

Perturbation Calculations of the Interaction Energies between Non-Bonded Hydrogen Atoms

Part 2. *

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Calculations of the interaction energy between non-bonded hydrogen atoms in the fragments A—H---H'—A' for selected displacements of the hydrogen atoms enable one to evaluate corrections to the force field due to the non-bonded interactions and to discuss the changes in the stretching vibration frequencies of the interacting fragments.

In the previous paper ¹ (hereafter referred to as I) the non-bonded interaction energies between the rigid fragments AH and BH were examined in some detail. Particular attention was given to the analysis of the various contributions to the interaction energy in the region of large non-bonded overlap.† In those calculations the position of the fragments with respect to one another was varied, keeping the bond-lengths of the fragments fixed. As a result the "non-bonded" potential energy of approach of the two fragments was studied. Clearly, in many physical situations the nuclei A and B may be held at fixed positions within a molecular framework, and one should enquire as to the effect of the non-bonded interaction on the energy and equilibrium position of the hydrogen atoms. In particular, one might consider a linear case A—H---H'—A' where $R_{AA'}$ is held constant and R_{AH} and $R_{A'H'}$ are varied in an appropriate manner.‡ Such calculations would not only provide some insight into the magnitude and nature of non-bonded interactions in a molecular framework, but also yield theoretical values for the corrections to the force field and consequently allow investigation of the perturbation of stretching vibration frequencies of the interacting fragments.

THE INTERACTION ENERGY

THE MODEL

Two cases were examined: $R_{AA'} = 7.7$ a.u., where the intermolecular overlap is quite significant, and $R_{AA'} = 10.0$ a.u., where the contributions to the interaction energy, which are dependent on the non-bonded overlap, are small. In each case the bond-lengths R_{AH} and $R_{A'H'}$ were varied symmetrically and asymmetrically (see fig. 1) from 1.6 a.u. to 2.6 a.u. about an equilibrium bond-length value of 2.1 a.u. In order to describe the symmetric and asymmetric bond-length variations, the variables d_s and d_a are introduced

$$\begin{aligned}d_s &= \Delta R_{AH} + \Delta R_{A'H'} \\d_a &= \Delta R_{AH} - \Delta R_{A'H'}\end{aligned}$$

* Part 1 is ref. (1).

† This refers to the overlap between two non-bonded fragments where the fragments may or may not be part of the same molecule.

‡ The notation A'H' for the second fragment is used to indicate that the two interacting fragments are the same. The orbitals on A'H' will still be denoted by b and b' .

where ΔR_{AH} and $\Delta R_{A'H'}$ are the extensions of the AH and A'H' bond-lengths respectively.

The description of the fragments and the method of calculating the interaction energies were the same as in I and the parameters were selected to represent, within

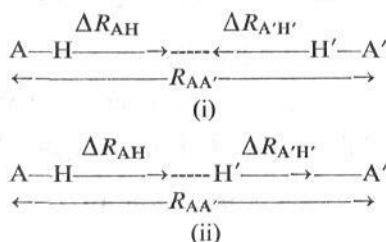


FIG. 1.—(i) Symmetric variation of the AH and A'H' bond-lengths. (ii) Asymmetric variation of the AH and A'H' bond-lengths.

the limitations of the model, two interacting CH fragments. The orbital exponents were given the Slater values: for hydrogen $\zeta_H = \zeta_{H'} = 1.0$ and for carbon $\zeta_A = \zeta_{A'} = 1.625$. In order to assess the effect of changes in bond polarity, calculations were carried out for three values* of the bond parameter l .

ANALYSIS OF THE INTERACTION ENERGY

Results of the calculations for the total interaction energy $\dagger E_{\text{int, tot}} = E_{\text{coul}} + E_{\text{exch}} + E_{\text{ind}} + E_{\text{disp}}$ are presented in fig. 1 and 2. Due to both a larger separation and the concomitant decrease in overlap between the fragments, the interaction energies for $R_{AA'} = 10.0$ a.u. (fig. 2 and 3) are smaller than for $R_{AA'} = 7.7$ a.u. (fig. 2 and 3). Our calculations show that this difference is most notably due to the sharp decrease in E_{exch} . However, the dependence of the various contributions to the interaction energy on the bond-length variations is essentially the same for both AA' distances. Since the separation 7.7 a.u. is approximately equal to the observed C₁—C₈ distance in 1,8-bisdehydro[14]annulene² and should be typical for such intramolecular interactions, the discussion is presented in terms of the results for this distance.

From fig. 4 to 7 it can be seen that a variation in d_s has a large influence on all contributions to the interaction energy whereas changes in d_a affect them only slightly. Since the HH' separation changes on symmetric variation of the bond-lengths but is constant in the asymmetric variation, it follows that the interaction energy of the two fragments is a sensitive function of the HH' distance. Also the various contributions to the interaction energy are more sensitive functions of the bond parameter l for the symmetric displacement than for the asymmetric displacement.

As far as the significance of the changes in the various contributions is concerned, the (weak) dependence of the total interaction energy on d_a is almost completely due to the changes in E_{coul} with d_a . For symmetric bond-length variation, the characteristic features of the variation in $E_{\text{int, tot}}$ are mainly due to E_{coul} and E_{exch} ; however,

* The l values selected here were 0.6, 0.7 and 0.8; see I, pp. 1840-1841 for a discussion pertaining to the selection of appropriate l values to represent a CH fragment. Note that in this work the bond parameter is denoted by l rather than k to avoid confusion with the common use of k for the force constants.

† In this paper the total interaction energy will be denoted by $E_{\text{int, tot}}$ instead of E_{tot} , the notation used in I. Further, the total interaction energy for $d_a = 0$ will be denoted by $E_{\text{int, tot}}^0$ and for $d_s = 0$ by $E_{\text{int, tot}}^A$.

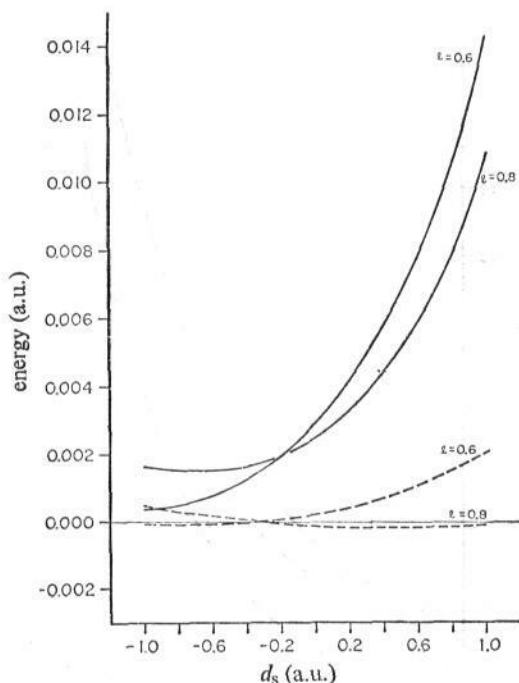


FIG. 2.—Total interaction energy for $d_a = 0$. The solid curve gives the values for $R_{AA'} = 7.7$ a.u. and the broken curve gives the values for $R_{AA'} = 10.0$ a.u.

the changes in E_{ind} and E_{disp} are by no means insignificant. The above-mentioned contributions were therefore analyzed in some detail.

In I an attempt was made to analyse E_{coul} , E_{ind} and E_{disp} , using electrostatic formulae and it was found that for HH' separations less than 6.0 a.u. only the dispersion energy is satisfactorily reproduced. Since for $R_{AA'} = 7.7$ a.u., the HH'

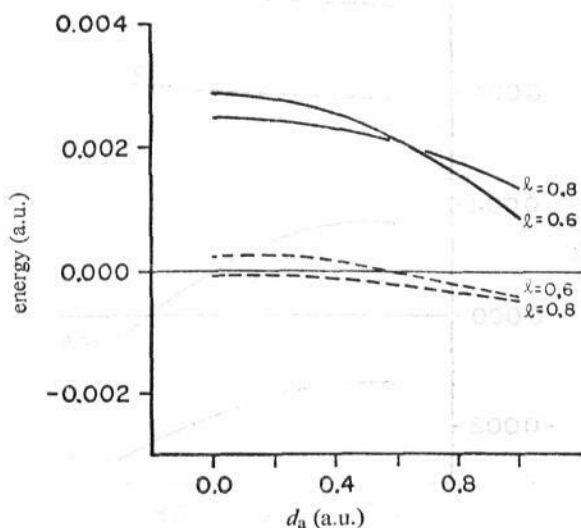


FIG. 3.—Total interaction energy for $d_s = 0$. The solid curve gives the values for $R_{AA'} = 7.7$ a.u. and the broken curve gives the values for $R_{AA'} = 10.0$ a.u.

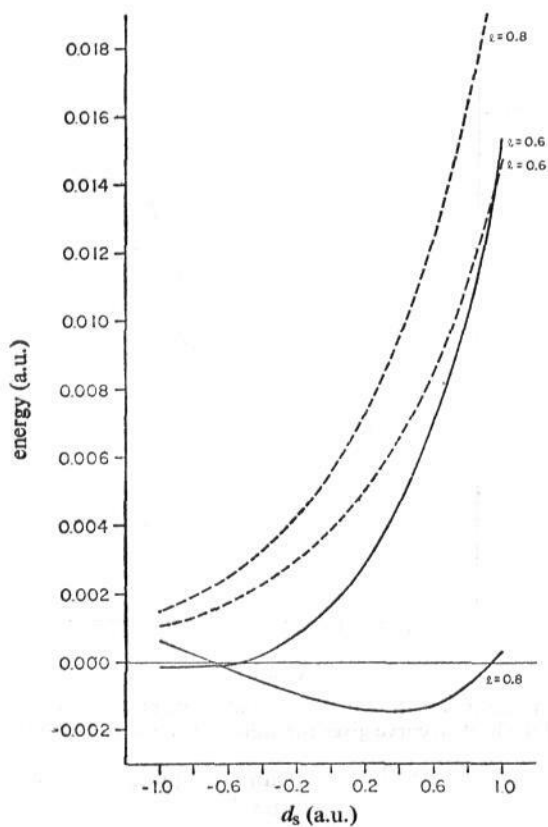


FIG. 4.— E_{coul} (—) and E_{exch} (---) for $R_{AA'} = 7.7$ a.u. and $d_a = 0$.

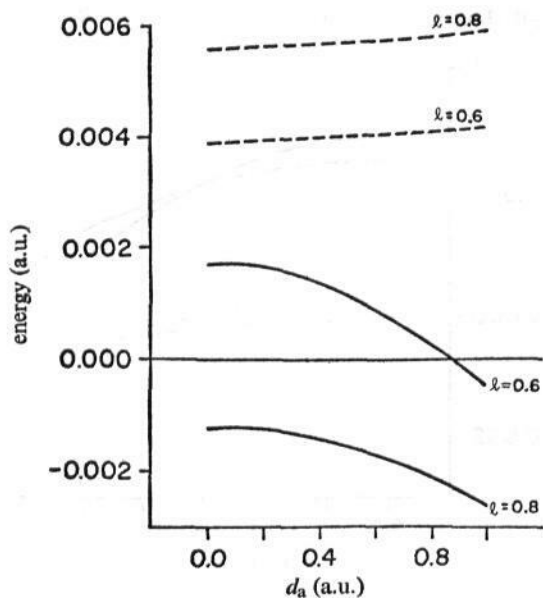


FIG. 5.— E_{coul} (—) and E_{exch} (---) for $R_{AA'} = 7.7$ a.u. and $d_s = 0$.

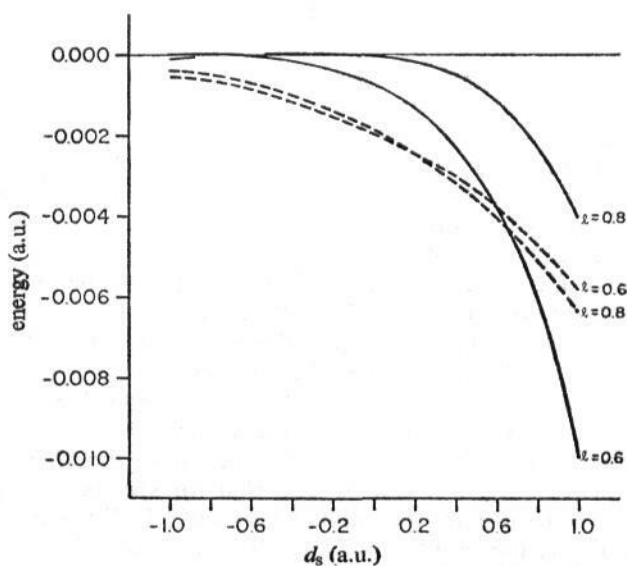


FIG. 6.— E_{ind} (—) and E_{disp} (---) for $R_{AA'} = 7.7$ a.u. and $d_a = 0$.

separation is always smaller than 6.0 a.u., the behaviour of E_{coul} and E_{ind} can only be understood from their perturbation theoretic expressions (I, eqn. (1) and (3) respectively).

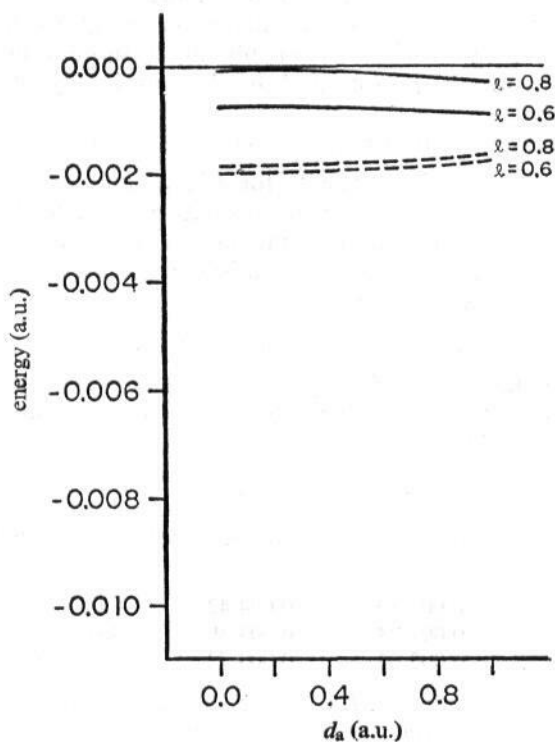


FIG. 7.— E_{ind} (—) and E_{disp} (---) for $R_{AA'} = 7.7$ a.u. and $d_s = 0$.

The dependence of E_{coul} on d_s and l is best understood in terms of the relative magnitude of proton-proton repulsion terms in the expression for E_{coul} . For increasing values of l the proton attraction terms become more important, e.g., in the case of $l = 0.8$ and small values of d_s they outweigh the increase in proton-proton repulsion with increasing d_s . For very large values of d_s the proton-proton repulsion contribution of course becomes dominant for all l values. Although the behaviour of E_{coul} is characteristic of the change in $E_{\text{int, tot}}$ for a variation of d_s , it was not possible to identify in the perturbation theoretic expression those terms which dominate the behaviour of E_{coul} as a function of d_s .

The behaviour of E_{ind} as a function of d_s and l can again be understood as the balance of two contributions, that is $(aa' | V^{AH})$ depends on the relative magnitude of the proton attraction term $(aa' | H_A^{-1})$ and the electron repulsion term $2(aa' | b^2)$. For small values of d_s and large l values the latter term is larger than the former with the result that $(aa' | V^{AH})$ is repulsive. For increasing values of d_s the proton attraction term increases faster than the electron repulsion term with the result that $(aa' | V^{AH})$ becomes increasingly attractive with increasing bond-length, especially for small l values. From fig. 6 it can be seen that for specific values of d_s and l , E_{ind} is zero. These of course are the points where $(aa' | V^{AH})$ changes sign.

As mentioned above, the results for E_{disp} can be reproduced by an electrostatic expression (I, p. 1835). Thus in this case the increase in the dispersion energy (fig. 6) can be attributed to the increase in the polarizabilities of the bonds and the decrease in effective distance, R , with increasing d_s .

In I it was found that E_{exch} is a sensitive function of the non-bonded overlap and the distance, and it can be seen that in the present situation these trends are maintained—that is, E_{exch} increases with increasing values of d_s and l .

In summary then, the sensitivity of the interaction energy to the HH' distance for the symmetric bond-length variation is mainly due to those terms in E_{coul} , E_{exch} , E_{disp} and E_{ind} which involve the protons and the electron density about the protons.

REPRESENTATION OF THE INTERACTION ENERGY

To facilitate applications of the results for $E_{\text{int, tot}}^s$ and $E_{\text{int, tot}}^a$, a functional representation of these quantities in terms of, respectively, d_s and d_a was attempted. Specifically a least squares fit of the total interaction energy in terms of a power series was carried out. In order to obtain a satisfactory representation for $E_{\text{int, tot}}^s$, terms to third order in d_s were required as

$$E_{\text{int, tot}}^s = a_0 + a_1^s d_s + a_2^s d_s^2 + a_3^s d_s^3. \quad (1)$$

Since $E_{\text{int, tot}}^a$ is an even function of d_a only even powers of d_a need be included in the expansion. It was found that $E_{\text{int, tot}}^a$ can be represented quite accurately by the sum of a constant and a quadratic term as

$$E_{\text{int, tot}}^a = a_0 + a_2^a d_a^2. \quad (2)$$

TABLE I.—CONSTANTS IN EQN* (1) AND (2). VALUES IN ATOMIC UNITS

	a_0	a_1^s	a_2^s	a_3^s	a_2^a
0.6	0.002 88	0.005 59	0.004 42	0.001 37	-0.002 01
0.7	0.002 29	0.004 08	0.003 93	0.001 32	-0.001 54
0.8	0.002 48	0.003 24	0.003 72	0.001 37	-0.001 11

* In the fitting procedure the values of $E_{\text{int, tot}}^s$ at $d_s = -1.0, -0.6, -0.4, -0.2, 0.0, 0.2, 0.4, 0.6$ and 1.0 a.u. were used. The standard deviation was less than 5.10^{-5} a.u. In the fitting of $E_{\text{int, tot}}^a$ the values at $d_a = 0.0, 0.2, 0.4, 0.6$ and 1.0 a.u. were used. The standard deviation was less than 1.10^{-5} a.u.

The constant term a_0 in eqn (1) and (2) has the same value, as it represents the interaction energy for the case $d_s = d_a = 0$. The results of the fitting are given in table 1.

APPLICATION OF THE EVALUATION OF CORRECTIONS TO THE FORCE FIELD AND VIBRATION FREQUENCIES

CORRECTIONS TO THE FORCE FIELD

Molecular force fields are commonly evaluated by means of a comparison between calculated and observed frequencies (see for example ref. (3) and (4)). However, it is not always clear whether the force field constants so generated are physically meaningful. This is particularly true with regard to the interaction constants. For interaction constants which are principally due to non-bonded interactions, perturbation calculations could be useful in determining the approximate magnitude of these constants. For example, the calculations discussed in the preceding section indicate that the non-bonded interaction in this case gives rise to interaction constants of the order of 0.1 md/Å. While not bearing a one to one relation, these values might be compared to the values obtained for the force field constants from fitting the spectroscopic data. For example, in propane four CH bonds of the terminal methyl groups are in close proximity and in their calculations Gayles *et al.*⁵ found that inclusion of a bending interaction constant for the eclipsed CH bonds of 0.06 md/Å and one for the CH bonds on opposite sides of the CCC plane of 0.05 md/Å improved the fit. In the case of H₂S and H₂S₄ it was found that intramolecular S—H---H—S stretching and bending interaction constants of 0.01 md/Å had to be included in the force field in order to reproduce the splitting observed for the SH stretching and bending vibrations.⁶

Direct comparison of the interaction constants obtained in the preceding section is of course only possible within the context of the normal coordinate analysis of the entire system. As an illustration we have analyzed the simple C—H---H—C system with fixed R_{CC} for both the interaction force constant and the correction to the diagonal force constant when the non-bonded interaction is taken into account.

The total potential energy for the motion of the hydrogen atoms can be considered as the sum of the vibrational potential energy of the isolated fragment and the interaction energy between them. If cubic and higher terms are neglected, the vibrational potential energy of the *isolated* fragments can be written in the form

$$\begin{aligned} V_{\text{vib}} &= \frac{1}{2}k(\Delta R_{\text{AH}}^2 + \Delta R_{\text{A'H'}}^2) \\ &= \frac{1}{4}k(d_s^2 + d_a^2) \end{aligned} \quad (3)$$

where k is the bond stretching force constant. Using the same approximation as for V_{vib} , the total potential energy for constant AA' distance can be expressed as

$$\begin{aligned} V_{\text{tot}} &= a_0 + \frac{1}{2}f\Delta R_{\text{AH}}^2 + f'\Delta R_{\text{AH}}\Delta R_{\text{A'H'}} + \frac{1}{2}f\Delta R_{\text{A'H'}}^2 \\ &= a_0 + \frac{1}{4}(f+f')d_s^2 + \frac{1}{4}(f-f')d_a^2 \end{aligned} \quad (4)$$

But $V_{\text{tot}} = V_{\text{vib}} + E_{\text{int, tot}}$ and if we consider V_{tot}^s only (i.e., $d_a = 0$) then

$$V_{\text{tot}}^s = a_0 + a_1^s d_s + (\frac{1}{4}k + a_2^s) d_s^2 + a_3^s d_s^3 \quad (5)$$

which we wish to identify with

$$V_{\text{tot}}^s = a_0 + \frac{1}{4}(f+f')d_s^2. \quad (6)$$

The minimum in the potential given by eqn (5) is shifted slightly ($d_s^{\min} \approx -a_1^s / 2(\frac{1}{4}k + a_2^s)$). However, this value of d_s^{\min} is small and consequently the representation in terms of d_s as in eqn (6) is reasonable. Furthermore non-quadratic terms will only affect the energy in the second order perturbation. Since a_0 will be the same in both equations one can identify

$$\frac{1}{4}(f - f') = \frac{1}{4}k + a_2^s. \quad (7)$$

For $d_s = 0$ there was in addition to the constant only a quadratic term in d_a , consequently one obtains

$$\frac{1}{4}(f + f') = \frac{1}{4}k + a_2^a. \quad (8)$$

Eqn (7) and (8) yield

$$f = k + 2(a_2^s + a_2^a) \quad (9)$$

$$f' = 2(a_2^s - a_2^a). \quad (10)$$

The results for the correction to the bond stretching force constant and the interaction constant are given in table 2. Keeping in mind that the bond stretching force constant for a CH bond is roughly 4.7-5.9 md/Å it can be seen that the corrections to this constant are of the order of 1.5 % and that the interaction constant is of the order of 4 % of the bond stretching force constant.

TABLE 2.—CORRECTIONS TO THE FORCE FIELD. VALUES IN md/Å

l	$2(a_2^s + a_2^a)$	$2(a_2^s - a_2^a)$
0.6	0.075	0.200
0.7	0.067	0.178
0.8	0.076	0.156

PERTURBED VIBRATION FREQUENCIES

In order to use these results in the calculation of the stretching vibration frequencies of the fragments, the vibrational motions of the system have to be analyzed in terms of normal modes and characteristic frequencies. In the following this will be done under the restrictions that the system as a whole remains linear and the AA' distance is constant. This last requirement is made for convenience and is of course an approximation to the molecular situation.

The system described above has two vibrational degrees of freedom, and from symmetry considerations it is clear that d_s and d_a correspond to the normal coordinates. In order to find the characteristic frequencies of the normal modes, not only the vibrational potential energy must be known but also the vibrational kinetic energy. The vibrational kinetic energy is obtained by subtracting from the total kinetic energy the kinetic energy of the centre of mass motion. One obtains

$$T_{\text{vib}} = \frac{1}{4}m_{\text{H}}d_s^2 + \frac{1}{4}\mu d_a^2 \quad (11)$$

where m_{H} is the atomic mass of hydrogen and μ is the reduced mass of CH. From the expressions for V_{tot} and T_{vib} , as given by eqn (4) and (11) it follows that the characteristic frequencies of the symmetric and asymmetric vibrations are given by

$$\omega_s = \sqrt{\frac{f + f'}{m_{\text{H}}}} \quad (12)$$

$$\omega_a = \sqrt{\frac{f - f'}{\mu}}. \quad (13)$$

The difference in mass effect can be understood from the fact that the symmetric motion of the hydrogen atoms leaves the centre of mass at its place, whereas in the asymmetric motion this is not the case. It should also be emphasized that this is a result of the analysis of the normal modes for a case where $R_{AA'}$ is held constant.

In table 3 some results for ω_s and ω_a are given, for the case that the interacting fragments are CH bonds and the unperturbed CH bond-stretching vibration frequency is 3000 cm^{-1} . The calculations show that both ω_s and ω_a are lower than the un-

TABLE 3.—PERTURBED VIBRATION FREQUENCIES. VALUES IN cm^{-1}

l	ω_s	ω_a
0.6	2962	2961
0.7	2954	2966
0.8	2950	2976

perturbed frequency, the shift being of the order of $25\text{--}50\text{ cm}^{-1}$. It might also be noted that only for $l = 0.6$ is ω_s higher than ω_a . Both this effect as well as the fact that the splitting increases with decreasing interaction constant is of course due to the mass effect mentioned above.

SUMMARY

The results of the calculations presented in this paper show that the interaction energy of the linear system $A\text{--}H\text{--}H'\text{--}A'$ is a sensitive function of the HH' separation. Further, the variation in the total interaction energy, both for the symmetric motion of the hydrogen atoms as well as for the asymmetric motion, is the strongest for small l values, i.e., for a bond polarity in the sense $A\text{--}H^+$. The result is that the interaction constant increases with increasing polarity in the sense $A\text{--}H^+$. Therefore it is expected that the interaction constant will increase in going from interacting CH bonds to NH, OH and FH bonds.

As far as the calculation of the perturbed vibrational frequencies is concerned, the different mass factors that were found for the symmetric and asymmetric vibration play a very important role in the shift and splitting of the frequencies of the vibrations. However, the restrictions placed upon the motion of the A and A' atoms is the source of the mass effect and may not represent the mass effect obtained from the vibrational analysis in the appropriate molecular situation.

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