PRAMANA
— journal of
physics

Vol. 59, No. 3
September 2002
pp. 487–496

CO_2 laser photoacoustic spectra and vibrational modes of heroin, morphine and narcotine

R L PRASAD[1], S N THAKUR[*] and G C BHAR[2]
Department of Physics, Banaras Hindu University, Varanasi 221 005, India
[1]Presently at Physics Department, IIT, Kanpur, India
[2]Department of Physics, Burdwan University, India
[*]Corresponding author
Email: snthakur1@yahoo.com

MS received 3 July 2001; revised 1 February 2002

Abstract. Heroin, morphine and narcotine are very large molecules having 50, 40 and 53 atoms respectively. Moderately high resolution photoacoustic (PA) spectra have been recorded in 9.6 μm and 10.6 μm regions of CO_2 laser. It is very difficult to assign the modes of vibrations for PA bands by comparison with conventional low resolution IR spectra. The *ab initio* quantum chemical calculations were used for determining the molecular geometries and normal mode frequencies of vibrations of these molecules for assignments of PA spectra.

Keywords. Laser photoacoustic spectroscopy; spectrochemical analysis; infrared spectroscopy.

PACS Nos 33.20.Ea; 33.20.Vq; 33.20.-t; 78.30.-j

1. Introduction

Heroin (dimorphine), morphine and narcotine are extremely harmful drugs and trace detection in powder form is of paramount importance in a good security system in order to check clandestine transport of these harmful compounds. Infrared spectroscopy with conventional excitation source has been employed to study the liquid phase spectra for qualitative analysis of drugs [1] but no work has been done in the most common powder form in which these drugs are generally used. Photoacoustic spectroscopy is a sensitive technique that requires little sample preparation and spectra can be recorded in solid, liquid and vapor phase with equal case. Highly resolved vibrational bands of these molecules have been recorded with rotational line tunable CO_2 laser in the 9.6 μm and 10.6 μm regions. The assignment of these bands have been done in the light of *ab initio* calculations of normal mode frequencies. The rotational lines of CO_2 laser emission fall in the very important Fingerprint region of the infrared spectrum and a close match between the spectrum of a known compound and that of an unknown sample constitutes strong evidence for the identity of the unknown sample. The moderately high resolution resulting from the

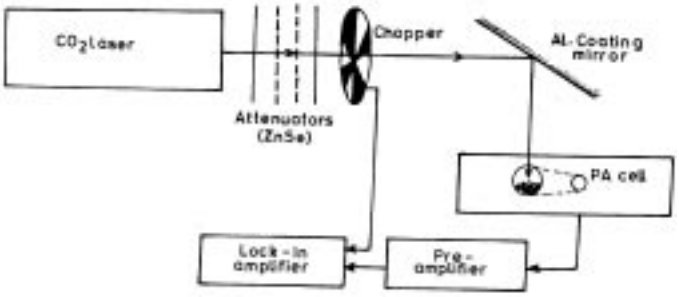

Figure 1. Experimental set up for recording PA spectra of solid samples.

rotational line tunable laser source gives PAS bands with an uncertainty of ± 1 cm $^{-1}$ in their frequencies in the present case, which is an order of magnitude better than that reported by earlier workers [1,2].

2. Experimental

The drug samples were obtained from Central Forensic Science Laboratory, Calcutta having almost 100% purity. The block diagram of experimental arrangement for recording PA spectra of powder sample is shown in figure 1.

The rotational line tunable CW CO_2 laser (Model 8822 of M/S Ultra Lasertech. Inc. Canada) has maximum power of 15 Watts which may be reduced up to 50 mW by using attenuators (ZnSe) to avoid the saturation effect. The power of laser radiation was measured by using a pyro-electric power meter (Model RKP 360, M/S Laser Precision Corporation, USA) and the unfocussed laser beam of 6 mm diameter was made to fall on the sample. Each wavelength was monitored by using a CO_2 spectrum analyzer (Model 16A, M/S Optical Engineering, USA). Some of the rotational lines of CO_2 did not lase and the color of the sample did not change as a result of irradiation. The attenuated CO_2 laser beam was chopped at 22 Hz by a mechanical chopper (Model SR 540, Standford Research Inc.) before entering into the photoacoustic cell containing powder samples. The absorption of CO_2 laser radiation by the sample causes heat generation and leads to pressure fluctuations at chopping frequency which were detected by a sensitive condenser microphone located inside the airtight cell. The output of microphone was fed to pre-amplifier and amplified signal was processed by the lock-in amplifier (EG&G, Princeton Applied Research, Model 186A). The resultant PA signal was read from the panel meter of the lock-in amplifier. The PA signals measured at each of the rotationally tunable wavelengths from the CO_2 laser for drug samples, were normalized by the PA signal for carbon black at the same wavelength. The normalized data was plotted against laser wavelengths using Sigma Plot 3.0 plotting program and the resulting spectra for heroin, morphine and narcotine are shown in figures 2, 3 and 4 respectively. The quality of PA spectra is greatly improved as compared to the conventional infrared spectra [1,2] and hence they are better suited for spectrochemical analysis in view of being free from overlapping which occurs at lower resolution.

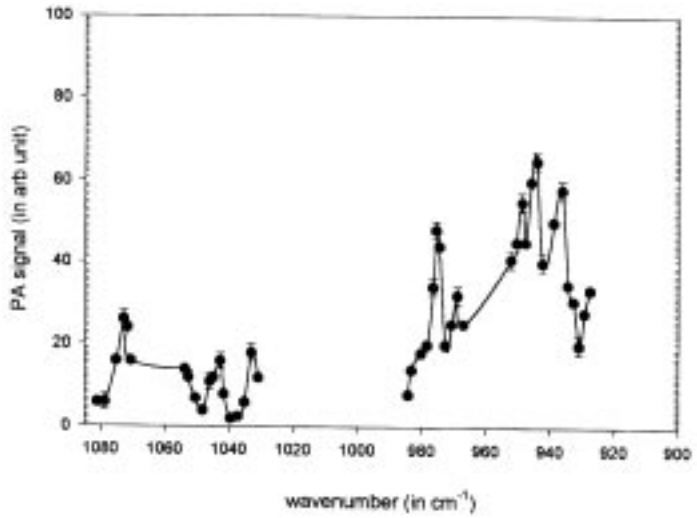

Figure 2. PA spectra of heroin powder.

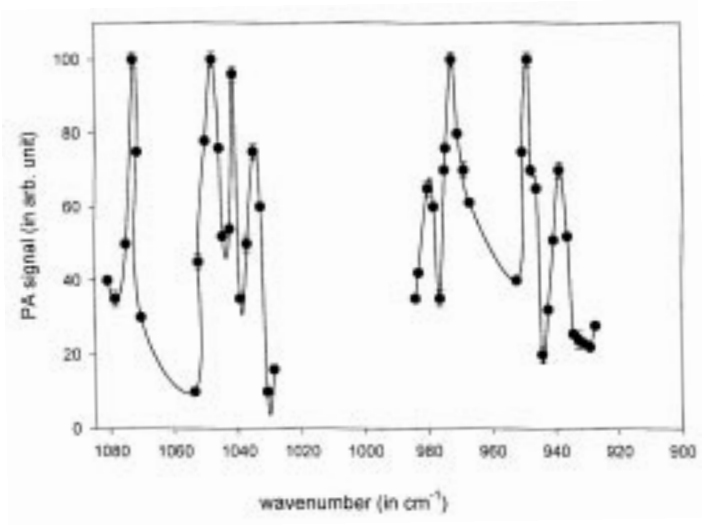

Figure 3. PA spectra of morphine powder.

3. Description of observed spectra

The low resolution infrared spectra of heroin, morphine and narcotine are reported in refs [1,2] and the present PA spectra (figures 2–4) are in general agreement with their corresponding infrared spectra but the number of observed bands are more compared to those reported by earlier authors [1,2].

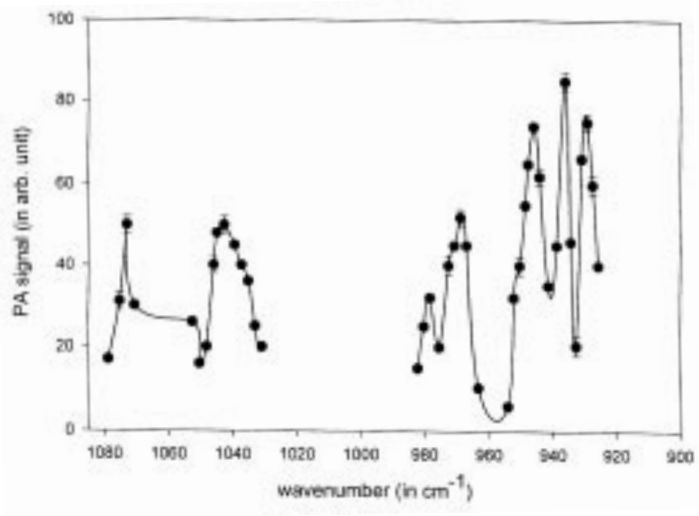

Figure 4. PA spectra of narcotin powder.

Heroin and morphine have similar chemical composition which is reflected in their PA spectra with 4 peaks in 9.6 μm region and 5 peaks in 10.6 μm region. There are, however, significant differences in the relative intensities and finer details of the two spectra. The spectral intensities of observed bands in the 10.6 μm region are comparable for the two compounds but those of morphine in the 9.6 μm region are much larger than in the case of heroin (figures 2 and 3). The differences in the band positions of PA spectrum in the 10.6 μm region is very striking. The strong peak at 949 cm^{-1} and the weak one at 947 cm^{-1} in morphine are in contrast with the weak peak at 949 cm^{-1}and a strong one at 944 cm^{-1} in heroin. Similarly the pattern of a weak peak at 980 cm^{-1} and strong peak at 973 cm^{-1} in morphine is replaced by a strong peak at 976 cm^{-1} and weaker one at 969 cm^{-1} in heroin. Thus we can easily distinguish the spectrum of one compound from the other. There is a sharp peak at 1073 cm^{-1} and a relatively broad one at 1043 cm^{-1} in 9.6 μm region and 5 peaks at 978, 969, 946, 936 and 929 cm^{-1} in 10.6 μm region in narcotine with the band of largest intensity appearing at 936 cm^{-1} (see figure 4).

4. Analysis of vibrational bands

The infrared bands observed in the PA spectra of heroin, morphine and narcotine are compared with their respective infrared spectra in tables 1, 2 and 3 respectively. It is found that in the case of heroin there are strong infrared bands at 1054, 1040 and 1020 cm^{-1}, weak bands at 990 and 950 cm^{-1} and a very weak band at 975 cm^{-1}. These bands are relatively broad due to low resolution but the number of bands observed in the PA spectrum is many more. The strongest band in the PA spectrum is observed at 944 cm^{-1} and the weaker ones are located at 1054 cm^{-1} and 1043 cm^{-1} as can be seen in table 1. It is to be noted that the intensity of band in the PA spectrum depends on the product of absorption cross

section and the non-radiative de-excitation cross section. This excludes a direct correlation between the IR and the PA bands on the basis of their relative intensities. It may also happen that the upper vibrational level of a weak infrared band has a very large non-radiative de-excitation cross section which will make the corresponding band in the PA spectrum much more prominent than in the IR spectrum. In the reverse situation a strong band in the IR spectrum may appear as a very weak one in the PA spectrum. The prominent IR bands at 1054 and 1040 cm^{-1} in heroin may be correlated with the weak bands at 1054 and 1043 cm^{-1} on the basis of their identical frequencies. In contrast the strong PA band at 949 cm^{-1} is correlated with the weak IR band at 950 cm^{-1}. The very weak band at 975 cm^{-1} in the IR spectrum may be identified with the strong band in the PA spectrum of heroin at 969 cm^{-1}.

Table 1. Comparison of PA and IR spectra of heroin.

Frequency of PA bands (cm^{-1})	Relative intensity of PA bands	Frequency of IR bands (cm^{-1}) (ref. [1])	Relative intensity of IR bands
1073	26		
1054	14	1054	Very strong
1043	16	1040	Strong
1033	18	1020	Strong
976	47	990	Weak
969	33	975	Very weak
949	45	950	Weak
944	65		
936	47		

Table 2. Comparison of PA and IR spectra of morphine.

Frequency of PA bands (cm^{-1})	Relative intensity of PA bands	Frequency of IR bands (cm^{-1}) (ref. [2])	Relative intensity of IR bands
1073	100	1075	Weak
1048	100	1050	Strong
1042	96		
1035	75	1025	Strong
980	65	980	Strong
973	100	960	Weak
949	100		
947	70	945	Very strong
938	70		

Table 3. Comparison of PA and IR spectra of narcotine.

Frequency of PA bands (cm^{-1})	Relative intensity of PA bands	Frequency of IR bands (cm^{-1}) (ref. [2])	Relative intensity of IR bands
1073	50	1050	Weak
1043	50	1035	Very strong
978	32	990	Strong
969	52	970	Weak
946	74		
936	85	935	Weak
929	75		

Table 2 shows a comparison between the IR and PA spectra of morphine. The weak IR band at 1075 cm^{-1} may correspond to the strong band at 1073 cm^{-1} in the PA spectrum and the strong band at 1050 cm^{-1} in the former may correspond to the strong band at 1048 cm^{-1} in the latter. There is no PA band in close proximity of IR band at 1025 cm^{-1} and we identify it with the PA band at 1035 cm^{-1}. The strong bands at 980 cm^{-1} in the two spectra are easily identified but there is a frequency difference of 13 cm^{-1} between the IR band at 960 cm^{-1} and PA band at 973 cm^{-1}. Finally it seems that IR peak at 945 cm^{-1} is a broad envelope which has been resolved into three sharp peaks at 949, 947 and 938 cm^{-1} in the PA spectrum (table 2).

The frequencies and relative intensities of bands in IR and PA spectra of narcotine are given in table 3. It is difficult to identify all the PA bands with the IR bands and we can correlate only the three IR bands at 1035, 970 and 935 cm^{-1} with the PA bands at 1043, 969 and 936 cm^{-1} respectively. The observed IR band at 1050 cm^{-1} is weak and has a frequency separation of 23 cm^{-1} from the PA band at 1073 cm^{-1} with which it is correlated (see table 3).

5. Geometry and normal mode calculations

Heroin consists of 50 atoms, morphine has 40 atoms and narcotine has 53 atoms. In order to identify the vibrational bands observed in the photoacoustic spectra, we have calculated the vibrational frequencies using quantum chemical methods. Pulay *et al* [3,4] have developed a method of *ab initio* gradient calculation of molecular geometries and intra-molecular force constants which can be applied to molecules of the size of benzene or even to larger molecules. Molecular geometry is optimized corresponding to the global energy minimum on the potential energy surface of the N-atomic molecule. The potential energy V depends on the set of $3N$ coordinates $x_1, x_2, \ldots x_{3N}$ of the constituent atoms and the configuration at the minimum energy must satisfy the following relations:

$$\frac{\partial V}{\partial x_i} = 0; \quad \frac{\partial^2 V}{\partial x_i^2} > 0. \tag{1}$$

In the present work TURBOMOLE program [5] has been used which is based on the method of derivative minimization. The molecular potential energy is expanded in a power series of small displacement from reference geometry and displacements are represented by a complete and nonredundant set of internal coordinates $\{q_i\}$.

$$V = V_0 + \sum_i \phi_i \Delta q_i + \frac{1}{2!}\sum_{ij} F_{ij}\Delta q_i \Delta q_j + \frac{1}{3!}\sum_{ijk} F_{ijk}\Delta q_i \Delta q_j \Delta q_k \tag{2}$$

where

$$\phi_i = \frac{\partial V}{\partial q_i}; \quad F_{ij} = \frac{\partial^2 V}{\partial q_i \partial q_j}; \quad F_{ijk} = \frac{\partial^3 V}{\partial q_i \partial q_j \partial q_k} \tag{3}$$

at the reference geometry and $\Delta q_i = q_i - q_i^e$, q_i^e corresponds to the reference geometry. The completeness and nonredundancy of $\{q_i\}$ assures that eq. (2) is unique. It is also

necessary to take care that the following transformation connecting internal coordinates q_i with Cartesian's x is not singular

$$\mathbf{q} = \mathbf{B}(\mathbf{x} - \mathbf{x}_0). \tag{4}$$

This criterion is best stated by the requirement that the matrix $\mathbf{BB}^+$ is not singular. If we truncate eq. (2) after second derivative terms we get

$$V = \sum_i \phi_i \Delta q_i + \frac{1}{2!} \sum_{ij} F_{ij} \Delta q_i \Delta q_j. \tag{5}$$

If we minimize the potential energy in eq. (5) with respect to Δq_i we get

$$\sum \phi_i + \sum F_{ij} \Delta q_i = 0. \tag{6}$$

The set of linear equations represented by eq. (6) can be written in the matrix form

$$\Delta \mathbf{q} = -\mathbf{F}^{-1} \boldsymbol{\phi}. \tag{7}$$

In eq. (7) $\boldsymbol{\phi}$ is the gradient vector and $\mathbf{F}$ is the force constant matrix. For quadratic surfaces, eq. (5) can be solved exactly in one step but in practice the surfaces are not quadratic and eq. (5) must be solved iteratively using Newton–Ralphson method. This method is quite suitable for molecules with less than 100 atoms but it is very time consuming due to the evaluation of force constant matrix at each iteration. An improvement is found by using a family of iteration methods called quasi-Newton methods which lead to very efficient geometry optimization.

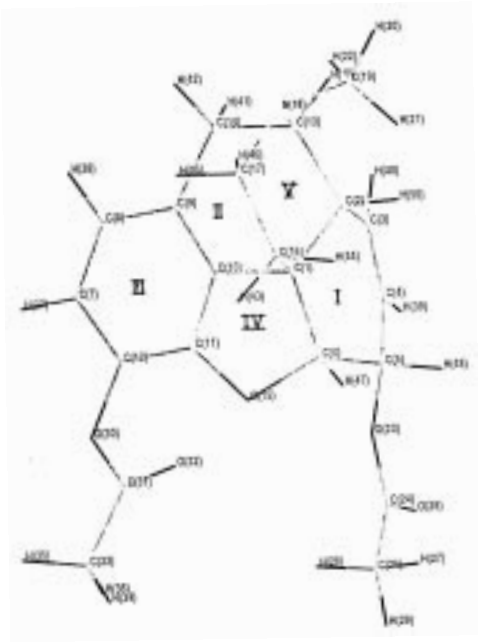

Figure 5. Computationally optimized structure of heroin.

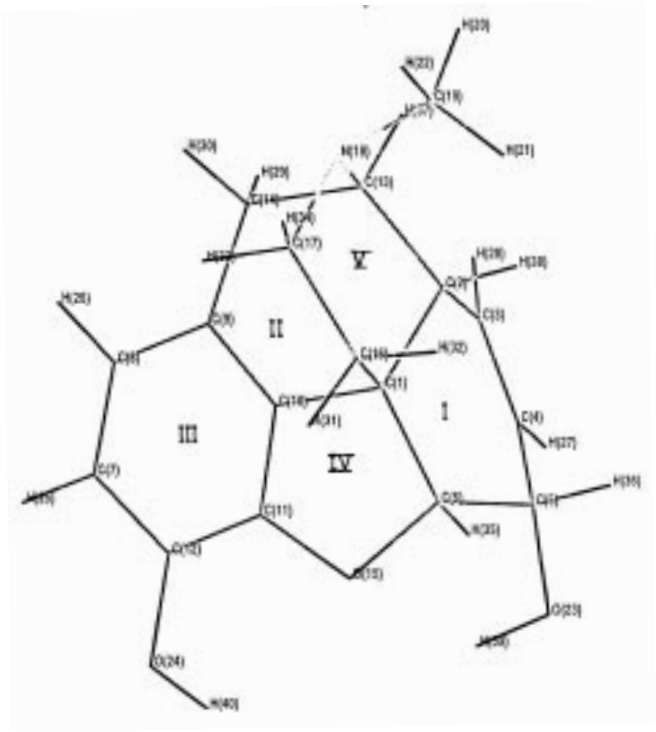

Figure 6. Computationally optimized structure of morphine.

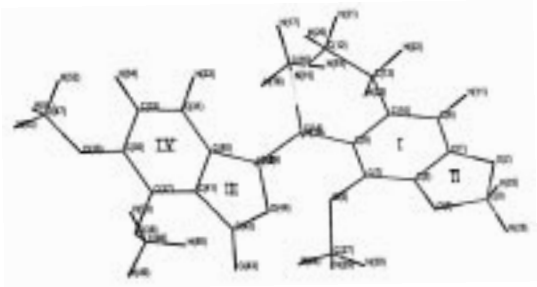

Figure 7. Computationally optimized structure of narcotine.

The computed geometry of heroin is shown in figure 5 which has five rings numbered I to V. The structure of morphine is given in figure 6 which also contains five rings marked I to V. The number of rings in the structure of narcotine is four numbered I to IV as shown in figure 7. The calculated frequencies were scaled using a scaling factor of 1.13 (obtained by comparing observed and calculated C–H stretching frequencies) in all cases. The calculated frequencies which match with the observed frequencies in the PA spectra of heroin, morphine and narcotine are given in tables 4–6 for the three cases with a qualitative

Table 4. PA bands, calculated frequencies and forms of modes of the vibration of heroin.

Frequency of PA bands (cm^{-1})	Calculated frequency (cm^{-1})	Forms of modes of vibration
1073	1063	Deformation of rings I and V
1054	1051	Deformation of rings I and V
1043	1046	C_{13}–C_{14} stretching in ring II
1033	1032	N–CH_3 bend. in ring V
976	996	Bending of acetate group in ring I
969	979	C_6–O_{15} stretching in ring IV
949	967	Distortion of ring III
944	936	Twisting of C_{16}–C_{17} bond. in ring V
936	934	C_2–C_1 stretching in rings I, II and V

Table 5. PA bands, calculated frequencies and forms of modes of vibration of morphine.

Frequency of PA bands (cm^{-1})	Calculated frequency (cm^{-1})	Forms of modes of vibration
1073	1086	C–C stretching in bond common to ring I and IV + C–C stretching in ring I
1048	1055	C–O stretching in ring III + deformation of ring V
1042	1044	Deformation in ring I and V
1035	1039	Deformation of ring V + C–H bend. in ring I
980	999	C–H bending in ring III
973	963	C–H bending in ring III
949	954	C–O stretching in ring IV
947	934	C–C stretching in rings II and IV
938	929	C–C stretching in ring II and deformation of ring V

Table 6. PA bands, calculated frequencies and forms of modes of vibration of narcotine.

Frequency of PA bands (cm^{-1})	Calculated frequency (cm^{-1})	Forms of modes of vibration
1073	1070	C–C stretching in rings I and IV
1043	1055	O_{36}–C_{47} stretching in ring I
978	993	Deformation of rings I, III and IV
969	990	C–O stretching in ring II
946	956	C–C stretching in ring IV
936	943	Deformation in ring I
929	913	C_6–H_{11} bending

description of the normal modes in the last columns of these tables. To obtain the form of normal vibration a computer program (Molden Program) was used which alternately displays, the equilibrium geometry and that corresponding to maximum displacement of constituent atoms during a particular mode of vibration on the screen. This periodic display

gives a visual impression of the motion of the constituent atoms in the molecule and provides a means of qualitatively describing the normal modes which are given in tables 4–6. The number of vibrational frequencies and corresponding normal modes for heroin, morphine and narcotine are 144, 114 and 153 respectively and the list of calculated frequencies can be obtained from the authors on request.

6. Conclusions

The bands in the CO_2 laser PA spectra of heroin, morphine and narcotine (noscapine) are more numerous and sharp in each case as compared to the respective conventional IR spectra. In the case of heroin and narcotine, PA bands in the 10.6 μm region are the best suited for qualitative as well as quantitative estimate of the compound for trace detection. In the case of morphine, however, the PA bands in both the 9.6 μm and 10.6 μm regions are very pronounced and these can be used for its trace detection.

The normal mode description of photoacoustic bands has been attempted with the help of quantum chemical calculations which indicate that most of the vibrations involve complicated deformation motions of the various rings in these molecules (see tables 4–6). There are, however, a few transitions which may be described in terms of stretching or bending of specific bonds, e.g., 1043, 1033, 969, 944 and 936 cm^{-1} in heroin (table 4), 980, 973 and 949 cm^{-1} in morphine (table 5) and 1073, 1043, 969, 946 and 929 in narcotine (table 6). We hope that further work on these compounds using isotopic substitutions will give a much more accurate description of the vibrational motions.

Aknowledgements

We are thankful to R Prasad and P Chandra for their help in calculating normal mode frequencies and to A K Choudhary for providing the sample and to S Das for his help in doing the experiment.

References

[1] W D Breazley, *J. Forensic Sci.* **30**, 915 (1985)
[2] E C G Clarke, *Clarke's isolation and identification of drugs* (The Pharmaceutical Press, London, 1986) pp. 747 and 749
[3] P Pulay and G Fogarasi, *J. Chem. Phys.* **74**, 3999 (1981)
[4] P Pulay, G Fogarasi, F Pang and J E Boggs, *J. Am. Chem. Soc.* **101**, 2550 (1979)
[5] TURBOMOLE – A program package for *ab initio* calculations mainly based on the SCF level of theory by Hans Horn, M Christoph, Koelunel Michael Baer, Marco Haeser and R Ahlrichs, Quantum Chemistry Group, University Karlsruhe