence (LIF) is one of the more interesting methods. It can give detailed information about the distribution of states after the laser irradiation.¹⁶ Unfortunately, wide application of this method has been limited so far by the lack of suitable laser sources. Recently two interesting free jet studies have

reported the application of Stimulated Raman Spectroscopy¹⁷ and infrared diode laser absorption spectroscopy¹⁸ for investigating the MPE of SF₆. Both these experiments have demonstrated the strong dependence of the multiple-photon excitation on the initial rotational state of the molecules.

A different molecular beam method, which is based on the Opto-Thermal technique,^{19,20} has been developed²¹⁻²⁵ in the past few years. The basic idea of the method is to measure the energy absorbed by the molecular beam by means of a fast superconducting bolometer. The result of the measurements is the average number of photons absorbed by each molecule. The analogy between the Opto-Thermal and the Optoacoustic methods is straightforward. The major difference is that, in the first case, the experimental results are strictly collisionless, independently from the laser conditions.

In this paper we present the results of molecular beam Opto-Thermal experiments aimed at investigating the multiple-photon excitation of CF₃Br. Several papers describing the multiple-photon dissociation (MPD) of this molecule have appeared in the literature during the last few years.²⁶⁻³² A recent molecular beam study³² has shown the existence of strong structures in the MPD spectrum which have been attributed to two and three photon resonances.

The MPE spectrum has been recently calculated by Capitelli and coworkers³³ who compared the theoretical calculations with the results of an Optoacoustic cell measurement. Strong differences between theory and experiment have been shown. Our collisionless results show a much better agreement with the theory. We have studied in detail the effects of the laser fluence and of the initial state of the molecules on the multiple-photon excitation yield. Two strong structures of the MPE spectrum have been identified around about 1081 and 1084 cm⁻¹. The existence of another structure placed near 1075 cm⁻¹ is discussed.

2. EXPERIMENTAL

The experimental apparatus, shown schematically in Figure 1, consists of two vacuum chambers. The molecular beam is produced in the first chamber by supersonic expansion of pure CF₃Br through a variable temperature nozzle (diameter 75 ± 5 μm). The source temperature is

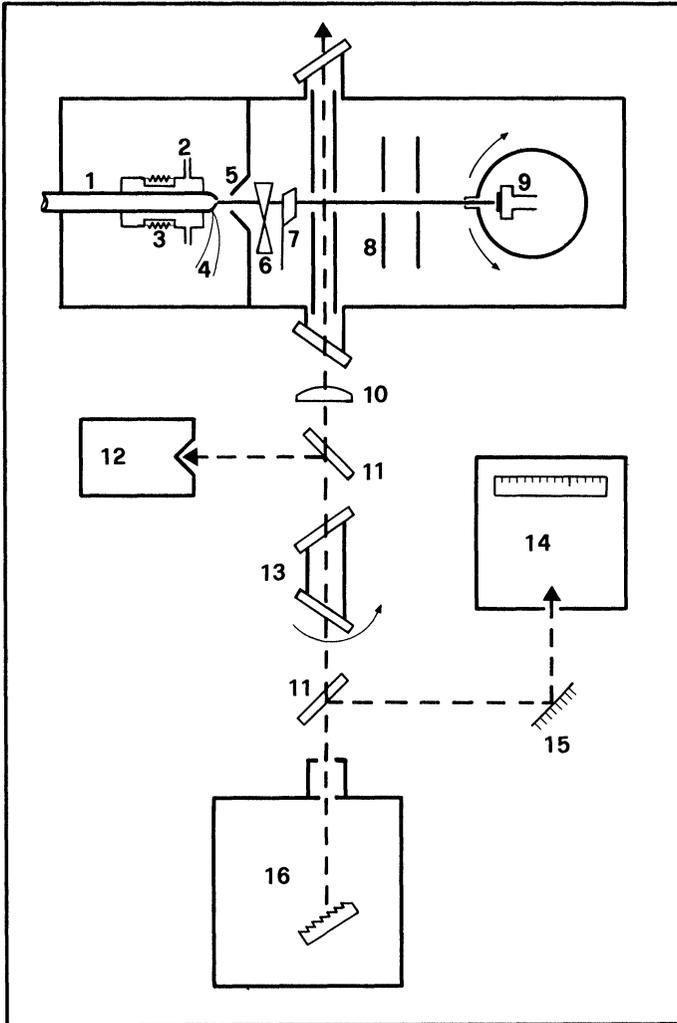


FIGURE 1 Schematic view of the experimental apparatus: (1) molecular beam source; (2) liquid nitrogen cooling system; (3) electric heater; (4) thermocouple; (5) skimmer; (6) mechanical chopper; (7) beam shutter; (8) optical baffles; (9) cryogenic detector; (10) cylindrical lens; (11) beam splitter; (12) power meter; (13) variable attenuator; (14) spectrum analyzer; (15) mirror; (16) line tunable CO_2 pulsed laser.

regulated with an accuracy of ± 0.1 K by means of liquid nitrogen and an electric heater. The temperature may range from 100 to 400 K.

The two vacuum chambers are connected through a conical skimmer which samples the core of the jet expansion. The second chamber contains a liquid helium cryostat on the bottom of which the superconducting bolometer is mounted. It consists of a thin layer of tin which is temperature stabilized around the center of its superconducting transition at 3.7 K. The liquid helium bath is pumped below the He λ -point to reduce thermal fluctuations of the cryostat. The operating temperature of the bolometer is regulated by means of an electric heater.²³

When the molecular beam impinges on the bolometer a small change of temperature is produced. This change is proportional to the molecular beam power and may be detected as a change of the bolometric resistance. The bolometric signal is amplified by a wide-band transformer and by a low-noise amplifier. A mechanical beam chopper and a beam flag are used for measuring the beam intensity by means of the conventional lock-in method.

The infrared source is a line-tunable Lumonics TEA-820 CO₂ laser which produces 2 J pulses with a maximum repetition rate of 20 Hz. The laser energy and wavelength are measured with, respectively, a Scientech power meter (model 38-0102) and a spectrum analyzer. The laser light is vertically polarized and the intensity of the different laser lines is equalized by means of a variable attenuator. The laser beam is focused on the molecular beam by a cylindrical lens (focal length 30 cm). The laser fluence experienced by the molecules is varied by changing the lens position. Several optical baffles are inserted into the vacuum chamber to prevent the diffused laser light from reaching the bolometric detector.

A typical opto-thermal measurement is carried out using a continuous molecular beam and detecting by means of the fast detector the bunch of excited molecules which are produced by each laser pulse. Two checks have been made in order to be sure that the measurements are free from systematic errors. The first one is carried out to exclude the presence in the beam of dimers or clusters which may undergo vibrational predissociation after laser irradiation,²¹ and therefore affect our experiment. The other source of error may be due to the natural infrared fluorescence of the excited molecules. Measurements with different times of flight between the illuminated region

and the detector show that this effect is negligible in our experimental conditions.

An example of bolometric signal is shown in Figure 2. The horizontal scale gives the time of flight of the molecules. Its origin coincides with the laser pulse. One of the main advantages of the fast bolometer is that it makes possible to separate in time the spurious signals, originating from the laser discharge and the diffused radiation, from the true signal produced by the vibrationally excited molecules. This last signal is extracted from the random noise by means of a micro-computer based signal averager.³⁴ The same micro-computer is used for analyzing the averaged signal which may be directly related to the velocity distribution of the molecule. A fit of the experimental data is shown in Figure 2 in full line. It gives information about the mean square velocity $\langle v^2 \rangle$ and the translational temperature T_{tra} of the molecular beam. These quantities are used as parameters for an enthalpy balance computer program²⁴ which calculates the vibrational temperature T_{vib} of the molecules before the laser irradiation. The balance has been calculated assuming that the initial rotational temperature of the beam

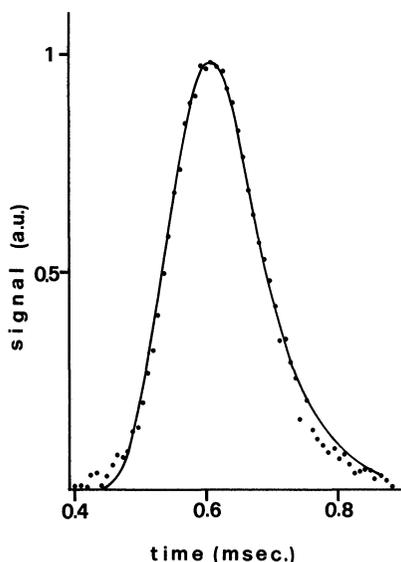


FIGURE 2 An example of the time resolved detector signal. The full line is the result of a best-fit which gives the velocity distribution of the supersonic beam. See text for detail.

is equal to the translational one. This assumption is not too crude for large molecules for which the rotational constants are low. Anyhow, the contribution of the rotational specific heat to the molecular enthalpy is small in our molecular beam conditions and consequently our assumption does not affect too much the calculated value of T_{vib} . A much more drastic approximation is due to the assumption of a single vibrational temperature. Recent measurements carried out by Reuss and co-workers³⁵ have demonstrated the existence of strongly mode dependent vibrational temperatures in a molecular beam of CF₃Br. Nevertheless in our experiment the vibrational relaxation in the beam expansion is quite small, because our beam source is operated at the low constant pressure of 350 mbar. For this reason we expect that the differences between the different modes are less dramatic than in the results of Ref. 35. In any case our value of T_{vib} must be considered as an average over the normal vibrational modes of the molecule. The results of the signal analysis and of the enthalpy balance are shown in Figure 3 for different temperatures of the molecular beam source.

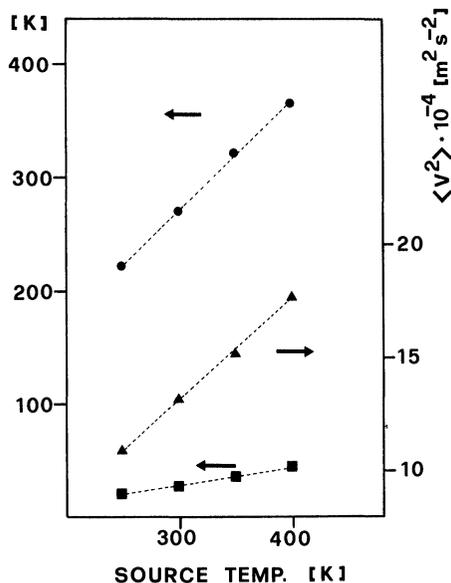


FIGURE 3 The vibrational (●) and the translational (■) temperatures of the molecular beam as a function of the source temperature. The mean square molecular velocity (v^2) (▲) is also shown. The source pressure is set at the fixed value of 350 mbar.

The information about the average number of photons absorbed by each molecule is obtained by integrating the detector signal. Details about the methods used for data reduction may be found in Refs. 21 and 24.

3. THE MULTIPLE-PHOTON EXCITATION OF CF_3Br

CF_3Br is a symmetric-top molecule without a centre of inversion. It has six vibrational modes, three of which are doubly degenerate. The spectroscopic constants of CF_3Br may be found in Ref. 35 and references therein. The ν_1 mode which corresponds to the C-F stretch has an absorption band which lies in the *R* branch of the $9.6 \mu\text{m}$ band of the CO_2 laser.

The MPE spectrum of CF_3Br is shown in Figure 4 for three different laser fluences, at the constant source temperature of 248 K. As mentioned in the previous section the conditions of the molecular beam

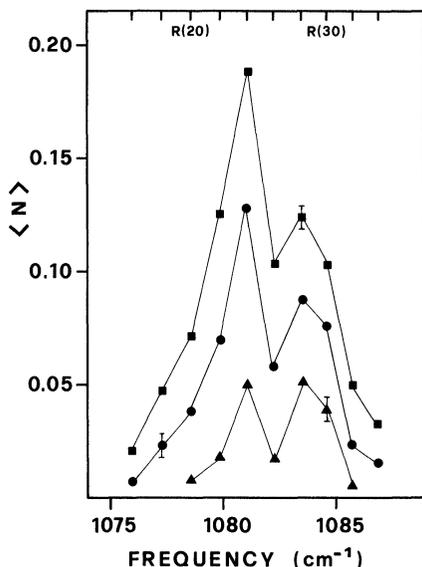


FIGURE 4 The multiple-photon excitation spectrum of CF_3Br for 3 different laser fluences ($\blacktriangle = 0.1 \text{ J cm}^{-2}$; $\bullet = 0.75 \text{ J cm}^{-2}$; $\blacksquare = 2.2 \text{ J cm}^{-2}$). The vertical scale gives the average number of photons absorbed by each molecule. The molecular beam source temperature and pressure are respectively 248 K and 350 mbar.

before the laser irradiation are given in Figure 3. The MPE spectrum is characterized by a well defined two peaks structure. The peak around 1084 cm⁻¹ lies near to the centre of the ν_1 linear absorption spectrum and the second one is placed around 1081 cm⁻¹. There are two possible explanations of the second peak. First of all a two-photon process in the transition $\nu_1 = 2 \leftarrow \nu_1 = 0$ may give rise to such structure because the distance between the two peaks corresponds to the expected anharmonic shift between the single and the two-photon transitions ($X_{11} = -3.4$ cm⁻¹³⁶). On the other hand the position of this peak is near to the expected maximum of the *P*-branch of the single-photon absorption spectrum. This effect has been previously observed by Reuss and co-workers³⁵ who have recently reported the results of a free jet study aimed to study the collision-assisted excitation of CF₃Br by means of a C.W. low power CO₂ laser. In this experiment the laser has been focused very close to the supersonic nozzle and the vibrational excitation of CF₃Br has been monitored by means of the Raman probe. The absorption spectrum shows two peaks at 1080 and 1085 cm⁻¹ which have been attributed respectively to the *P* and *Q* branches of the linear spectrum.

These results cannot be compared with our data because the spectrum reported in Ref. 35 has been obtained under different experimental conditions. In fact Reuss investigated a collision-assisted phenomenon at a rotational temperature of about 100 K. In our conditions (Figure 4) the rotational temperature has been estimated to be about 24 K and the photon-molecule interaction is strictly collisionless. At such a low rotational temperature the maximum of the *P* branch is expected to be around 1082.6 cm⁻¹. Even taking into account that our estimation of the rotational temperature may be affected by a consistent systematic error the separation between the observed peak and the position of the *P* branch maximum seems to be significant. This point may be further clarified by considering the fluence dependence of our spectra. At the lowest fluence (0.1 J cm⁻²) the two peaks have roughly the same intensity while as the fluence increases the 1081 cm⁻¹ peak grows faster. This is a hint that the absorption mechanisms of the two peaks are different and suggests that the 1081 cm⁻¹ peak is more likely due to a two-photon transition.

Figure 5 shows similar measurements carried out at a higher source temperature (398 K). These spectra look very different from those of Figure 4. A first major difference is in the low-frequency range where

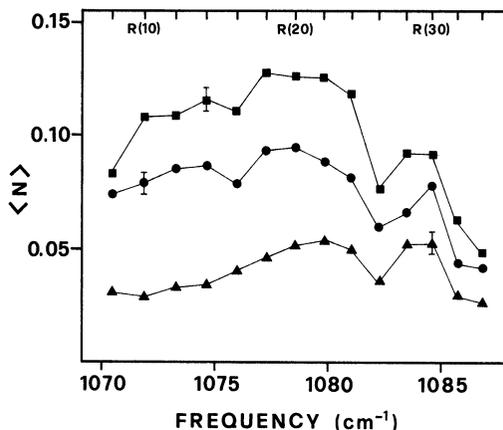


FIGURE 5. The multiple-photon excitation spectrum of CF_3Br for 3 different laser fluences. ($\blacktriangle = 0.26 \text{ J cm}^{-2}$; $\bullet = 0.75 \text{ J cm}^{-2}$; $\blacksquare = 1.3 \text{ J cm}^{-2}$). The molecular beam source temperature and pressure are respectively 398 K and 350 mbar.

a much higher absorption is observed when the source temperature is higher. This low-frequency absorption enhancement changes the shape and the position of the maximum which is significantly shifted. This behaviour may be explained taking into account that the contribution due to the presence of hot bands becomes more and more important at higher temperatures. Furthermore also the beam rotational temperature varies significantly (see Figure 3) giving another contribution to the change of the spectrum. From the point of view of the relative intensities it is interesting to note that the ratio between the low and the high frequency maxima increases as a function of the laser fluence, confirming the behaviour observed in Figure 4.

The temperature dependence of the MPE spectrum is shown in Figure 6. The three sets of data have been obtained at the same laser fluence (0.75 J cm^{-2}) for three different source temperatures. In the same figure is also drawn the result of a theoretical calculation by Capitelli and co-workers.³³ The theoretical calculations have been carried out by a numerical analysis based on the “heat-bath feed-back” model.^{37,38} They calculated the multiple-photon excitation of the molecule as a solution of Bloch equations for the first four discrete levels and of the incoherent master equations for the so-called quasicontinuum.

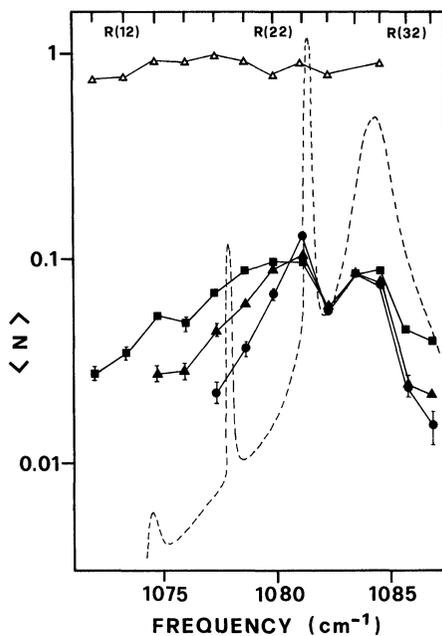


FIGURE 6 The multiple-photon excitation spectrum of CF₃Br for 3 different molecular beam temperatures (● = 248 K; ▲ = 298 K; ■ = 348 K). The dashed line is the result of a theoretical calculation taken from Ref. 33 (Figure 1b). The laser fluence is set at the fixed value of 0.75 J cm⁻². For comparison are shown the results of a cell experiment (△ Ref. 33 Figure 3a) carried out under similar laser conditions.

A relaxation time T_2 term was included into the model to take into account the intramolecular dephasing processes.

The theoretical spectrum shows four distinct peaks at 1084.7, 1081.4, 1078 and 1074.7 cm⁻¹. They are associated respectively with one, two, three and four photon resonances.

A comparison between this theory and our experimental results confirms the above mentioned assignment of the one and two-photon peaks. The theoretical three-photon peak falls between two adjacent CO₂ laser lines, and cannot be measured with our present experimental set-up. The highest temperature experimental data show also a feature corresponding to the expected four-photon resonance. The 1074.7 cm⁻¹ peak can be attributed to both a four-photon $\nu_1 = 4 \leftarrow \nu_1 = 0$ transition and a two-photon $\nu_1 = 3 \leftarrow \nu_1 = 1$ transition of thermally excited molecules.³³ We do not have enough information to assign

the observed peak to a well defined transition but high source temperature data suggest that it is more likely to be due to a two-photon hot transition.

A comparison of the theoretical and experimental spectral intensities shows two major differences. The low-frequency part of the experimental spectrum is much more intense while the part on the high-frequency side is lower than the theoretical predictions. These effects may be explained taking into account that the theory does not include the contributions arising from the rotational states and from the vibrationally excited "hot bands". The thermal behaviour of our experimental data suggests that both these contributions are important.

The analysis of the absorption intensities shows that the average number of photons $\langle N \rangle$ absorbed by each molecule is quite low even at laser fluences near to the dissociation threshold.

The comparison of our data with a room temperature cell MPE experiment (see Figure 6) has shown that the molecular beam MPE yield is at least a factor of 10 less than in the cell. This result is not surprising because a multiple-photon dissociation cell experiment²⁹ has shown that dissociation yield of CF_3Br is consistently increased when the cell pressure is raised from 0.1 to 1 torr.

The differences between our data and those of Ref. 33 may be attributed both to the absence of collisions and to the cooling of the ro-vibrational population which characterizes molecular beam experiments. The small value of $\langle N \rangle$ and its behaviour as a function of the laser fluence may be explained assuming that most of the molecules are bottlenecked into the ground and the $\nu_1 = 1$ vibrational state. Only a small fraction of molecules is excited to the quasi continuum and their contribution to the "average excitation" $\langle N \rangle$ is of the same order of magnitude of the $\nu_1 = 1 \leftarrow \nu_1 = 0$ single-photon absorption. In order to further clarify this point it should be interesting to measure the vibrational population of the molecules after a strictly collisionless multiple-photon excitation. Unfortunately the sensitivity of the presently available probe techniques is not sufficient to carry out this measurement with low density molecular beams.

4. CONCLUSIONS

The multiple-photon excitation of trifluorobromomethane has been investigated under strictly collisionless conditions by means of a

molecular beam opto-thermal experiment. The molecules have been prepared in ro-vibrational distributions very different from those of conventional cell experiments and the effect of the initial distribution on the MPE yield has been studied in detail. The MPE spectrum shows strong structures which have been attributed to different orders of multiple-photon resonances. The comparison of our experimental data with an available theoretical calculation confirms these assignments and shows a strong effect due to the presence of vibrationally excited "hot band" and to the residual rotational excitation of the beam.

Further advances in molecular beam MPE spectroscopy may be achieved by using continuously tunable CO₂ lasers, which are needed for investigating narrow resonance structures in the spectrum. From the theoretical point of view an effort should be devoted to extend the available "heat-bath feed-back" model to the realistic molecular beam conditions. This should be possible because the molecular beam rotational temperature is reasonably low and therefore the computer time needed to carry out such a calculation should be much smaller than for the conditions of cell experiments.

Acknowledgements

The financial supports of the Italian National Research Council (C.N.R.-G.N.S.M.), the Italian Ministry for Public Education (M.P.I.) and the Istituto per la Ricerca Scientifica e Tecnologica (I.R.S.T.) are gratefully acknowledged.

The authors thank R. Dallapiccola, C. Mezzena and the mechanical staff of the Physics Department at Trento for constant help and cooperation.

References

1. J. L. Lyman, R. G. Anderson, R. A. Fisher and B. J. Feldman, *Chem. Phys.* **45**, 325 (1980).
2. V. N. Bagratashvili, I. N. Knyazev, V. S. Letokhov and V. V. Lobko, *Optics Commun.* **18**, 525 (1976).
3. J. G. Black, P. Kolodner, M. J. Shultz, Eli Yablonovitch and N. Bloembergen, *Phys. Rev. A* **19**, 704 (1979).
4. R. C. Sharp, Eli Yablonovitch and N. Bloembergen, *J. Chem. Phys.* **74**, 5357 (1981).
5. W. Fuss, J. Hartman and W. E. Schmid, *Appl. Phys.* **15**, 297 (1978).
6. T. F. Deutsch and S. R. J. Brueck, *J. Chem. Phys.* **70**, 2063 (1979).
7. V. N. Bagratashvili, Yu. G. Vainer, V. S. Doljnikov, S. F. Koliakov, A. A. Makarov, L. P. Malyavkin, E. A. Ryabov, E. G. Silkis and V. D. Titov, *Appl. Phys.* **22**, 101 (1980).
8. V. N. Bagratashvili, Yu. G. Vainer, V. S. Doljnikov, V. S. Letokhov, A. A. Makarov, L. P. Malyavkin, E. A. Ryabov and E. G. Silkis, *Optics Lett.* **6**, 148 (1981).
9. V. N. Bagratashvili, V. S. Doljnikov, V. S. Letokhov, A. A. Makarov, L. P. Malyavkin, E. A. Ryabov, E. G. Silkis and Yu. G. Vainer *Optics Commun.* **38**, 31 (1981).

10. J. W. Hudgens and J. D. McDonald, *J. Chem. Phys.* **76**, 173 (1982).
11. S. Ruhman and Y. Haas, *J. Chem. Phys.* **76**, 1317 (1982).
12. T. B. Simpson, E. Mazur, K. K. Lehmann, I. Burak and N. Bloembergen, *J. Chem. Phys.* **79**, 3374 (1983).
13. R. V. Ambartzumian, G. N. Makarov and A. A. Puretzky, *Optics Comm.* **34**, 81 (1980).
14. H. S. Kwok, Eli Yablonovitch and N. Bloembergen, *Phys. Rev. A* **23**, 3094 (1981).
15. D. Bassi, S. Iannotta and S. Niccolini, *Rev. Sci. Instr.* **52**, 8 (1981).
16. D. M. Brenner, *J. Chem. Phys.* **74**, 2293 (1981).
17. P. Esherick, A. J. Grimley and A. Owyong, *Chem. Phys.* **73**, 271 (1982).
18. V. M. Apatin, V. M. Krivtsun, Yu. A. Kuritsyn, G. N. Makarov and I. Pak, *Optics Commun.* **47**, 251 (1983).
19. T. E. Gough, R. E. Miller and G. Scoles, *Appl. Phys. Letters* **30**, 338 (1977).
20. D. Bassi, A. Boschetti, S. Marchetti, G. Scoles and M. Zen, *J. Chem. Phys.* **74**, 2221 (1981).
21. D. Bassi, A. Boschetti, G. Scoles, M. Scotoni and M. Zen, *Chem. Phys.* **71**, 239 (1982).
22. M. Zen, D. Bassi, A. Boschetti and M. Scotoni, in: *Laser Spectroscopy VI*, eds. H. P. Weber and W. Lüthy (Springer, Berlin 1983) p. 359.
23. D. Bassi, A. Boschetti, M. Scotoni and M. Zen, *Appl. Phys. B* **26**, 99 (1981).
24. A. Boschetti, M. Zen, D. Bassi and M. Scotoni, *Chem. Phys.* **87**, 131 (1984).
25. (a) V. M. Apatin and G. N. Makarov, *Appl. Phys. B* **28**, 367 (1982); (b) V. M. Apatin, T. V. Bezuglova and G. N. Makarov, *Optics Comm.* **42**, 255 (1982).
26. Aa. S. Sudbø, P. A. Schulz, E. R. Grant, Y. R. Shen and Y. T. Lee, *J. Chem. Phys.* **70**, 912 (1979).
27. E. Würzberg, L. J. Kovalenko and P. L. Houston, *Chem. Phys.* **35**, 317 (1978).
28. W. A. Jalenak and N. S. Nogar, *Chem. Phys.* **41**, 407 (1979).
29. M. Gauthier, P. A. Hackett and C. Willis, *Chem. Phys.* **45**, 39 (1980).
30. V. S. Doljnikov, Yu. R. Kolomisky and E. A. Ryabov, *Chem. Phys. Letters* **80**, 433 (1981).
31. M. Nève de Mévergnies, *Appl. Phys. B* **29**, 125 (1982).
32. E. Borsella, R. Fantoni, A. Giardini-Guidoni, D. Masci, A. Palucci and J. Reuss, *Chem. Phys. Letters* **93**, 523 (1982).
33. E. Borsella, D. Masci, M. Capitelli and M. Dilonardo, *Chem. Phys.* **77**, 401 (1983).
34. M. Anderle, D. Bassi, A. Boschetti, S. Iannotta, M. Scotoni and M. Zen, *J. Phys. E* **17**, 276 (1984).
35. G. Luijks, S. Stolte and J. Reuss, *Chem. Phys. Letters* **94**, 48 (1983).
36. H. Bürger, K. Burchzijk, P. Schulz and A. Ruoff, *Spectra Chimica Acta* **38A**, 627 (1982) and references therein.
37. J. A. Horsely, J. Stone, M. F. Goodman and D. A. Dows, *Chem. Phys. Letters* **66**, 461 (1979).
38. M. Dilonardo, G. Petrocelli and M. Capitelli, *Chem. Phys.* **70**, 247 (1982).