Theoret. Chim. Acta (Berl.) 36, 25–36 (1974)

# Calculated Vibrational Spectra of Weak Hydrogen Bonds

## I. Methanethiol Dimer

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Received May 28, 1974

Potential energy and dipole moment surfaces for the H-bond SH...S in the dimeric methanethiol have been calculated by the SCF-MO-LCGO method, and the vibrational spectrum – transition frequencies and IR absorption intensities at 20 °K – computed. This spectrum is compared with that of the monomeric species and with experimental results. The resulting dimerization energy is 1.4 kcal/mole.

*Key words:* Weak hydrogen bonds – Methanethiol dimer – Vibrational spectra

## 1. Introduction

IR spectra of weak H-bonds XH...Y show a manifold of partially weak and poorly resolved absorptions in the region of the XH stretching mode. The assignment of these transitions to specific vibrational modes is therefore often difficult. The aim of the assignment of transitions is the determination of potential parameter such as the anharmonicity of a potential curve or the anharmonic coupling of vibrational modes. Furthermore the transitions in the range of the XH stretching mode are also able to give one information about the low frequency H-bond stretching vibrations X...Y which are weak and not easily observed directly.

The manifold of absorptions in the XH stretching region is caused by vibrational coupling. This has been shown theoretically by means of a model which well reproduces observed vibrational spectra [1]. Due to the magnitude of the numerical calculation, until now, we can only consider one vibration coupled with the XH stretching vibration. For the coupled vibration the H-bond stretching vibration X...Y has been taken into account by several authors [2–6]; in other cases the H-bond bending vibration or a second XH vibration in a neighbouring XH...Y bond have been coupled with a XH vibration in an H-bond [7, 8]. In the above mentioned model, the XH and the X...Y vibrations are treated within the adiabatic approximation under the condition $\nu_{XH} \gg \nu_{X...Y}$ [1]. The potential parameters are adjusted by means of experimental data.

In the present work, however, no use of the adiabatic approximation is made but the two-dimensional Schrödinger equation for the nuclear motion will be

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solved. Furthermore the potential energy and the dipole moment as functions of the nuclear coordinates of motion are obtained from HF-SCF calculations. Accordingly this calculation of vibrational spectra may be called non-empirical.

The system investigated is the dimeric methanethiol in which extremely weak SH...S bonds are present. Until now no definite statement about the coupling between the SH and the S...S vibration has been made by the use of observed spectra [9]. Barnes *et al.* [10] have used the matrix isolation technique and have varied the concentration at a temperature of 20 °K and from the observed IR spectra it has been possible to assign some absorptions to dimeric methanethiol. In the present work an explanation of these spectra will be considered by means of the calculated spectra.

## 2. Method of Calculation

The computational procedure may be subdivided into three parts:

1) The SCF-MO-LCGO method which gives the total energy $V(q_1, q_2)$ and the dipole moment $\mu(q_1, q_2)$ where $q_1$, $q_2$ are internal coordinates of nuclear motion [11].

2) The two-dimensional least square method which yields analytical expressions in the form of polynomials in $q_1$, $q_2$ for the representation of $V$ and $\mu$ [12].

3) The nuclear CI method for solving the two-dimensional Schrödinger equation of the nuclear motion. A second order perturbation calculation is also included. The results using $V$ are transition frequencies and vibrational states which together by means of $\mu$ yield IR intensities including temperature dependency [13].

The geometry of the monomeric $CH_3SH$ is assumed to be that of Kilb [14], given in [15], with only a small change, namely that in order to get a more symmetrical molecule the S atom is placed on the symmetry axis of the methyl group. The geometry of the dimer is represented in Fig. 1. In the monomeric species only the SH distance has been varied whereas in the dimer only the H-bonded SH distance as well as the S...S distance have been varied independently in order

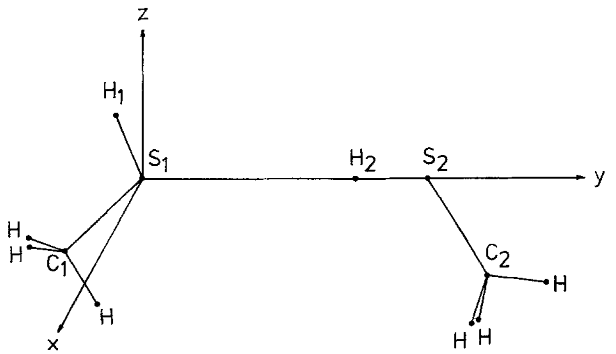

Fig. 1. Geometry of the methanethiol dimer (open chain structure). The $(x, y)$ plane is defined by $H_1$, $S_1$, $C_1$; the $(y, z)$ plane is defined by $H_2$, $S_2$, $C_2$

Table 1. Gaussian basis set used for the methanethiol dimer

| Atom | Type | Nr. | Exponent | Coefficient |
|---|---|---|---|---|
| S | *s* | 1 | 254.622 | 1.0 |
| | | | 44.931 | 2.3 |
| | | 2 | 6.061 | 1.0 |
| | | 3 | 2.448 | 1.0 |
| | | 4 | 0.604 | 1.0 |
| | | 5 | 0.230 | 1.0 |
| | *p* | 1 | 17.260 | 1.0 |
| | | | 3.680 | 1.74 |
| | | 2 | 0.737 | 1.0 |
| | | 3 | 0.202 | 1.0 |
| C | *s* | 1 | 27.380 | 1.0 |
| | | | 4.874 | 1.76 |
| | | 2 | 0.387 | 3.1 |
| | | | 0.147 | 1.0 |
| | *p* | 1 | 1.294 | 1.0 |
| | | | 0.260 | 1.77 |
| H(S) | *s* | 1 | 1.127 | 1.0 |
| | | 2 | 0.201 | 1.0 |
| H(C) | *s* | 1 | 0.397 | 1.0 |

to generate the surfaces $V$ and $\mu$. The non-bonded SH bond has been taken from the results on the monomer.

The basis set used to build up the SCF molecular orbitals is composed of pure spherical Gaussians. The *p* functions are simulated by a suitable contraction of two spherical Gaussians. The distance between them, $\varrho$, is given by the formula $\varrho = 0.2/\sqrt{\eta}$, where $\eta$ is the exponential parameter of the function. All numerical values presented in this paper are in atomic units unless otherwise stated. The values of exponential parameters stated in Table 1 are as follows: for the S atom the (6*s*, 4*p*) basis set of Claxton and Smith [16] contracted to (5*s*, 3*p*) is used; for the remaining atoms the expansion of Slater functions into Gaussians performed by Hehre *et al.* [17] are used with the scaling factors given for $CH_3SH$ in the first column of Table 8 in their paper. In our basis set only one Gaussian function is used for H atoms from the methyl group, two Gaussians for the H atoms bonded with S and a (4*s*, 2*p*) basis set, contracted to (2*s*, 1*p*), for the C atom.

In order to test the part of the basis set describing the SH bond some calculations have also been performed for the S atom and the $H_2S$ molecule. The energy minimum SH distances and the dipole moments for $CH_3SH$ and for $H_2S$ are both greater than their experimental values. In order to make the dipole moments smaller, the two smallest *s*-exponents and the two smallest *p*-exponents of the Gaussian basis set on S have been multiplied by a common scaling factor which has been optimized to give the energy minimum. As a result the exponents have been multiplied by the factor 1.44. Further improvement of the dipole moment of the $CH_3SH$ molecule and a small improvement of its energy has been obtained in an analogous manner by placing the smallest *p*-exponent of the C atom to

0.26. After these improvements of the basis set the SH distance has been optimized and the appropriate Gaussians have been contracted at the calculated equilibrium SH distance. The resulting exponents and contraction coefficients are given in Table 1.

In the next stage of the calculation, the SH distance for the monomer with contracted Gaussians was varied, and the resulting potential energy as well as dipole moment curves were fitted to the polynomial formulae. The axes of the $p$ orbitals of the monomers are so chosen that both monomers are physically equivalent, so that the energy of the dimer for the infinite distance between them is exactly equal to the energy of the monomer multiplied by two.

At the beginning of the calculations for the dimer the S...S distance is varied for fixed geometries of monomers at their calculated equilibrium SH distances. After the energy minimum has been obtained the SH distance in the H-bond SH...S is varied, the S...S equilibrium distance and other geometry parameters being fixed. Furthermore additional points are calculated in the plane which is defined by the SH and S...S coordinates, so that the SH and S...S distance are seen to be independent variables.

The resulting total energy and dipole moment components are two-dimensionally fitted to the polynomials

$$\sum_{k,l} a_{kl} q_1^k q_2^l , \tag{1}$$

where $q_1$ stands for the SH distance and $q_2$ for the S...S distance. With weak H-bonds the cross terms ($k \neq 0$, $l \neq 0$) in the total energy representation are very small but significant for the origin of spectra. This will be discussed later in comparing the spectra for a potential energy without cross terms (complete decoupling of the SH and the S...S modes) with those for coupled modes. The restriction for the coupling terms in the total energy representation was $k+l \leqq 3$. The dipole moment surface underlies the restriction $k+l \leqq 2$.

The results of these fits are used for the calculations of vibrational frequencies and intensities, solving the two-dimensional Schrödinger equation for the nuclear motion. The Schrödinger equation is solved by a CI method using configurations of the type

$$\varphi_1^m(q_1) \cdot \varphi_2^n(q_2) \tag{2}$$

where $\varphi_i^k$ are harmonic oscillator eigenfunctions with the quantum number $k$. With the restriction $m+n \leqq 16$ the total number of configurations was 120. This method is described in more detail in [8].

## 3. Results and Discussion

The results of the HF-SCF calculations for the dimeric methanethiol are given in Table 2. The calculated H-bond of the type SH...S is extremely weak. If the changes of the SH bond on the formation of the H-bond are of interest, the interpolation of the results from Table 2 has to be performed carefully since only slight changes are to be expected.

Table 2. Total energy $E$ and dipole moment components for various SH and S...S distances, all in atomic units (distance: 1 a.u. = 0.52917 Å; energy: 1 a.u. = 219474 $cm^{-1}$; dipole moment: 1 a.u. = 2.54 D)

| SH | S...S | $E+850$ | $\mu_x$ | $\mu_y$ | $\mu_z$ |
|---|---|---|---|---|---|
| 2.31 | 8.124 | −0.6455674 | 0.005895 | −1.311101 | −0.739922 |
| 2.41 | 8.124 | −0.6547270 | 0.005991 | −1.305360 | −0.741693 |
| 2.51 | 8.124 | −0.6599927 | 0.006114 | −1.299320 | −0.742913 |
| 2.61 | 8.124 | −0.6622627 | 0.006271 | −1.293654 | −0.743515 |
| 2.658 | 8.124 | −0.6624908 | 0.006362 | −1.291286 | −0.743577 |
| 2.71 | 8.124 | −0.6622022 | 0.006473 | −1.289116 | −0.743478 |
| 2.81 | 8.124 | −0.6603038 | 0.006731 | −1.286501 | −0.742824 |
| 2.91 | 8.124 | −0.6569371 | 0.007055 | −1.286631 | −0.741596 |
| 3.01 | 8.124 | −0.6523867 | 0.007462 | −1.290344 | −0.739841 |
| 3.11 | 8.124 | −0.6468796 | 0.007904 | −1.298512 | −0.737600 |
| 2.51 | 7.924 | −0.6599869 | 0.006632 | −1.321486 | −0.739757 |
| 2.61 | 7.924 | −0.6622196 | 0.006835 | −1.318677 | −0.740045 |
| 2.658 | 7.924 | −0.6624296 | 0.006954 | −1.317883 | −0.739935 |
| 2.71 | 7.924 | −0.6621215 | 0.007101 | −1.317582 | −0.739636 |
| 2.81 | 7.924 | −0.6601864 | 0.007443 | −1.311911 | −0.738559 |
| 2.51 | 8.324 | −0.6599051 | 0.005613 | −1.279057 | −0.745672 |
| 2.61 | 8.324 | −0.6622028 | 0.005739 | −1.270981 | −0.746534 |
| 2.658 | 8.324 | −0.6624446 | 0.005810 | −1.267298 | −0.746736 |
| 2.71 | 8.324 | −0.6621709 | 0.005896 | −1.263569 | −0.746805 |
| 2.81 | 8.324 | −0.6603012 | 0.006091 | −1.257528 | −0.746515 |
| 2.658 | 7.50 | −0.6617237 | 0.00839 | −1.38371 | −0.73033 |
| 2.658 | 7.70 | −0.6621782 | 0.00768 | −1.35095 | −0.73521 |
| 2.658 | 7.80 | −0.6623188 | 0.00735 | −1.33574 | −0.73741 |
| 2.658 | 8.00 | −0.6624681 | 0.00672 | −1.30746 | −0.74138 |
| 2.658 | 8.20 | −0.6624839 | 0.00615 | −1.28186 | −0.74483 |
| 2.658 | 8.40 | −0.6624062 | 0.00561 | −1.25885 | −0.74782 |
| 2.658 | 8.50 | −0.6623427 | 0.00535 | −1.24830 | −0.74916 |
| 2.658 | 9.00 | −0.6619032 | 0.00418 | −1.20486 | −0.75454 |

In Table 3 some properties of the SH bond in the monomeric species are compared with the results for the dimeric methanethiol. The least square treatment is performed using 5, 8, and 10 points, respectively, so that random errors due to the choice of the points have been excluded. The SH equilibrium distance shows a slight decrease on the formation of the dimer. However, this decrease is of the magnitude of the range of uncertainty of the least square method. Thus the SH distance is unchanged within the accuracy of the computational methods as well as within the accuracy of experimental technique. This SH distance of $2.656 \pm 0.001$ a.u. is greater than the value of 2.51 a.u. observed for the monomer. The calculated S...S equilibrium distance of 8.12 a.u. is found to be in the same range as that for the system $(H_2S)_2$ for which Sabin has calculated the value of 8.50 a.u. [18]. Our calculated equilibrium distance for $H_2S$ is found to be 2.66 a.u. and the equilibrium angle HSH 94°. The experimental values of these parameters are 2.51 a.u. and 92.2°, respectively [15]. The agreement between the calculated and experimental values of geometry parameter is a little better than by those calculated by Sabin [18] with the very strongly contracted basis of Veillard [20], which needs much more computation time than our basis. Our differences between

Table 3. Distances (a.u.), potential parameters (a.u.), and frequencies ($cm^{-1}$) of the SH bonds using 5, 8, and 10 points for the least square fit (PT: second order perturbation theory)

| | 5 | | 8 | | 10 | | |
|---|---|---|---|---|---|---|---|
| | mon | dim | mon | dim | mon | dim | mon (uncontracted basis) |
| SH | 2.658 | 2.656 | 2.658 | 2.656 | 2.657 | 2.655 | 2.655 |
| $a_{20}$ | 0.10271 | 0.10368 | 0.10396 | 0.10428 | 0.10413 | 0.10489 | 0.10522 |
| $a_{30}$ | −0.08236 | −0.08304 | −0.08437 | −0.08574 | −0.08900 | −0.08954 | −0.09028 |
| $a_{40}$ | 0.06212 | 0.06016 | 0.04666 | 0.05303 | 0.05402 | 0.05467 | 0.05454 |
| $\nu$ | 2347 | 2331 | 2320 | 2313 | 2324 | 2312 | 2335 |
| $2\nu$ | 4714 | 4675 | 4613 | 4615 | 4628 | 4606 | 4651 |
| $\nu_{PT}$ | 2310 | 2297 | 2297 | 2285 | 2293 | 2282 | 2305 |
| $2\nu_{PT}$ | 4561 | 4534 | 4512 | 4494 | 4497 | 4478 | 4519 |

the theoretical and experimental values have the same sign as the Sabin's, probably because the bases are related.

The calculated H-bond binding energy $|E_{dim} - 2E_{mon}| = 1.4$ kcal/mole provides an extremely weak H-bond, the force constant $2a_{20}$ of the SH bond in Table 3 showing a slight increase on the formation of the dimer. However, this apparent abnormal effect is so small that it does not yield a wrong frequency shift to higher wavenumbers. Namely, the increase of the reduced mass of 2% is the dominating origin of the frequency shift to lower wavenumbers. It is interesting to note that if the potential energy curve for the SH bond in the dimer were identical with that in the monomer, the frequency shift would be exactly equal to the observed value of 1 %. The one-dimensionally calculated fundamental frequencies for the SH stretching mode are 2324 and 2312 $cm^{-1}$ for the monomer and the dimer, respectively; the corresponding observed values are 2603 and 2576 $cm^{-1}$ [10].

The last column in Table 3 contains the results for the monomeric species using a non-contracted Gaussian basis. The results show in some sense that our contraction of the basis set lowering the computer time by almost 50% does not change essentially the calculated properties.

The anharmonicity $X = \nu - \frac{1}{2}(2\nu)$, calculated by the variational method, is seen to be very sensitive to the number of points used for the calculation. With 5 points a negative anharmonicity of about $-10\,cm^{-1}$ results; with 8 and 10 points, respectively, an anharmonicity of about $10\,cm^{-1}$ is calculated, both for the monomer and the dimer. The anharmonicity calculated with 8 and 10 points, respectively, by the second order perturbation theory is of about $40\,cm^{-1}$, both for the monomer and the dimer. These results are in qualitative agreement with experiments on self-associated thiols in the liquid state, where relatively weak anharmonicities of the order of $50\,cm^{-1}$ are found, both for the free and the associated species [19].

The results of a two-dimensional least square fitting are given in Table 4a for the total energy and in Table 4b for the dipole moment. The coefficient of the harmonic coupling term $a_{11}q_1q_2$ in the total energy representation is so small,

Table 4. (a) Energy surface parameter $a_{kl}$ for the representation (1); parameter after transformation to normal coordinates in parentheses. (b) Dipole moment surface parameter $\mathbf{a}_{kl}$ for the representation (1) (all in a.u.)

| $k$ $l$ | 0 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| (a) | | | | | |
| 0 | 0.0<br>(0.0) | 0.0<br>(0.0) | 0.10489<br>(0.10490) | −0.08954<br>(−0.08954) | 0.05467<br>(0.05466) |
| 1 | 0.0<br>(0.0) | −0.00162<br>(0.0) | 0.00066<br>(−0.00140) | | |
| 2 | 0.00133<br>(0.00132) | −0.00272<br>(−0.00271) | | | |
| 3 | −0.00087<br>(−0.00089) | | | | |
| 4 | 0.00025<br>(0.00025) | | | | |
| (b) | | | | | |
| 0 | 0.00636<br>−1.29129<br>−0.74358 | 0.00217<br>0.03204<br>−0.00023 | 0.00265<br>−0.09670<br>0.02953 | | |
| 1 | −0.00291<br>0.12718<br>−0.01740 | −0.00250<br>0.14648<br>−0.01752 | | | |
| 2 | 0.00049<br>−0.03270<br>0.00565 | | | | |

that its influence on the vibrational frequencies after the transformation from internal coordinates $q_1 = \mathrm{SH}$, $q_2 = \mathrm{S}\ldots\mathrm{S}$ to normal coordinates is negligibly small. This may be seen in Table 4a from the potential parameter after the transformation from internal to normal coordinates (values in parentheses). This transformation causes the disappearance of the harmonic coupling term. Only the anharmonic coupling term $a_{21} q_1^2 q_2$ is changed essentially so that its sign has been reversed. This anharmonic coupling term will be used later for discussing the calculated spectrum. The use of internal coordinates as normal modes within the one-dimensional treatment is now to be justified. The reciprocal reduced masses for the system $CH_3SH\ldots SHCH_3$ are

$$1/m(CH_3SH) + 1/m(CH_3SH)$$

and

$$1/m(H) + 1/(m(CH_3SH) + m(CH_3S))$$

for the S...S and the SH vibration, respectively.

The use of the potential energy from Table 4a and the reduced masses in the Schrödinger equation for the nuclear motion yields vibrational states which are drawn schematically in Fig. 2. The assignment of the states to pairs of quantum

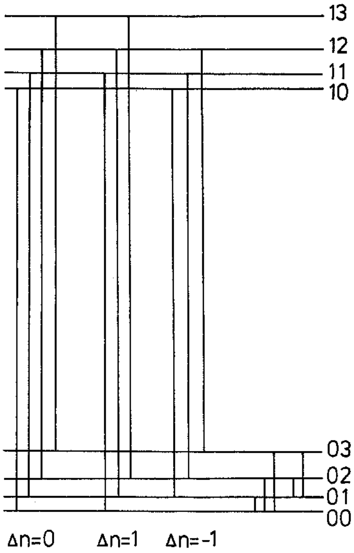

Fig. 2. Schematical representation of the vibrational level scheme for the SH and the S...S vibration in the methanethiol dimer

numbers is straightforward for the lower states and is performed by the use of the dominating coefficient in the expansion of the eigenvector by configurations of the type (2). The level scheme in Fig. 2 shows that there are many transitions in the range of the fundamental stretching vibration. They can be classified by means of the change of the quantum number $\Delta n$ of the S...S vibration. At that stage the influence of the anharmonic coupling in the potential energy shall be discussed.

### *3.1. Neglect of Vibrational Coupling*

The neglect of all cross-terms in the potential energy implies that the Schrödinger equation may be solved by separation with respect to $q_1$ and $q_2$. The results are two independent level schemes for the vibrational states, in the sense, that all fundamental transitions within $\Delta n = 0$ have a common wavenumber; all transitions for $\Delta n = 1$ have a common wavenumber, etc. In other words, the transitions of the S...S mode are independent from the vibrational state of the SH mode.

Furthermore, the neglect of all cross-terms in the dipole moment makes all transitions with $\Delta n \neq 0$ forbidden. For example, the transition 00–11 is possible only with the dipole coupling term $q_1 q_2$ so that $\langle 00|q_1 q_2|11\rangle = \langle 0|q_1|1\rangle \cdot \langle 0|q_2|1\rangle \neq 0$.

The result of the neglect of both the mechanical as well as the electrical coupling is only one wavenumber for the fundamental SH transition together with some hot transitions. This calculated wavenumber is given in Table 5 as 2312 cm$^{-1}$.

Table 5. Transition frequencies and logarithmic intensities ($I$) for the methanethiol dimer with coupling and without coupling (one-dimensional treatment) at 20 °K

| | Transition | With coupling | | Without coupling | |
|---|---|---|---|---|---|
| | | $\nu$[cm$^{-1}$] | log $I$ | $\nu$[cm$^{-1}$] | log $I$ |
| S...S | 00-01 | 48 | 4.23477 | 52 | 4.21956 |
| | 01-02 | 44 | 2.98363 | 49 | 2.86153 |
| | 02-03 | 41 | 1.71600 | 47 | 1.44716 |
| | 03-04 | 40 | 0.47712 | 46 | 0.0 |
| | 00-02 | 92 | 3.13258 | 101 | 3.04139 |
| | 01-03 | 85 | 2.10037 | 97 | 1.88081 |
| | 02-04 | 81 | 0.95424 | 94 | 0.60206 |
| | 00-03 | 132 | 2.07918 | 148 | 1.79934 |
| | 01-04 | 124 | 1.17609 | 143 | 0.77815 |
| | 00-04 | 172 | 1.07918 | 195 | 0.60206 |
| SH | 00-10 | 2309 | 4.52004 | 2312 | 4.12707 |
| | 01-11 | 2301 | 3.40722 | 2312 | 2.51587 |
| | 02-12 | 2290 | 2.22789 | 2312 | 0.95424 |
| | 03-13 | 2284 | 1.00000 | 2312 | <0 |
| | 00-11 | 2348 | 4.27448 | | |
| | 01-12 | 2334 | 2.71265 | | |
| | 02-13 | 2325 | 0.95424 | | |
| | 03-14 | 2326 | 0.0 | | |
| | 00-12 | 2382 | 3.62829 | | |
| | 01-13 | 2369 | 2.71096 | | |
| | 02-14 | 2367 | 1.50515 | | |
| | 00-13 | 2417 | 2.57403 | | |
| | 01-14 | 2411 | 1.69897 | | |
| | 00-14 | 2459 | 0.0 | | |
| | 01-10 | 2261 | 3.12352 | | |
| | 02-11 | 2257 | 2.22272 | | |
| | 03-12 | 2250 | 1.25527 | | |
| | 02-10 | 2217 | <0 | | |
| | 03-11 | 2216 | 0.0 | | |
| | 03-10 | 2176 | <0 | | |
| | 00-20 | 4599 | | 4606 | |

The S...S transitions are found in the region of about 50 cm$^{-1}$. All intensities in Table 5 are calculated at 20 °K in order to compare them with observed spectra [10]. The dipole moment surface resulting from HF-SCF calculations is a very sensitive quantity, so that intensities for different kinds of vibration should be compared with great care. The intensities for the S...S transitions in Table 5 seem to have been overestimated to a large extent with respect to the SH transitions.

### *3.2. Effect of Vibrational Coupling*

The effect of vibrational coupling on the S... S transitions is of little importance. All wavenumbers decrease by about 10%, but no new transitions arise.

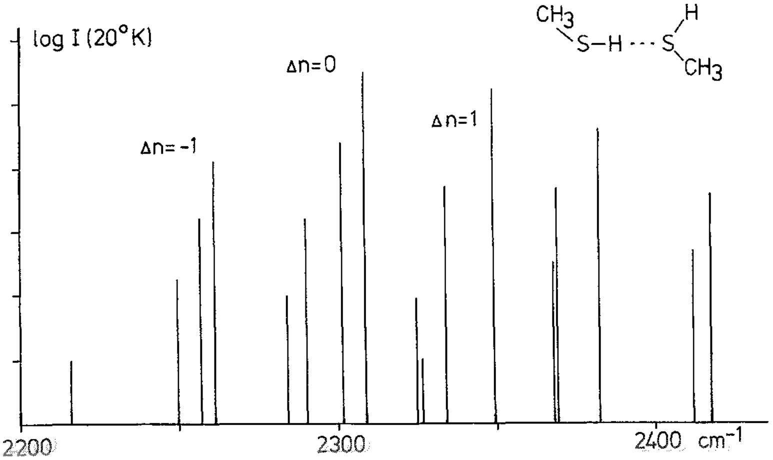

Fig. 3. Calculated IR absorption spectrum for the methanethiol dimer in the range of the SH stretching mode at 20 °K. (For comparison with experiment see Ref. [10])

With the SH fundamental transitions, however, many new transitions occur due to the coupling. They are spread out from 2250 – 2450 cm$^{-1}$ and are structured as seen in Fig. 3. The most intensive transitions at 20 °K are those from the lower vibrational states 00 and 01. Each has some hot transitions which are situated to lower wavenumber. The negative anharmonic coupling term $a_{21} q_1^2 q_2$ is responsible for this shift. The most intensive transitions 01–10, 00–10, 00–11, 00–12 have almost common wavenumber distances among each other, namely about 40 – 50 cm$^{-1}$, which represents the wavenumber of the S…S vibration.

The calculated spectrum in Fig. 3 shall now be compared with the observed one from Barnes *et al.*, shown in their Fig. 1(a). With concentrations $M/A = 1000$, 300, and 100 three absorptions at 2603, 2576, and 2550 cm$^{-1}$ are observed. They were assigned by the authors to the free SH stretching mode, the SH stretching mode in an open chain dimer, and the SH stretching mode in a multimer assumed to be a cyclic tetramer, respectively. The question arises now: Why is the frequency shift from the free SH bond to the dimeric SH bond the same as those from the dimeric SH bond to a tetramer?

From our calculated spectrum the following explanation may be put forward: The absorption at 2576 cm$^{-1}$ corresponds to the dimeric transition 00–10 with $\Delta n = 0$, for which a wavenumber of 2309 cm$^{-1}$ was calculated. The two observed satellites at lower wavenumbers for $M/A = 300$ (2570 and 2564 cm$^{-1}$) show a possible agreement with our hot transitions 01–11 and 02–12 at 2301 and 2290 cm$^{-1}$, respectively. The agreement is also confirmed by the behaviour of intensities.

Even the absorption of the free SH bound at 2603 cm$^{-1}$ has such a satellite for a lower wavenumber (2593 cm$^{-1}$). The calculated dimeric SH absorption for $\Delta n = 1$ (00–11: 2348 cm$^{-1}$; 01–12: 2334 cm$^{-1}$) should possibly be found in the observed spectrum coincident with the monomeric SH absorption, so that the existence of the satellite is explained.

The observed absorptions at 2550 and 2552 $\text{cm}^{-1}$ may be explained by the calculated transitions for $\Delta n = -1$ (01–10: 2261 $\text{cm}^{-1}$; 02–11: 2257 $\text{cm}^{-1}$), providing an explanation of the doublet.

These interpretations give an observed S...S vibrational wavenumber of about 26 $\text{cm}^{-1}$; the corresponding calculated wavenumber is about 40 $\text{cm}^{-1}$.

## 4. Conclusion

In the dimeric methanethiol very weak H-bonds of the type SH...S are present with an H-bond binding energy of less than 1.4 kcal/mole. The present non-empirical theoretical treatment suggests, that the SH distance and the potential curve for the SH stretching are practically unchanged upon H-bond formation. Therefore, the wavenumber shift of the SH mode to lower wavenumber is solely caused by the increasing reduced mass. The anharmonic coupling of the SH mode with the S...S mode is found to be the origin for band broadening and the structure of the absorption band in the range of the SH stretching mode. In spite of the discrepancy of 300 $\text{cm}^{-1}$ between the calculated and the observed SH wavenumber the structure of the calculated vibrational spectrum seems to agree with the observed one. The wavenumber for the S...S stretching vibration seems to coincide with the wavenumber shift of 26 $\text{cm}^{-1}$.

*Acknowledgements.* The authors are indebted to Prof. C. Sandorfy, Departement de Chimie, Université de Montreal, Canada, for suggesting them the problem. We wish also to express our thanks to Prof. H. E. Hallam, University of Swansea, Great Britain, and Dr. B. Webster, University of Glasgow, Great Britain, for stimulating discussions.

One of the authors (K.P.) wishes to thank the Alexander von Humboldt-Stiftung for the fellowship and Prof. H. Preuß for the hospitality extended to him as the guest at the Institut für Theoretische Chemie. He should also like to thank the Polish Academy of Sciences for the partial support of his investigations within the project PAN-3.

## References

1. Marechal, Y., Witkowski, A.: J. Chem. Phys. **48**, 3697 (1968)
2. Ibers, J. A.: J. Chem. Phys. **41**, 25 (1964)
3. Singh, T. R., Wood, J. L.: J. Chem. Phys. **48**, 4567 (1968)
4. Almlöf, J.: Chem. Phys. Letters **17**, 49 (1972)
5. Janoschek, R., Weidemann, E. G., Zundel, G.: Faraday Transactions II **69**, 505 (1973)
6. Janoschek, R.: Theoret. Chim. Acta (Berl.) **29**, 57 (1973)
7. Brickmann, J., Licha, A., Zimmermann, H.: Ber. Bunsenges. Phys. Chem. **75**, 1324 (1971)
8. Janoschek, R.: Theoret. Chim. Acta (Berl.) **32**, 49 (1973)
9. Sandorfy, C.: Private communication
10. Barnes, A. J., Hallam, H. E., Howells, J. D. R.: Faraday Transactions II **68**, 737 (1972)
11. Meyer, W., Pulay, P.: Program Molpro II, München, Stuttgart 1969
12. Janoschek, R.: Program Polfit 2, Stuttgart 1970
13. Janoschek, R.: Program Nucmot 2, Stuttgart 1971
14. Kilb, R. W.: J. Chem. Phys. **23**, 1736 (1955)

15. Tables of interatomic distances and configurations in molecules and ions. London: The Chemical Society 1958
16. Claxton, T. A., Smith, N. A.: Theoret. Chim. Acta (Berl.) **22**, 378 (1971)
17. Hehre, W. J., Ditchfield, R., Stewart, R. F., Pople, J. A.: J. Chem. Phys. **52**, 2769 (1970)
18. Sabin, J. R.: J. Am. Chem. Soc. **93**, 3613 (1971)
19. Bicca de Alencastro, R., Sandorfy, C.: Can. J. Chem. **50**, 3594 (1972)
20. Veillard, A.: Theoret. Chim. Acta (Berl.) **12**, 405 (1968)

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