



Long-range interactions within the H₂O molecule

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Abstract

The long-range interactions between the atoms and diatoms in their ground and first excited states as they appear as fragments on the water dissociation have been modeled. The computed long-range coefficients, which are function of the interaction angle and the interatomic distance of the diatomic, are used to build potential energy functions to represent the long-range energies within this system.

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1. Introduction

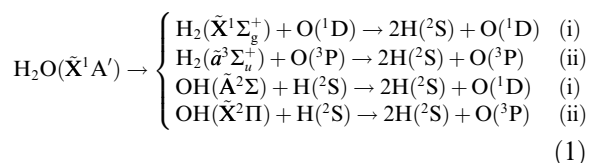
Although there have been a lot of studies on the potential energy surface for the \tilde{X}^1A_1 ground state of the H₂O molecule [1–6], there is a lack of studies on the long-range interactions within this system.

In the absence of those studies and mainly interested on the rovibrational spectra of water, the published potential energy surfaces do not reproduce the long-range interactions or use a simplified form to emulate them neglecting the intra-molecular dependence of the atom–diatom dispersion coefficients. In addition, none of them aims to reproduce the electrostatic quadrupole–quadrupole interaction between the O atom and the H₂ diatom.

In contrast with this situation, the O(¹D) + H₂(¹Σ_g⁺) → OH(²Π) + H(²S) reaction, which oc-

curs mainly in this system, is believed to have a null activation barrier. So, the long-range forces between the O atom and the H₂ diatom should play an important role [7] on the dynamics of this important reaction in atmospheric and combustion chemistry. Despite that, this has been ignored in recent theoretical studies for this reaction [1,7,8].

The \tilde{X}^1A' ground state of the water molecule correlates with the atoms and diatoms in their ground and first excited states allowed by spin and symmetric correlation rules as described by the following equations:



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In this work we aim to study the diabatic long-range interactions between those fragments and

represent them by using analytical functions, including the dependences on the angular and interatomic coordinates.

2. Calculations

In order to represent such interactions we have done MCSCF ab initio calculations of the dipole and quadrupole charge distributions, as well as for the dipolar polarizabilities. Those calculations have been made for the different atoms and diatoms, at different R values, in their ground and first excited state as they appear in Eq. (1). To model the dispersion anisotropy by a 2-term Legendre expansion, we have computed the perpendicular and parallel components of the polarizability. To cover all configurational space we have also done calculations on the united atom limits, F and He atoms, in the corresponding electronic states.

All the calculations have been made using the suite programs GAMESS [9] and augmented triple-zeta quality basis set: (10s5p3d1f/4s3p2d1f) augmented with tight functions (2s2p1d) and diffuse (1s1p1d1f) for O and F atoms [10], (5s2p1d/3s2p1d) with diffuse (1s1p1d) functions for H atom [11] and (6s2p1d/3s2p1d) with diffuse (1s1p1d) functions for He atom [12]. Test calculations using this basis and one of Sadlej [13] (optimized for electrical properties) have shown that they give similar polarizability values but the augmented triple-zeta gives lower energies. To define the active space for the multiconfiguration calculations we have used all the molecular orbitals generated from the 1s and 2s orbitals of H atom and 1s, 2s, 2p, 3s and 3p orbitals of O atom. We have considered all the configurations generated within this space. Test calculations have shown that a MCSCF calculation within this active space gives lower energy values than a MR-CI using the 1s orbital for the H atoms and 1s, 2s and 2p orbitals for the O atom as active space and single and double excitations from this valence space to external orbitals, usually named CASSCF-CI. The polarizabilities have been calculated using the finite electric field method as implemented in GAMESS.

3. Results

For some of the systems here studied, in particular for H atom and H₂, we can found accurate values in the literature to compare with. Those results serve as tests of our calculations showing a reasonable agreement in all cases. When available, we use the more accurate values.

To our knowledge only the value for the quadrupolar moment of O atom, ³P state, is quoted in literature [14]. For consistency we have calculated its value for both ³P (−0.992 a.u.) and ¹D (0.917 a.u.) states.

The R dependence of the values obtained for the diatomics was defined by fitting them to the functional form

$$F(R) = A + \left(\sum_{i=0}^3 B_i R^i \right) \exp \left(- \sum_{i=1}^3 C_i R^i \right) + (1 - \exp(-D_3 R^5)) E_3 / R^3 + (1 - \exp(-D_6 R^8)) E_6 / R^6. \quad (2)$$

This function has a short range term made by a polynomial multiplied by an exponential, with another polynomial on the exponent, added to a long-range R^{-n} term, $n = 3$ or 6 , properly damped, as proposed for the long-range polarizability of the He₂ [15]. Tables 1–3 display the fitted coefficients. In those tables and in all this work we use *atomic units*.

In all cases the fitting is good and some of them are shown in Figs. 1 and 2.

4. Functional representation

The long-range interactions are, as usually, expressed as r^{-n} series. In order to avoid their effect at intermediate and short distances, this series must be suitably damped. In this work we use the general damping functions $\chi_n(r)$ [16].

Due to the similarities between the dissociation channels (i) and (ii) the following expressions fit to any one of them. So, from now on we will not label the electronic state of the atom and diatom involved in the specific interaction.

Table 1

Fitted coefficients (in a.u.) for function (2), to represent the quadrupolar moment for H₂ and the dipolar moment for OH

| Term | Θ H ₂ (¹ Σ _g ⁺) | Θ H ₂ (³ Σ _u ⁺) | μ OH (² Π) | μ OH (² Σ) |
|----------------|--|--|----------------------------|----------------------------|
| A | | | | |
| B ₀ | | -1.2E+1 | 3.34634E-6 | |
| B ₁ | 9.22929E-2 | | 1.10145 | -5.35373E-1 |
| B ₂ | -1.01879E-2 | | -9.24344E-1 | 6.44911E-1 |
| B ₃ | 1.03075E-2 | | 3.47117E-1 | 8.53312E-3 |
| C ₁ | -1.06356 | 1.99302E-2 | -3.62597E-1 | 1.28817 |
| C ₂ | 2.84762E-1 | 6.07726E-1 | 3.67325E-1 | -7.47762E-1 |
| C ₃ | 1.19616E-8 | | | 1.83918E-1 |
| D ₃ | 1.34734E-2 | 1.24088E-2 | 6.83140E-3 | 1.35063E-2 |
| E ₃ | 3.90374 | -2.55326E+1 | 2.39261 | 5.53301 |
| D ₆ | | | | |
| E ₆ | | | | |

Table 2

Fitted coefficients (in a.u.) for function (2), to represent the parallel and the perpendicular components of polarizabilities for H₂

| Term | α_{\perp} H ₂ (¹ Σ _g ⁺) | α_{\parallel} H ₂ (¹ Σ _g ⁺) | α_{\perp} H ₂ (³ Σ _u ⁺) | α_{\parallel} H ₂ (³ Σ _u ⁺) |
|----------------|--|--|--|--|
| A | 9.0 | 9.0 | 9.0 | 9.0 |
| B ₀ | -7.61700 | -7.61700 | 9.20910 | 9.20910 |
| B ₁ | 4.87503 | 6.31342 | 7.76381E+1 | 3.73782E+3 |
| B ₂ | -1.86843 | -2.86774 | | |
| B ₃ | 3.82230E-1 | 7.77710E-1 | | |
| C ₁ | -5.63545E-1 | -7.69666E-1 | 1.69641 | 4.93109 |
| C ₂ | 2.81068E-1 | 2.81168E-1 | 4.34410E-9 | -7.25382 |
| C ₃ | | | 2.75347E-1 | 4.26734 |
| D ₃ | 1.78618E-3 | 4.15672E-3 | 4.77254E-3 | 3.89702E-2 |
| E ₃ | -2.82744E+1 | 1.50746E+2 | -5.81647E+1 | 1.34470E+1 |
| D ₆ | | | | 2.47694E-2 |
| E ₆ | | | | 8.99229E+2 |

Table 3

Fitted coefficients (in a.u.) for function (2), to represent the parallel and perpendicular components of polarizabilities for OH

| Term | α_{\perp} OH(² Σ) | α_{\parallel} OH(² Σ) | α_{\perp} OH(² Π) | α_{\parallel} OH(² Π) |
|----------------|--------------------------------------|--|--------------------------------------|--|
| A | 9.63784 | 8.77530 | 9.60613 | 9.33810 |
| B ₀ | -6.09815 | -5.63591 | -6.06644 | -6.19871 |
| B ₁ | | 7.77847 | | 5.29573 |
| B ₂ | | -3.77081 | | -1.36949 |
| B ₃ | | 6.32319E-1 | | 1.13441E-1 |
| C ₁ | -1.59966E-3 | -1.12258 | 4.86487E-1 | -7.30744E-1 |
| C ₂ | 3.22130E-1 | -7.20865E-1 | -1.31992E-1 | -2.89381E-1 |
| C ₃ | 1.43778E-2 | 2.73829E-1 | 4.24270E-2 | 7.29806E-2 |
| D ₃ | 2.36155E-3 | | 2.17251E-4 | 4.27100E-3 |
| E ₃ | -4.62767E+1 | | -2.55359E+1 | 1.20166E+2 |
| D ₆ | | 1.73020E-5 | | |
| E ₆ | | 2.92449E+4 | | |

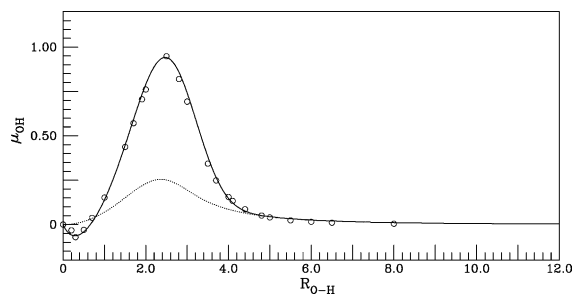


Fig. 1. Dipolar moment of OH($^2\Sigma^+$); line (—) corresponds to the fitted points \circ , line (\cdots) corresponds to the R^{-3} term.

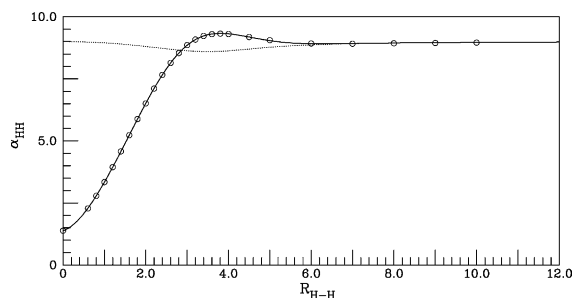


Fig. 2. Perpendicular component of polarizability for H $_2$ ($^1\Sigma_g^+$); line (—) corresponds to the fitted points \circ , line (\cdots) corresponds to the R^{-3} term.

Atom–diatom long-range interactions are best described using Jacobi coordinates, where R represents the interatomic distance in the diatomic, r is the distance from the diatomic mass center to the atom and θ the angle between both. However to obtain a potential interaction valid for all the configurational space we should build a function of the three interatomic distances, R_1 , R_2 and R_3 , where 1 labels the diatomic H–H, and the other two represent the two heteronuclear diatomics OH. To convert the internuclear distances to Jacobi coordinates we need to define the angular coordinate. As in earlier work [17], to avoid the non-analyticity when an atom is at the middle of the other two, we approximate $\cos\theta_i$ by $(R_j - R_k)/R_i$.

4.1. Electrostatic energy

With the quadrupole values for the O atom and H $_2$ diatom, we have been able to model

the electrostatic interaction between those species. The general form for this energy contribution is

$$V_{\text{ele}}^{(3)} = \frac{3}{4} \Theta_{\text{H}_2}(R) \Theta_{\text{O}} \mathcal{A}(\omega) \chi_5(r) r^{-5}. \quad (3)$$

To represent the angular function $\mathcal{A}(\omega)$ we used a ‘adiabatic’ approach [18] allowing the O atom to orient its quadrupolar axis in order to minimize the interaction energy. This minimal function is accurately represented by a 3-term Fourier expansion whose coefficients have been determined elsewhere [19]. Note that, the quadrupole of the singlet ground state of H $_2$ is positive and it is negative for the triplet state but, as the same happens to the quadrupole moments of the O atom, the angular dependence of this minimal interaction is the same for both interactions.

4.2. Induction energy

With the dipole moments of OH and the dipolar polarizability of the H atom, 4.5 a.u. [20], we have been able to study the induction term for the interaction between each H atom and the remaining OH diatomic

$$V_{\text{ind}}^{(3)} = - \sum_{i=2}^3 \mu_{\text{OH}_i}^2(R_i) \alpha_{\text{H}} (3 \cos^2 \theta_i + 1) \chi_6(r_i) / (2r_i^6). \quad (4)$$

4.3. Correlation energy

The dispersion contribution for the long-range forces has been semi-empirically modeled using the Kirkwood method [21] to estimate the C_6 coefficient, and its radial and angular dependencies, Eqs. (5) and (6). As input data, we use the parallel and perpendicular values for the polarizabilities for the diatomics we have computed. For the O atom, ^3P and ^1D states, we consider the polarizabilities of the components $m_l = 1$ (5.393 a.u.) [22] and $m_l = 0$ (5.621 a.u.) [23] respectively, which correlate with the corresponding OH diatomic states. These data are complemented with an *effective number of electrons*, N_{eff} , obtained from the dispersion coefficients of other interactions with

known dispersion energy, in particular, between identical species

$$C_6^{\parallel,\perp}(\text{AB} - \text{C})(R) = \frac{3}{2} \alpha_{\text{AB}}^{\parallel,\perp}(0)(R) \alpha_{\text{C}}(0) \times \left[\left(\frac{\alpha_{\text{AB}}^{\parallel,\perp}(0)(R)}{N_{\text{eff}}^{\text{AB}}(R)} \right)^{1/2} + \left(\frac{\alpha_{\text{C}}(0)}{N_{\text{eff}}^{\text{C}}(R)} \right)^{1/2} \right]^{-1}, \quad (5)$$

$$C_n(R_i, \theta_i) = \frac{1}{3} (2C_n^{\perp}(R) + C_n^{\parallel}(R)) + \frac{1}{3} (C_n^{\parallel}(R) - C_n^{\perp}(R)) (3 \cos^2 \theta_i - 1). \quad (6)$$

We found it convenient to use expression (7) for the variation of N_{eff} with the diatomic distance.

$$N_{\text{eff}}(R) = N_{\infty} + [a + b(R - R_c)] \exp[c(R - R_c)]. \quad (7)$$

The parameters a , b and c have been defined in order to reproduce the united atom and far apart, N_{∞} , limits as well as an equilibrium value, if known. Only for the ${}^2\Pi$ state of OH, where the $N_{\text{eff}}(R_c)$ value is greater than the asymptotic limits, we needed to include the b parameter. It has been determined in order to give a maximum for N_{eff} at R_c . Table 4 quotes their values.

To better model the dispersion interaction we need the coefficients $C_n(\text{AB} - \text{C})(R)$, $n = 8$ and 10 . When available we have used literature values [24], otherwise, we have semiempirically estimated those coefficients from C_6 using a universal correlation [25]

$$C_n^{\parallel,\perp}(\text{AB} - \text{C})(R) = C_6^{\parallel,\perp}(\text{AB} - \text{C})(R) k_n R_0^{[a(n-6)/2]} \times (\text{AB} - \text{C})(R). \quad (8)$$

In lack of accurate values for the Le Roy's parameter, $R_0(\text{AB} - \text{C})(R)$, we have estimated it using Eq. (9), where we use the mean polarizability of the diatomic as a measure of the diatomic volume and the atomic radius is taken from literature [26]

$$R_0(\text{AB} - \text{C})(R) = 2[\langle \bar{\alpha}_{\text{AB}}(0)(R) \rangle^{1/3} + \langle r_c^2 \rangle^{1/2}] f_{\text{corr}}^n(R). \quad (9)$$

To keep consistency between the estimated and known values for the asymptotic limits of R_0 or C_8 and C_{10} coefficients, we needed to introduce a correction function $f_{\text{corr}}^n(R)$. We consider enough to use expression (10), where c assumes the same value as in Eq. (7), f_{inf}^n is defined in order to accomplish the dissociation limit and d^n by the united atom. Table 4 quotes their values

$$f_{\text{corr}}^n = f_{\text{inf}}^n + d^n \exp(-cR). \quad (10)$$

In Fig. 3, we present, as an example, the results obtained with expression (9), for the interaction H–OH (${}^2\Pi$), as a function of the distance O–H.

Using Eqs. (5)–(10) we are able to obtain the dispersion coefficients C_8 and C_{10} for each atom–diatom interaction. As an example we show in Fig. 4 the parallel component of the dispersion coefficients, C_n ($n = 6, 8$ and 10), for the interaction H–OH (${}^2\Pi$), as a function of the distance O–H.

We now address to the problem of joining together all these interactions in a closed form, function of the three interatomic distances. This

Table 4
Coefficients (in a.u.) for expressions (7) and (10)

| Term | OH (${}^2\Pi$) | OH (${}^2\Sigma$) | H ₂ (${}^3\Sigma_u^+$) | H ₂ (${}^1\Sigma_g^+$) |
|-----------------------|------------------|---------------------|-------------------------------------|-------------------------------------|
| N_{∞} | 3.52 | 4.2594 | 1.77778 | 1.77778 |
| R_c | 1.8344 | | 1.449 | 1.449 |
| a | 1.04 | -2.96361E-1 | -1.47800E-1 | -1.47800E-1 |
| b | 5.84820E-1 | 0.0 | 0.0 | 0.0 |
| c | 5.62327E-1 | 5.62327E-1 | 6.06347E-1 | 6.06347E-1 |
| d^8 | 8.96375E-2 | -1.05085E-1 | 7.87947E-2 | 9.16471E-2 |
| f_{inf}^8 | 8.29597E-1 | 1.02432 | 9.06209E-1 | 9.05984E-1 |
| d^{10} | 6.57061E-2 | -2.30734E-2 | 7.87947E-2 | 9.16471E-2 |
| f_{inf}^{10} | 8.53528E-1 | 9.42308E-1 | 9.06209E-1 | 9.05984E-1 |

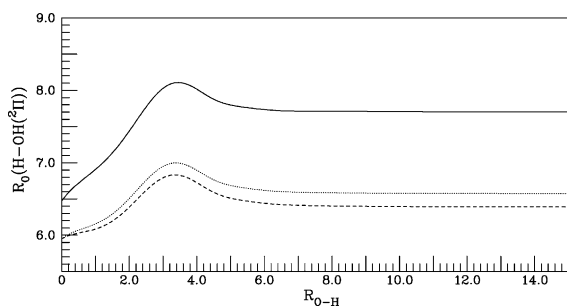


Fig. 3. Parameter R_0 for the interaction H–OH ($^2\Pi$), as a function of the distance O–H. Line (—) refers to the parameter R_0 without correction. While lines (---) and (···) refer to the parameter R_0 with corrections to obtain the coefficients C_8 and C_{10} , respectively.

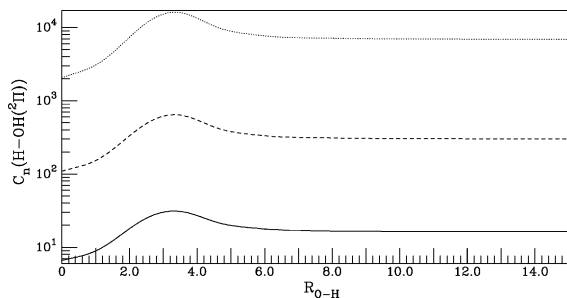


Fig. 4. Parallel dispersion coefficients C_6 , line (—), C_8 , line (---) and C_{10} , line (···), for the interaction H–OH ($^2\Pi$), as a function of the distance O–H.

problem didn't occur when dealing with the electrostatic, which is pair-additive, and induction energies since they result from well defined pairs.

When one atom is far apart from the diatomic the total dispersion energy is the sum of the atom–diatom interaction with the dispersion energy of the diatomic. When they approach each other we need to consider all the interaction pairs. The total interaction should be the sum of the three atom–diatom dispersion energies weighted by a switch function. This function depends on the triatomic geometry and defines the contribution of each atom–diatom configuration. We found it appropriate to use Eq. (11) to define this switch function, $S(R, r)$ [27], and also use it to compute the weight of each diatomic.

$$S(R, r) = \frac{1}{2} \left\{ 1 + \tanh \left[4.5 \left(\frac{r}{R} - 2 \right) \right] \right\}. \quad (11)$$

Then, the total dispersion interaction is computed as

$$V_{dc} = \sum_{i=1}^3 S(R_i, r_i) \sum_{n=6}^{10} C_n^i(R_i, \theta_i) \chi_n(r_i) r_i^{-n} + \sum_{i=1}^3 \left[\prod_{j \neq i} (1 - S(R_j, r_j)^2) \right] \sum_{n=6}^{10} C_n^i \chi_n(R_i) R_i^{-n}, \quad (12)$$

where $\prod_{j \neq i} (1 - S(R_j, r_j)^2)$ is used to select the diatomic contribution.

5. Conclusions

Using high quality ab initio calculations for the fragments and semiempirically modelling the interaction, we have been able to represent the long-range interactions within the H_2O system including their anisotropy and dependence on the diatomic coordinate.

To illustrate the different components of the long-range interaction, we present in Fig. 5 the perpendicular approach of the O (1D) atom to the HH ($^1\Sigma_g^+$) diatomic. Note that the main contribution comes from the dispersion energy but the small electrostatic interaction should be considered.

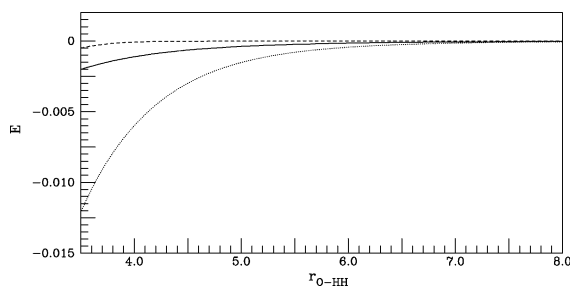


Fig. 5. Electrostatic energy (—), induction energy (---) and dynamic correlation (···), for the perpendicular approach of the O (1D) atom to the HH ($^1\Sigma_g^+$) diatomic, fixed at the equilibrium distance ($1.401 a_0$), as a function of the $r_{\text{O-HH}}$.

Acknowledgements

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References

- [1] T.S. Ho, T. Hollebeek, H. Rabitz, L.B. Harding, G.C. Schatz, *J. Chem. Phys.* 105 (1996) 10472.
- [2] O.L. Polyansky, P. Jensen, J. Tennyson, *J. Chem. Phys.* 105 (1996) 6490.
- [3] A.J.C. Varandas, *J. Chem. Phys.* 105 (1996) 3524.
- [4] H. Partridge, D.W. Schwenke, *J. Chem. Phys.* 106 (1997) 4618.
- [5] A.J.C. Varandas, *J. Chem. Phys.* 107 (1997) 867.
- [6] A.J. Dobbyn, P.J. Knowles, *Mol. Phys.* 91 (1997) 1107.
- [7] A.J.C. Varandas, A.I. Voronin, A. Riganelli, P.J.S.B. Caridade, *Chem. Phys. Lett.* 278 (1997) 325.
- [8] A.J. Alexander, F.J. Aoiz, L. Bañares, M. Bruard, V.J. Herrero, J.P. Simons, *Chem. Phys. Lett.* 278 (1997) 313.
- [9] M.W. Schmidt et al., *J. Comput. Chem.* 14 (1993) 1347.
- [10] R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, *J. Chem. Phys.* 96 (1992) 6769.
- [11] T.H. Dunning Jr., *J. Chem. Phys.* 90 (1989) 1007.
- [12] D.E. Woon, T.H. Dunning Jr., *J. Chem. Phys.* 100 (1994) 2975.
- [13] A.J. Sadlej, *Collection Czechoslovak Chem. Commun.* 53 (1988) 1995.
- [14] C.F. Fisher, *At. Data* 12 (1973) 87.
- [15] P.R. Certain, P.J. Fortune, *J. Chem. Phys.* 55 (1971) 5818.
- [16] A.J.C. Varandas, J. Brandão, *Mol. Phys.* 45 (1982) 857.
- [17] M.R. Pastrana, L.A.M. Quintales, J. Brandão, A.J.C. Varandas, *J. Phys. Chem.* 94 (1990) 8073.
- [18] A.J.C. Varandas, J. Brandão, L.A.M. Quintales, *J. Phys. Chem.* 92 (1988) 3732.
- [19] A.J.C. Varandas, A.A.C.C. Pais, *Mol. Phys.* 65 (1988) 843.
- [20] F.E. Cummings, *J. Chem. Phys.* 63 (1975) 4960.
- [21] J.G. Kirkwood, *Phys. Z.* 33 (1932) 57.
- [22] H.U. Kelly, *Phys. Rev.* 182 (1969) 84.
- [23] H.U. Kelly, *Phys. Rev.* 152 (1966) 62.
- [24] M.A. Matías, A.J.C. Varandas, *Mol. Phys.* 70 (1990) 623.
- [25] A.J.C. Varandas, J. Dias da Silva, *J. Chem. Soc., Faraday Trans. 2* 82 (1986) 593.
- [26] J.P. Descleaux, *At. Data* 12 (1973) 311.
- [27] A.A.C.C. Pais, private communication.