A Comparative Study of the BJH- and MCYL-Type Potentials Applied to the Gaseous Water Dimer

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Various refined potentials describing the intra- and inter-molecular force fields of water molecules are used to calculate the properties of the gas-phase water dimer. The intra-molecular parts have been taken from spectroscopic or quantum-chemical sources. The minimum energy structure was found iteratively using the first derivatives of the potential; the force-constant matrix was constructed by numerical differentation. A quite close agreement between the Bopp-Jancsó-Heinzinger and the Matsuoka-Clementi-Yoshimine-Lie potentials is found. The treatment is applied to seven observed water-dimer isotopomeric isomerizations.

Introduction

Theoretical and computational studies of various properties of the water dimer [1–75] have become an essential part of the present-day water research. A crucial role is played by the inter-water potentials [4–6]. Recently, potentials allowing for motions of the atoms within the water molecules have been introduced [7–14]. The intra-molecular potential contributions were originally described together with inter-molecular interactions by means of the so called CF (central force, i.e., depending only on two-centre distances) models introduced by Lemberg and Stillinger [7] (CF [7], CF1 [8], CF2 [9]). However, the versatility of the potentials can be increased [6] using more sophisticated intra-molecular forces. So, Bopp, Jancsó, and Heinzinger (BJH) [10, 11] combined the CF2-type inter-molecular potentials with the quartic force field obtained by Carney, Curtiss, and Langhoff (CCL) from a spectroscopic fit [15]. Similarly, the potentials [16–18] based on the form introduced by Matsuoka, Clementi, and Yoshimine (MCY) [16] were later on expanded by Lie and Clementi (MCYL) [13] through an addition of a quartic potential of the free water molecule from the quantum-chemical evaluation by Bartlett, Shavitt, and Purvis (BSP) [19]. Also Morse functions [12] or even harmonic force field [20–22] were originally considered in this connection. However, the BJH [10, 11] and MCYL [13, 14] potentials have most widely been used, the former having also been applied to liquid methanol [23], aqueous electrolyte solutions [3] and water-metal interface simulations [24, 25].

In spite of the vigorous interest in the computational treatment of the gas-phase water dimer, the BJH and MCYL potentials have practically not been exploited for studying this dimer. In view of the growing amount of observed information on the gaseous water dimer (for recent contributions, see [76–82]) it seemed useful to model it also with the BJH and MCYL potentials. Moreover, a comparison of both potentials under various conditions was desirable.

The Potentials

For the gas-phase water dimer the change ΔE of the potential energy with respect to the infinitely separated monomers is composed of inter- and intra-molecular terms:

$$\Delta E = \Delta E_{\text{inter}} + \Delta E_{\text{intra}} \,. \tag{1}$$

(ΔE_{intra} can further be decomposed into contributions of the first and second molecular unit.) Table 1 lists eight potentials considered in this study. Within the central-force model, three approximations of the inter-molecular contributions are considered: CF1 [8], CF2 [9] and BJH [10, 11] (the latter two differ in the H-H interaction potential, cf. [11]). BJH is a combination of CF with the CCL intra-molecular force-field of gaseous water [15]. The spectroscopic potential was

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Table 1. Survey of the refined water-water interaction potentials studied.

Potential acronyme	Inter-molecular part	Intra-molecular part
CF1/G	CF1 [8]	CCL [15]
CF2/G	CF2 [9]	CCL [15]
BJH/G	BJH [10, 11]	CCL [15]
BJH/L	BJH [10, 11]	BJH [10]
MCY-I	MCYI[a] [16]	BSP [19]
MCY-L	MCYII[b] [16]	BSP [19]
MCY-B	MCYB [17]	BSP [19]
MCY-C	MCYC [18]	BSP [19]

[a] The potential based on the full correlation contribution [16].
[b] The potential based on inter-molecular correlation contribution [16].

derived [15] from the quartic force field [83], adopting a new expansion parameter [84], viz. the term $\Delta R/R$ instead of ΔR. The intra-molecular potential is coded as G (gas) throughout. There exists also a modification of the intra-molecular potential [15] adjusted [10] to liquid-phase conditions. For the sake of completeness the latter is considered, too (coded by L).

Up to now, there are four parametric versions of the ab initio rigid MCY potential [16]. Originally, two modifications of the MCY potential were derived from the self consistent field configuration interaction results [16], differing in the electron-correlation contribution treatment (the full electron correlation: MCYI; the inter-molecular electron-correlation only: MCYII). The MCYII potential was found [21] to yield a better agreement with observed gas-phase water-dimer data. In fact, the MCYII potential was also selected for combination with the BSP intra-molecular force field to yield the MCYL potential [13]. Later on, Bounds [17] found a new solution of the MCYII fitting problem, leading to a substantial decrease in the mean standard deviation (MCYB potential). Finally, Carravetta and Clementi [18] re-evaluated the electron-correlation contribution, producing the fourth (MCYC) potential. In order to follow the way in which the MCYL potential was created [13], also in our connections the four MCY inter-molecular potential versions were combined with the BSP intra-molecular force field [19]. The latter force field was constructed within the standard ΔR expansion [85]. Throughout the paper the refined MCY potentials are denoted as MCY-X (X = I, L, B or C – see Table 1; clearly enough our acronyme MCY-L denotes the same potential as the original short name MCYL, however, e.g., the potentials MCYI and MCY-I are different).

The Potential Treating

The BJH- and MCYL-type potentials differ in their origin, functional forms and employed coordinate sets. Concerning the last mentioned point, the MCYL potentials are more complex as they involve, in addition to usual interatomic distances (and bond angles in the intra-molecular parts), also distances from negative-charge centres * (not residing on any atom). Nevertheless, both coordinate systems exhibit a redundancy (i.e., the coordinates are not independent – there are binding, redundancy conditions between them). This is not convenient from the point of view of energy-minimum location. While in a general, redundancy-free coordinate set R_i the first derivatives of energy are equal to zero in a stationary point,

$$\left(\frac{\partial \Delta E}{\partial R_i}\right)_0 = 0, \tag{2}$$

it is not true in a redundant coordinate set. Then, the Lagrange multiplier method is a technique of choice. However, if we still want to use the treatments designed for optimization without constraints we have to pass to a redundancy-free coordinate set. A convenient choice ** is the set of 18 Cartesian coordinates ξ_i of the six atoms in $(H_2O)_2$. Derivatives with respect to these coordinates are given, e.g., in the terms of the original 15 coordinates $R_i^{(15)}$ used in the BJH-type potentials as follows:

$$\left(\frac{\partial \Delta E}{\partial \xi_i}\right)_0 = \sum_{j=1}^{15} \left(\frac{\partial \Delta E}{\partial R_j^{(15)}}\right)_0 \left(\frac{\partial R_j^{(15)}}{\partial \xi_i}\right)_0 . \tag{3}$$

An application of (3) presupposes knowledge of the internal coordinates R_i as functions of the Cartesian coordinates ξ_i, this being rather straightforward with the BJH-type potentials. However, such a procedure is more complex for the MCY potentials owing to the above mentioned distances from charge centres. In the

* The extension from rigid to the refined MCY-type potentials requires an additional information comparing to the BJH case, viz. a specification how positions of the negative-charge centres change with the monomer deformation. The suggestion [13] was followed, i.e. the charge points always reside on the related bond angle axis, obeying a distance-proportionality rule [13].

** Interestingly enough, the Cartesian coordinate set can, strictly speaking, be understood as abundant too. This remark is related to the problem of translation and rotation of the whole system, which after all is manifested in six (five) zero eigenvalues in the vibrational problem. However, this problem does not interfere in the geometry optimization, cf. [86].

latter case a double application of (3) has turned out be a more convenient alternative (in order to avoid too complex expressions), a third coordinate system being employed as an intermediate.

Having available the analytical potential-energy gradient in the redundance-free Cartesian coordinates, it is possible to apply one of the numerical iterative optimization techniques [87, 88]. The variable-metric method [89] was chosen for that purpose. Within this scheme, the position of the minimum-energy water-dimer structure can in principle be found with any required precision. A next step is a construction of the force-constant-matrix for both, checking the type of the stationary point found and carrying out the harmonic vibrational analysis [86].

In principle, the force-constant matrix elements could again be constructed analytically. Within the above coordinate interplay one has

$$\left(\frac{\partial^2 \Delta E}{\partial \xi_i \, \partial \xi_j}\right)_0 = \sum_{k=1}^{15} \left(\frac{\partial \Delta E}{\partial R_k^{(15)}}\right)_0 \left(\frac{\partial^2 R_k^{(15)}}{\partial \xi_i \, \partial \xi_j}\right)_0 + \sum_{k=1}^{15} \sum_{l=1}^{15} \left(\frac{\partial^2 \Delta E}{\partial R_k^{(15)} \, \partial R_l^{(15)}}\right)_0 \left(\frac{\partial R_k^{(15)}}{\partial \xi_i}\right)_0 \left(\frac{\partial R_l^{(15)}}{\partial \xi_j}\right)_0 . \quad (4)$$

However, with respect to previous experience with numerical differentiation [87] the force-constant matrix was also in our case constructed through numerical differentiation of the analytical potential-energy gradient. Nevertheless, (4) is worth of presenting for a deeper reasoning on the redundancy problem. One reason (avoiding the Lagrange multiplier method) for applying the redundancy-free coordinate set was already mentioned. However, it should also be realized that the standard vibrational analysis implicitly supposes that the first energy derivatives with respect to the coordinates applied vanish. If for a redundant coordinate system the first energy derivatives are nonzero in a stationary point, then one is faced with the problem how to incorporate the "linear" force constants. The first term on the right side of (4) is a way how to handle the "linear" terms (N.B.: if the R_i is a redundance-free coordinate set, then the contribution disappears). Moreover, there is a third reason for abandoning the original coordinates. This is related to the fact that the above mentioned distances from charge centres in the MCY-type potentials involve a point(s) with effectively zero mass. This is again a feature not considered in the standard vibrational-analysis scheme (*G* matrix elements contain reciprocal mass [86]).

Table 2. Structure and energy characteristics of the water dimer[a] in the BJH- and MCYL-type potentials[b].

Term[c]	CF1/G	CF2/G	BJH/G	BJH/L
$R(O_5-O_6)$[d] (Å)	2.854	2.825	2.828	2.828
$R(O_5-H_1)$ (Å)	0.9571	0.9571	0.9571	0.9571
$R(O_5-H_2)$ (Å)	0.9699	0.9686	0.9685	0.9689
$R(O_6-H_3)=$ $R(O_6-H_4)$ (Å)	0.9590	0.9591	0.9591	0.9591
$\angle\,\alpha$[e] (deg)	−3.28	−3.68	−3.77	−3.77
$\angle\,\beta$[f] (deg)	22.98	22.53	21.87	21.86
$\angle\,H_1O_5H_2$ (deg)	103.05	103.05	103.05	103.03
$\angle\,H_3O_6H_4$ (deg)	103.92	103.91	103.90	103.89
ΔE_{inter} (kJ/mol)	−26.53	−24.02	−24.00	−24.02
ΔE_{intra} (kJ/mol)	0.53	0.46	0.46	0.47
ΔE (kJ/mol)	−26.01	−23.56	−23.54	−23.55
Term[g]	MCY-I	MCY-L	MCY-B	MCY-C
$R(O_5-O_6)$[d] (Å)	2.985	2.870	2.976	2.835
$R(O_5-H_1)$ (Å)	0.9547	0.9546	0.9549	0.9552
$R(O_5-H_2)$ (Å)	0.9683	0.9693	0.9675	0.9689
$R(O_6-H_3)=$ $R(O_6-H_4)$ (Å)	0.9613	0.9614	0.9609	0.9612
$\angle\,\alpha$[e] (deg)	2.92	4.21	3.20	5.52
$\angle\,\beta$[f] (deg)	32.53	37.93	33.92	51.76
$\angle\,H_1O_5H_2$ (deg)	103.86	104.02	103.96	103.90
$\angle\,H_3O_6H_4$ (deg)	104.41	104.53	104.48	104.51
ΔE_{inter} (kJ/mol)	−24.73	−25.45	−24.26	−26.09
ΔE_{intra} (kJ/mol)	0.40	0.44	0.33	0.41
ΔE (kJ/mol)	−24.33	−25.01	−23.93	−25.68

[a] See Fig. 1 of Ref. [13] for structural-parameter definition.
[b] See Table 1 for specification of the potentials.
[c] The consistent geometry parameters of a free water molecule read 0.9572 Å and 104.52°.
[d] Observed value [90, 91]: 2.98(1) Å.
[e] Observed value [90, 91]: −1(6)°.
[f] Observed value [90, 91]: 58(6)°.
[g] Cf.[c]: 0.9576 Å and 104.59°.

Numerical differentiation of (3) straightforwardly leads to the force-constant matrix in Cartesian coordinates (once a coordinate shift is selected accordingly – *vide infra*). Each Cartesian coordinate was both increased and decreased by the same shift value (i.e., the potential-energy gradient (3) was evaluated for 36 distorted structures). The final value of a force constant was taken as the mean of the terms from both related shifts. Finally, the resulting force-constant matrix was applied in the harmonic vibrational analysis [86] within the mass-weighted Cartesian coordinates.

Results and Discussion

The key structural and geometrical features calculated for the water dimer with the eight potential versions considered are presented in Table 2. In agreement with the present-day observational and theoretical

consensus the water dimer exhibits C_s point-group symmetry and a near linear hydrogen bond. In all the potentials the twelve non-trivial vibrational frequencies are real so that we deal with a genuine energy minimum, indeed. The agreement with the available experimental geometry data [90, 91] is reasonably good (considering the vibrationally-averaged nature of the latter terms). It is, however, true that the acceptor-molecule deviation from the O-O axis is in practically all our calculations significantly lower than the observed term, this feature being also present in the newest, advanced water-dimer evaluation [74]. Incidentally, the value from the original CF potential [7] (differing slightly in its functional form from the CF1 and CF2 ones) is much closer to the experiment.

The results within both families of potentials are mostly quite close. This is particularly true in the triad CF2/G, BJH/G, BJH/L and (to a less extent) in the triad MCY-I, MCY-L, MCY-B. The CF1/G potential-energy term ΔE lies somewhat lower than in the remaining BJH-type potentials. Similarly, the MCY-C results differ a bit from those of the related triad. The largest shifts in the geometry of H_2O with respect to its free state are observed with the O-H bond of the donor molecule participating in the hydrogen bond and with the bond angle of the molecule. The bond is elongated by about 0.012 and 0.011 Å in the BJH- and MCYL-type potentials, respectively. The donor-molecule bond angle in the two approaches is decreased by about 1.5 and 0.7°. For the MCY-I, MCY-L and MCY-B treatments, the corresponding rigid potential results are available [21, 61, 92], being evaluated with the same precision of the optimization procedure, so that a direct comparison is possible. A considerable effect of the monomeric non-rigidity can be seen for the ΔE_{inter} term, which is lowered by about 0.8, 0.9 and 0.7 kJ/mol in the MCY-I, MCY-L and MCY-B potentials, respectively. However, the effect is reduced to about one half after adding the ΔE_{intra} term. Finally, when comparing the results between both types of the potentials it can be concluded that they are essentially similar, this being a non-trivial conclusion with respect to the considerably different origin and functional form of the potentials.

As the harmonic vibrational frequencies were evaluated using numerical differentiation [89] of the analytical potential-energy gradient, there is a question of precision of the vibrational data. For that purpose, the procedure was carried out in the FORTRAN extended (or quarter – about 35 valid decimal digits) precision, and the differentiation shift was varied in a wide interval. Table 3 serves as illustration. An optimum shift can be declared [93] as that one which produces the smallest (in the absolute value) frequencies which correspond to the overall translation and rotation (i.e., the six frequencies which should be exactly equal to zero). There is of course an arbitrarity in the choice of the criterion; for more symmetric species, for example, the requirement of smallest differences between essentially degenerate vibrational levels can be added [93]. It turns out that for both potentials considered in Table 3 (BJH/G and MCY-L), the optimum shift * is of the order of 10^{-11} Å and the corresponding lowest sum of the absolute values of the six trivial frequencies is about 3×10^{-6} and 1×10^{-6} cm^{-1}, respectively. Moreover, the sum changes with a shift change quite slowly. Changes in the non-trivial vibrational frequencies upon a shift change are even considerably smaller. It is evident from Table 3 that the shift could be changed considerably without having a significant effect on the frequencies. Similar comparison for the FORTRAN double

Table 3. Examples of numerical-differentiation stability with evaluation of harmonic vibrational frequencies (in cm^{-1}) of the water dimer in the BJH/G and MCY-L potentials.

Shift [a] (Å)	Sum of six zero frequencies [b]	The largest difference [c]
BJH/G		
1×10^{-7}	6×10^{-4}	-1×10^{-9}
1×10^{-9}	5×10^{-6}	-1×10^{-13}
1×10^{-11}	3×10^{-6}	0
1×10^{-13}	3×10^{-6}	2×10^{-17}
1×10^{-15}	4×10^{-6}	2×10^{-14}
MCY-L		
1×10^{-7}	8×10^{-4}	-8×10^{-10}
1×10^{-9}	8×10^{-6}	-8×10^{-14}
1×10^{-11}	1×10^{-6}	0
1×10^{-13}	1×10^{-6}	3×10^{-17}
1×10^{-15}	3×10^{-6}	6×10^{-15}

[a] The shift in Cartesian coordinates applied to numerical differentiation in the FORTRAN extended precision.
[b] The sum of the absolute values of the eigenvalues corresponding to translations and rotations.
[c] The largest difference in non-trivial frequencies comparing with the values belonging to the shift leading to the lowest sum [b].

* It does not necessarily mean that the geometry has to be precise to, or even below, this threshold (though actually it was the case). Generally speaking, it would depend on how close to harmonic behaviour a potential in the region is.

Table 4. Changes in vibrational zero-point energy (cm^{-1}) for the observed isomerizations [78] of the water-dimer isotopomers evaluated in the BJH- and MCYL-type potentials[a].

Isomerization	CF1/G	CF2/G	BJH/G	BJH/L	Observed [78]
$DOH.OH_2 = HOD.OH_2$	−69.1	−64.6	−64.4	−48.3	−(110−69)
$DOH.OHD = HOD.OHD$	−68.7	−64.2	−64.1	−47.9	−(70−60)
$DOH.OD_2 = HOD.OD_2$	−68.3	−63.9	−63.8	−47.6	−(68−50)
$DOD.OHD = HOD.OD_2$	3.1	3.1	1.7	3.4	−6− 4
$HOD.OH_2 = HOH.OHD$	77.5	72.8	70.8	56.4	40−60
$DOD.OHD = DOH.OD_2$	71.4	66.9	65.5	51.0	45−72
$DOD.OH_2 = HOH.OD_2$	80.2	75.4	72.1	59.4	30−50
$\sum \delta_i^2$ (cm^{-2})[b]	3071	2504	2174	2616	
Isomerization	MCY-I	MCY-L	MCY-B	MCY-C	Observed [78]
$DOH.OH_2 = HOD.OH_2$	−54.3	−58.2	−52.9	−60.5	−(110−69)
$DOH.OHD = HOD.OHD$	−54.6	−58.5	−53.2	−60.9	−(70−60)
$DOH.OD_2 = HOD.OD_2$	−54.9	−58.8	−53.5	−61.4	−(68−50)
$DOD.OHD = HOD.OD_2$	5.5	5.7	5.2	1.8	−6− 4
$HOD.OH_2 = HOH.OHD$	63.4	68.2	61.7	67.6	40−60
$DOD.OHD = DOH.OD_2$	60.4	64.5	58.7	63.2	45−72
$DOD.OH_2 = HOH.OD_2$	69.1	74.0	67.0	69.7	30−50
$\sum \delta_i^2$ (cm^{-2})[b]	2433	2588	2413	2087	

[a] See Table 1 for specification of the potentials.
[b] Sum of squares of differences between theory and experiment; the observed values represented by the mean of both limits.

precision leads to an optimum shift of the order of 10^{-6} Å but still securing a high numerical stability of the vibrational frequencies.

Comparison of computed results with observations for gas-phase molecular complexes is a rather difficult matter [94–99] owing, inter alia, to an incompleteness of the experimental data and an often somewhat different nature of the terms which are to be mutually compared. This is also valid for the individual vibrational frequencies of the gas-phase water dimer. They are incomplete [76, 77, 79] and of course they are of fundamental (and not harmonic) type. Nevertheless, there is a set of observed data on water-dimer vibrational properties which can be considered both sufficiently complete and (reasonably well) directly comparable with theoretical data, viz. energy changes at very low temperatures for seven different water-dimer isotopomer isomerizations reported recently by Engdahl and Nelander [78]. Moreover, their data have so far been practically unused for comparison with theory (cf. [70]). As to the very low temperatures, the energy changes correspond well to vibrational zero-point energy changes. Moreover, a substantial cancellation of anharmonicity terms can be expected along the isomerizations, and similarly so for effects of the krypton matrices used in the observations. Table 4 presents the vibrational zero-point energy changes for the eight potentials studied and compares them with the observations. In order to facilitate the comparisons, the sum of the squares of the differences between theory and experiment over the seven processes is considered. In the latter terms the best agreement with the observed data is, among the BJH-type potentials, exhibited by the BJH/G, and in the other family by the MCY-C potential. Incidentally, it is quite reasonable that the BJH/G modification works better than the BJH/L one; after all we deal with gas-phase properties. In summa, the agreement is quite good considering that in each of the seven isomerizations twelve vibrational frequencies have to be taken into account on each reaction side.

In conclusion, a surprisingly good agreement between the BJH- and MCYL-type potentials in evaluating the properties of the gas-phase water dimer can be stated (in spite of the different origin and functional form of the potentials) as well as an encouraging agreement with the selected experimental data. While the optimum structure and potential energy terms represent the final values within the potentials, vibrational properties can still be open to non-negligible changes owing to anharmonicity corrections entirely neglected within the present harmonic approach.

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[1] E. Clementi, Determination of Liquid Water Structure, Coordination Numbers for Ions and Solvation for Biological Molecules, Springer-Verlag, Berlin 1976.
[2] F. Franks, Anal. Sci. **4,** 441 (1988).
[3] K. Heinzinger, in Computer Modelling of Fluids, Polymers and Solids, Eds. C. R. A. Catlow, S. C. Parker, and M. P. Allen, Kluwer, Dordrecht 1990, p. 357.
[4] J. R. Reimers, R. O. Watts, and M. L. Klein, Chem. Phys. **64,** 95 (1982).
[5] J. L. Finney, J. E. Quinn, and J. O. Baum, Water Sci. Rev. **1,** 93 (1985).
[6] K. Heinzinger, P. Bopp, and G. Jancsó, Acta Chim. Hung. **121,** 27 (1986).
[7] H. L. Lemberg and F. H. Stillinger, J. Chem. Phys. **62,** 1677 (1975).
[8] A. Rahman, F. H. Stillinger, and H. L. Lemberg, J. Chem. Phys. **63,** 5223 (1975).
[9] F. H. Stillinger and A. Rahman, J. Chem. Phys. **68,** 666 (1978).
[10] P. Bopp, G. Jancsó, and K. Heinzinger, Chem. Phys. Lett. **98,** 129 (1983).
[11] G. Jancsó, P. Bopp, and K. Heinzinger, Chem. Phys. **85,** 377 (1984).
[12] J. R. Reimers and R. O. Watts, Chem. Phys. **85,** 83 (1984).
[13] G. C. Lie and E. Clementi, Phys. Rev. **A 33,** 2679 (1986).
[14] K. Refson, G. C. Lie, and E. Clementi, J. Chem. Phys. **87,** 3634 (187).
[15] G. D. Carney, L. A. Curtiss, and S. R. Langhoff, J. Mol. Spectr. **61,** 371 (1976).
[16] O. Matsuoka, E. Clementi, and M. Yoshimine, J. Chem. Phys. **64,** 1351 (1976).
[17] D. G. Bounds, Chem. Phys. Lett. **96,** 604 (1983).
[18] V. Carravetta and E. Clementi, J. Chem. Phys. **81,** 2646 (1984).
[19] R. J. Bartlett, I. Shavitt, and G. D. Purvis III, J. Chem. Phys. **71,** 281 (1979).
[20] Z. Slanina, J. Chem. Phys. **73,** 2519 (1980).
[21] Z. Slanina, Collect. Czech. Chem. Commun. **45,** 3417 (1980).
[22] Z. Slanina, Advan. Mol. Relax. Interact. Process. **19,** 117 (1981).
[23] G. Pálinkás, E. Hawlicka, and K. Heinzinger, J. Phys. Chem. **91,** 4334 (1987).
[24] K. Heinzinger and E. Spohr, Electrochim. Acta **34,** 1849 (1989).
[25] E. Spohr, J. Phys. Chem. **93,** 6171 (1989).
[26] N. D. Sokolov, Dokl. Akad. Nauk SSSR **58,** 611 (1947).
[27] K. Morokuma and L. Pedersen, J. Chem. Phys. **48,** 3275 (1968).
[28] J. P. O'Connell and J. M. Prausnitz, Ind. Eng. Chem., Fundam. **8,** 453 (1969).
[29] J. Chao, R. C. Wilhoit, and B. J. Zwolinski, J. Chem. Thermodyn. **3,** 195 (1971).
[30] H. Kistenmacher, G. C. Lie, H. Popkie, and E. Clementi, J. Chem. Phys. **61,** 546 (1974).
[31] C. Braun and H. Leidecker, J. Chem. Phys. **61,** 3104 (1974).
[32] J. Kroon, J. A. Kanters, J. G. C. M. van Duijneveldt – van de Rijdt, F. B. van Duijneveldt, and J. A. Vliegenthart, J. Mol. Struct. **24,** 109 (1975).
[33] L. A. Curtiss and J. A. Pople, J. Mol. Spectr. **55,** 1 (1975).
[34] J. C. Owicki, L. L. Shipman, and H. A. Scheraga, J. Phys. Chem. **79,** 1794 (1975); **79,** 3081 (1975).
[35] G. H. F. Diercksen, W. P. Kraemer, and B. O. Roos, Theor. Chim. Acta **36,** 249 (1975).
[36] E. Huler and A. Zunger, Chem. Phys. **13,** 433 (1976).
[37] P. A. Kollman, in Applications of Electronic Structure Theory, Ed. H. F. Schaefer III, Plenum, New York 1977.
[38] W. Thiel, Theor. Chim. Acta **48,** 357 (1978).
[39] P. M. Holland and A. W. Castleman, Jr., J. Chem. Phys. **72,** 5984 (1980).
[40] G. Brink and L. Glasser, J. Comput. Chem. **2,** 14 (1981).
[41] M. D. Morse and S. A. Rice, J. Chem. Phys. **76,** 650 (1982).
[42] G. Brink and L. Glasser, J. Comput. Chem. **3,** 47 (1982).
[43] Y. J. Park, Y. K. Kang, B. J. Yoon, and M. S. Jhon, Bull. Korean Chem. Soc. **3,** 50 (1982).
[44] D. F. Coker, J. R. Reimers, and R. O. Watts, Aust. J. Phys. **35,** 623 (1982).
[45] L. A. Curtiss, Chem. Phys. Lett. **96,** 442 (1983).
[46] E. Clementi and P. Habitz, J. Phys. Chem. **87,** 2815 (1983).
[47] S. Tomoda and K. Kimura, Chem. Phys. **82,** 215 (1983).
[48] D. J. Swanton, G. B. Bacskay, and N. S. Hush, Chem. Phys. **82,** 303 (1983).
[49] G. Jancsó and P. Bopp, Z. Naturforsch. **38a,** 206 (1983).
[50] M. J. Wójcik and J. Lindgren, Chem. Phys. Lett. **99,** 116 (1983).
[51] E. Clementi and G. Corongiu, Int. J. Quantum Chem., Quantum Biol. Symp. **10,** 31 (1983).
[52] B. A. Zilles and W. B. Person, J. Chem. Phys. **79,** 65 (1983).
[53] A. A. Vigasin, Zh. Strukt. Khim. **24,** 116 (1983).
[54] D. J. Swanton, G. B. Bacskay, and N. S. Hush, Chem. Phys. **83,** 69 (1984).
[55] G. Nielson and S. A. Rice, J. Chem. Phys. **80,** 4456 (1984).
[56] G. Brink and L. Glasser, J. Phys. Chem. **88,** 3412 (1984).
[57] J. Sauer, C. Morgeneyer, and K.-P. Schröder, J. Phys. Chem. **88,** 6375 (1984).
[58] L. A. Curtiss, Chem. Phys. Lett. **112,** 409 (1984).
[59] B. J. Yoon, K. Morokuma, and E. R. Davidson, J. Chem. Phys. **83,** 1223 (1985).
[60] A. A. Vigasin, Chem. Phys. Lett. **117,** 85 (1985).
[61] Z. Slanina, Chem. Phys. Lett. **127,** 67 (1986).
[62] K. S. Kim, M. Dupuis, G. C. Lie, and E. Clementi, Chem. Phys. Lett. **131,** 451 (1986).
[63] R. D. Amos, Chem. Phys. **104,** 145 (1986).
[64] M. J. Wójcik and S. A. Rice, J. Chem. Phys. **84,** 3042 (1986).
[65] D. F. Coker and R. O. Watts, J. Phys. Chem. **91,** 2513 (1987).
[66] E. Honegger and S. Leutwyler, J. Chem. Phys. **88,** 2582 (1988).
[67] K.-P. Schröder, Chem. Phys. **123,** 91 (1988).

[68] K. Hermansson and J. Lindgren, Chem. Phys. Lett. **146,** 459 (1988).
[69] K. Szalewicz, S. J. Cole, W. Kołos, and R. J. Bartlett, J. Chem. Phys. **89,** 3662 (1988).
[70] Z. Slanina, Chem. Phys. Lett. **149,** 497 (1988).
[71] Z. Slanina, J. Mol. Struct. **177,** 459 (1988).
[72] O. N. Ventura, E. L. Coitiño, A. Lledós, and J. Bertrán, J. Mol. Struct. (Theochem) **187,** 55 (1989).
[73] C. E. Dykstra, J. Chem. Phys. **91,** 6472 (1989).
[74] U. Niesar, G. Corongiu, M.-J. Huang, M. Dupuis, and E. Clementi, Int. J. Quantum Chem., Quantum Chem. Symp. **23,** 421 (1989).
[75] L. H. Coudert and J. T. Hougen, J. Mol. Spectr. **139,** 259 (1990).
[76] R. H. Page, J. G. Frey, Y.-R. Shen, and Y. T. Lee, Chem. Phys. Lett. **106,** 373 (1984).
[77] D. F. Coker, R. E. Miller, and R. O. Watts, J. Chem. Phys. **82,** 3554 (1985).
[78] A. Engdahl and B. Nelander, J. Chem. Phys. **86,** 1819 (1987).
[79] S. Wuelfert, D. Herren, and S. Leutwyler, J. Chem. Phys. **86,** 3751 (1987).
[80] J. K. Vij and F. Hufnagel, Chem. Phys. Lett. **155,** 153 (1989).
[81] H. Kleeberg and W. A. P. Luck, Z. Phys. Chem. Leipzig, **270,** 613 (1989).
[82] E. Zwart, J. J. Ter Meulen, and W. L. Meerts, Chem. Phys. Lett. **166,** 500 (1990).
[83] A. R. Hoy, I. M. Mills, and G. Strey, Mol. Phys. **24,** 1265 (1972).
[84] G. Simons, R. G. Parr, and J. M. Finlan, J. Chem. Phys. **59,** 3229 (1973).
[85] B. J. Rosenberg, W. C. Ermler, and I. Shavitt, J. Chem. Phys. **65,** 4072 (1976).
[86] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, Molecular Vibrations. The Theory of Infrared and Raman Vibrational Spectra, McGraw-Hill, New York 1955.
[87] S. R. Niketić and K. Rasmussen, The Consistent Force Field: A Documentation, Springer-Verlag, Berlin 1977.
[88] K. Rasmussen, Potential Energy Functions in Conformational Analysis, Springer-Verlag, Berlin 1985.
[89] J. W. McIver, Jr. and A. Komornicki, Chem. Phys. Lett. **10,** 303 (1971).
[90] T. R. Dyke, K. M. Mack, and J. S. Muenter, J. Chem. Phys. **66,** 498 (1977).
[91] J. A. Odutola and T. R. Dyke, J. Chem. Phys. **72,** 5062 (1980).
[92] Z. Slanina, Croat. Chim. Acta. **58,** 295 (1985).
[93] Z. Slanina, P. Kopáček, and S. Beran, Z. Phys. Chem. Leipzig **267,** 1159 (1986).
[94] A. W. Castleman, Jr. and R. G. Keesee, Ann. Rev. Phys. Chem. **37,** 525 (1986).
[95] A. C. Legon and D. J. Millen, Acc. Chem. Res. **20,** 39 (1987).
[96] A. C. Legon and D. J. Millen, Chem. Soc. Rev. **16,** 467 (1987).
[97] K. Toukan and A. Rahman, Phys. Rev. **B31,** 2643 (1985).
[98] P. Demontis, G. B. Suffritti, E. S. Fois, and A. Gamba, Chem. Phys. Lett. **127,** 456 (1986).
[99] L. X. Dang and B. M. Pettitt, J. Phys. Chem. **91,** 3349 (1987).