

## Commentationes

# PNO-CI and CEPA Studies of Electron Correlation Effects

## II. Potential Curves and Dipole Moment Functions of the OH Radical\*

Wilfried Meyer

Institut für Physikalische Chemie der Universität Mainz, Germany

Received June 21, 1974

*Ab initio* calculations of the potential curves of low lying electronic states of OH are performed on the basis of a variational configuration interaction wavefunction (PNO-CI) and the coupled electron pair approximation (CEPA).

The latter approach yields a ground state potential curve which deviates from the RKR curve by less than  $200\text{ cm}^{-1}$  in the region from 0.7 to 1.6 Å. Calculated ground state constants are as follows (experimental values in parentheses):  $r_e = 0.972$  (0.971) Å,  $B_e = 18.85$  (18.87)  $\text{cm}^{-1}$ ,  $\alpha_e = 0.727$  (0.714)  $\text{cm}^{-1}$ ,  $\omega_e = 3742$  (3739)  $\text{cm}^{-1}$ ,  $\omega_e x_e = 85.3$  (86.4)  $\text{cm}^{-1}$ ,  $\mu_0 = 1.686$  (1.66) D,  $D_e = 4.35$  (4.63) eV, IP = 12.78 (13.36?) eV, El.Aff. = 1.51 (1.83) eV,  $\nu_{00}(^2\Pi \leftrightarrow ^2\Sigma^+) = 32690$  (32440)  $\text{cm}^{-1}$ .

The correlation contributions to ionization, excitation and electron attachment are analyzed. On the basis of estimated CEPA-limits, which are in very good agreement with experiment for  $D_e$  and electron affinity, an IP of 13.0 eV is recommended. Dipole moment expectation values and some IR transition probabilities are calculated from the ground state dipole moment curves. The calculated crossing point of the  $^2\Sigma^-$  curve with the repulsive  $^4\Sigma^-$  state is not in agreement with the position deduced from intensity data.

*Key words:* OH-radial, potential curves of  $\sim$ , dipole moments of  $\sim$

### 1. Introduction

An efficient method previously proposed [1] for calculating highly correlated variational wavefunctions (PNO-CI) has been applied in Paper I of this series to several states of  $\text{CH}_4$  [2]. Comparing the variational results with those obtained from a new coupled electron pair approach (CEPA [1, 2]) and the familiar independent electron pair approximation, we concluded that the CEPA results are the most reasonable ones. In particular with respect to the stretching potential curve the correlation contributions according to the three methods vary significantly. Comparison with experiment is somewhat uncertain in  $\text{CH}_4$ . Here we investigate the usefulness of the CEPA for calculating potential curves by applying it to the OH radical, a system which can be treated sufficiently accurately and for which precise experimental results are available.

### 2. Methods for Calculating Energy Curves

In most cases the traditional one-determinant Hartree-Fock wavefunction does not allow for correct dissociation into atomic or molecular fractions. That

\* Dedicated to Professor Hermann Hartmann on the occasion of his 60<sup>th</sup> birthday.

not only makes this method inadequate for calculating potential curves but also renders the treatment of the electron correlation difficult. Ideally, one has to include in a variational CI calculation single and double substitutions with respect to all configurations which are required for proper dissociation. This represents a formidable problem. In order to reduce it, several well known procedures have been proposed: multiconfiguration SCF wavefunctions [3, 4], full CI with respect to a minimal basis set [5, 6], first order wavefunctions coupled with natural orbital iteration [7, 8]. These schemes have drastically improved upon the HF method. However, since they give only a small fraction of the total correlation, the curves corresponding to different electronic states will in general have to be shifted relative to each other by fitting them to data of the fractions. Their success with respect to the shape of the potential curve depends on a critical balance between the neglected parts of the "extra molecular correlation" (due to the restriction of number and type of the configurations) and the parts of the "atomic correlation" accounted for in the molecule.

Since there seems to be no unambiguous way of separating the extra molecular correlation, one would like to fully treat the valence shell of that part of the molecule which is involved in the deformation process. For internuclear distances not too far from the equilibrium geometry the Hartree-Fock configuration is usually the only dominant one, the coefficients of the additional configurations required for proper dissociation still being small though rapidly increasing with distance. Double substitutions with respect to these configurations are usually quadrupole substitutions with respect to the HF configuration. We may therefore argue that a coupled electron pair approach which approximately includes these types of configurations [2] should be able to adequately treat both the extra molecular correlation and the configurations of rapidly increasing importance. We thus expect this approach to yield reasonable spectroscopic constants representing the shape of the potential curve around the equilibrium.

With respect to potential surfaces we may characterize the CEPA in comparison with the MC-SCF as follows: The MC-SCF scheme rests on two assumptions about the neglected double substitutions of the explicitly considered configurations: a) they affect all configurations in the same way so that the spacing of the latter is unchanged, and b) their effect is constant during the deformation. The CEPA explicitly includes double substitutions of the HF configuration and uses only assumption (a) by transferring appropriate parts of the correlation energy calculated for the HF configuration to the other configurations of the CI. Since the orbitals of the CEPA wavefunction are not self-consistent, it is important to include single substitutions of all stronger occupied orbitals, i.e. those which are used to construct all the configurations required for proper dissociation.

### 3. The PNO-CI and CEPA Methods

We refer to I for a detailed discussion of the methods used here. They may be briefly characterized by the following steps:

- a) A conventional restricted Hartree-Fock calculation gives  $\Phi_0$ .

b) For each spin-irreducible pair  $P(a, b)$  of the orbitals  $a$  and  $b$  of  $\Phi_0$  a set of pseudonatural orbitals (PNO's  $\varphi_p^i$ ) is calculated perturbationally.

c) All doubly substituted configurations of diagonal form in the PNO's  $\Phi_p^i$ , which contribute to the energy more than a certain threshold value, are treated in a CI along with corresponding single substitutions. The partial nonorthogonality of the orbitals used in this PNO-CI is accepted in order to ensure optimal convergence.

d) Starting from the matrix eigenvalue equation of the PNO-CI ( $C_0 = 0, E_0 = 0$ )

$$\sum_P \sum_i \langle \Phi_0 | H | \Phi_P^i \rangle C_P^i = \sum_P E_P = E, \quad (1)$$

$$\langle \Phi_P^i | H | \Phi_0 \rangle + \sum_Q \sum_j \langle \Phi_P^i | H | \Phi_Q^j \rangle C_Q^j = E C_P^i \quad (2)$$

we obtain the CEPA equations by replacing the total correlation energy  $E$  in (2) by expressions of the pair energies defined in (1):

$$\text{Version 1: } \sum_Q E_{Q(c,d)} (\delta_{ac} + \delta_{ad} + \delta_{bc} + \delta_{bd})/4, \quad (3)$$

$$\text{Version 2: } E_{P(a,b)}. \quad (4)$$

This may be looked at as replacing  $\langle \Phi_P^i | H | \Phi_P^i \rangle$  by  $\langle \Phi_P^i | H | \Phi_P^i \rangle + \sum_{Q \neq P} E_Q$  (Version 2) and means assuming that the higher-order substitutions will affect the doubles  $\Phi_P^i$  in the same way as the doubles affect the reference configuration. It is safe to attribute to the untouched pairs  $Q \neq P$  in  $\Phi_P^i$  the correlation energies  $E_Q$  which are explicitly calculated for  $\Phi_0$ , but it is difficult to assess the correlation of the excited electrons in  $\Phi_P^i$  with all the others, i.e. the contribution of triple substitutions. Version 2 assumes that this correlation is unchanged by the excitation, Version 1 reduces it in a simple way according to how many orbitals are common to the involved spin-adapted pairs [2]. When we first suggested these coupled equations [1, 2] we were not aware that rather similar equations had been discussed some time ago by Kelly [9] (though seemingly never used). They are given in spin-orbital formulation and differ in that the sum of all pair energies of pairs  $Q$  having one orbital in common with pair  $P$  appears in place of  $E$  at the right hand side of (2), i.e. the correlation of the excited electrons in  $\Phi_P^i$  with the others is assumed zero.

The advantage of using the coupled equations is that the rather large three-body and four body effects contained in the coupling matrix elements are taken into account to all orders. From the difference between the upper bound PNO-CI energy and the CEPA energy we obtain rather reasonable numbers for the higher order contributions ranging from 2.5% for Ne and 4% for  $\text{H}_2\text{O}$  to 6% for  $\text{CH}_4$  [1, 2].

For calculating one-electron properties it is of course crucial to include single substitutions. No particular problem arises in the PNO-CI scheme, and in the CEPA equations the singles are simply treated as belonging to the corresponding intraorbital pair. It is straightforward to derive an expression for one-electron expectation values adequate for CEPA type wavefunctions. We will sketch this using arguments like those given above for the CEPA eigenvalue equations.

Defining pair correlation functions by  $|P\rangle = \sum_i \Phi_p^i C_p^i$  the expectation value for the operator  $F$  and the PNO-CI wavefunction is

$$\langle F \rangle_{\text{CI}} = \langle O|F|O \rangle + \left[ 2 \sum_P \langle P|F|O \rangle + \sum_{P,Q} \langle P|F - \langle O|F|O \rangle |Q \rangle \right] / \left( 1 + \sum_P \langle P|P \rangle \right). \quad (5)$$

Assuming now again that the higher order substitutions affect  $\langle P|F|P \rangle$  in the same way as the doubles affect  $\langle O|F|O \rangle$  we replace  $\langle P|F|P \rangle$  in (5) by  $\langle P|F|P \rangle + \langle P|P \rangle [2 \sum_{Q \neq P} \langle Q|F|O \rangle + \sum_{QR \neq P} \langle Q|F - \langle O|F|O \rangle |R \rangle]$  and obtain the CEPA expectation value

$$\begin{aligned} \langle F \rangle_{\text{CEPA}} = & \langle O|F|O \rangle + \left[ 2 \sum_P \langle P|F|O \rangle \left( 1 + \sum_{Q \neq P} \langle Q|Q \rangle \right) \right. \\ & \left. + \sum_{P,Q} \langle P|F - \langle O|F|O \rangle |Q \rangle \left( 1 + \sum_{R \neq P,Q} \langle R|R \rangle \right) \right] / \left( 1 + \sum_P \langle P|P \rangle \right). \end{aligned} \quad (6)$$

This shows of course the well known fact that the cluster contributions largely cancel the normalization denominator [10].

It is worth noting that the difference in expression (5) and (6) adds only a small contribution to the difference in the CI and the CEPA expectation value due to different coefficients  $C_p^i$  obtained in the corresponding eigenvalue equations.

#### 4. Potential Energy Curves and Spectroscopic Constants for OH( $^2\Pi$ ), OH ( $^2\Sigma^+$ ) and OH $^+$ ( $^2\Sigma^-$ )

Using a very extended and well optimized STO basis set, Cade and Huo [11] reported a Hartree-Fock potential curve for the ground state of OH which closely approaches the HF limit. In our calculations we employ a GTO basis set of the size: O: 11s, 6p, 2d, 1f/H: 5s, 2p, 1d<sub>σ</sub> with exponents derived from Huzinaga's [12] atomic sets. (For Oxygen, the *f*-exponent is identical with the third *p*-exponent, and the two *d*-exponents are half and twice that value, respectively. For Hydrogen, the *p*- and *d*<sub>σ</sub>-exponents are 0.25, 1.0, and 0.65, respectively.) Our HF energies are slightly above the values of Ref. [11] but both potential curves parallel each other completely. We therefore feel it justified to attribute all discrepancies of our curves with the RKR curve [13] to deficiencies in the treatment of the correlation.

OH potential curves which go beyond the HF approximation have been reported by Michels and Harris [6] (full CI on a minimal basis) and by Bondybey *et al.* [8] (first order wavefunction). Both methods have just been discussed. The latter paper gives rather good spectroscopic constants though slightly overcorrects the HF errors. The only calculation accounting for a large fraction of the correlation (about 70%) is apparently that of Bender and Davidson [14] which was restricted to the equilibrium distance however.

For calculating the potential curve we have restricted the CI to the valence-shell electrons. By employing an energy threshold value of  $10^{-4}$  Hartree, our ground state wavefunction contains 208 configurations constructed from 251 PNO's. At the equilibrium geometry 83% of the valence-shell correlation

Table 1. Experimental and calculated energies of OH at equilibrium distance (1.8348 bohr)

|                                                |          |
|------------------------------------------------|----------|
| Energy of separated atoms <sup>a</sup>         | 75.6101  |
| Binding energy <sup>b</sup>                    | 0.1617   |
| Zero point energy <sup>c</sup>                 | 0.0084   |
| Relativistic correction <sup>d</sup>           | - 0.0494 |
| Experimental nonrel. energy                    | 75.7309  |
| Hartree-Fock limit <sup>e</sup>                | 75.421   |
| Total correlation energy                       | 0.310    |
| Estimated valence shell correlation            | 0.252    |
| Calculated Hartree-Fock energy <sup>e</sup>    | 75.4192  |
| Valence correlation energies <sup>f</sup> :    |          |
| PNO-CI (upper bound)                           | 0.2085   |
| CEPA (1)                                       | 0.2164   |
| CEPA (2)                                       | 0.2187   |
| All electron correlation energies <sup>g</sup> |          |
| PNO-CI                                         | 0.2636   |
| CEPA (1)                                       | 0.2744   |
| CEPA (2)                                       | 0.2768   |

<sup>a</sup> Ref. [11].

<sup>b,c</sup> Ref. [30].

<sup>d</sup> Clementi, E., Roothaan, C. C., Yoshimine, M.:  
Phys. Rev. **127**, 1618 (1962).

<sup>e</sup> Basis (O: 11s, 6p, 2d, 1f/H: 5s, 2p, 1d<sub>σ</sub>).

<sup>f</sup> Threshold 10<sup>-4</sup>, 208 configurations.

<sup>g</sup> Threshold 10<sup>-4</sup>, 257 configurations.

energy has been obtained variationally (PNO-CI), and 86% results from the CEPA. Table 1 compares experimental and calculated energies at the equilibrium distance. It also shows the results of an all-electron calculation carried out only for this distance. Here we obtained 85% and 89% of the total experimental correlation energy by the PNO-CI and the CEPA methods, respectively. Our upper bound energy is 0.047 hartree above the nonrelativistic energy. The accuracy achieved is thus in line with what we have previously reported about H<sub>2</sub>O [1] and CH<sub>4</sub> [2] using similar basis sets and the same threshold value.

Calculated and experimental energies and dipole moments of the ground state at the classical turning points are given in Table 2. It can be seen that the CEPA indeed gives a potential curve in very good agreement with experiment over a relatively large region around the equilibrium. The correlation energy is a nearly linear function of the internuclear distance and its influence on the potential curve may be characterized by its slope. Putting the experimental slope at 100%, we obtained: HF: 0%, PNO-CI: 72%, CEPA: 95% or 102%, IEPA: 114% (localized) and 140% (canonical). The two versions of the CEPA seem to bracket the true situation as was conjectured in Ref. [2]. We have also checked the CEPA by carrying out a natural orbital iteration (in our scheme that involves the strongly occupied NO's only): there was no change in the slope for CEPA<sub>1</sub> and a decrease of only 0.5% for CEPA<sub>2</sub>.

Table 2. Potential energy curve and dipole moment curve of the ground state of OH<sup>a</sup>

| $r^{\text{obs}}$ | $E(r^{\text{OH}}) - E(r_e^{\text{OH}})$ |           |                   |                   | $\mu(r^{\text{OH}}) - \mu(r_e^{\text{OH}})$ |         |                   |                   | obs. <sup>d</sup> |
|------------------|-----------------------------------------|-----------|-------------------|-------------------|---------------------------------------------|---------|-------------------|-------------------|-------------------|
|                  | HF                                      | PNO-CI    | CEPA <sub>1</sub> | CEPA <sub>2</sub> | HF                                          | PNO-CI  | CEPA <sub>1</sub> | CEPA <sub>2</sub> |                   |
| 1.83485          | 0.0                                     | 0.0       | 0.0               | 0.0               | 0.0                                         | 0.0     | 0.0               | 0.0               | 0.0               |
| 1.66972          | 0.0050849                               | 0.0077495 | 0.0083374         | 0.0085304         | -0.0286                                     | -0.0212 | -0.0180           | -0.0175           | -0.0165           |
| 2.04234          | 0.0131239                               | 0.0096543 | 0.0087688         | 0.0084595         | 0.0332                                      | 0.0207  | 0.0156            | 0.0136            | 0.0152            |
| 1.57021          | 0.0196030                               | 0.0238110 | 0.0247109         | 0.0250021         | -0.0465                                     | -0.0355 | -0.0312           | -0.0302           | -0.0278           |
| 2.22809          | 0.0340191                               | 0.0272732 | 0.0254162         | 0.0247488         | 0.0600                                      | 0.0337  | 0.0216            | 0.0165            | 0.0216            |
| 1.51106          | 0.0341174                               | 0.0392218 | 0.0402942         | 0.0406384         | -0.0573                                     | -0.0441 | -0.0397           | -0.0385           | -0.0352           |
| 2.37704          | 0.0535647                               | 0.0440169 | 0.0412207         | 0.0401951         | 0.0794                                      | 0.0403  | 0.0206            | 0.0113            | 0.0202            |
| 1.46789          | 0.0481938                               | 0.0539415 | 0.0551338         | 0.0555146         | -0.0652                                     | -0.0505 | -0.0464           | -0.0448           | -0.0407           |
| 2.51367          | 0.0723405                               | 0.0600757 | 0.0562657         | 0.0548448         | 0.0959                                      | 0.0428  | 0.0130            | 0.0001            | 0.0123            |
| 1.43377          | 0.0617536                               | 0.0679992 | 0.0692824         | 0.0696905         | -0.0720                                     | -0.0568 | -0.0517           | -0.0498           | -0.0453           |
| 2.64535          | 0.0905521                               | 0.0757608 | 0.0708410         | 0.0689814         | 0.1118                                      | 0.0415  | 0.0015            | -0.0148           | -0.0024           |
| 1.40553          | 0.0748122                               | 0.0814689 | 0.0828247         | 0.0832544         | -0.0781                                     |         | -0.0561           | -0.0539           | -0.0491           |
| 2.77577          | 0.1083210                               | 0.0906627 | 0.0844267         | 0.0820392         | 0.1255                                      |         | -0.0173           | -0.0386           | -0.0251           |
| 2.90729          | 0.1257337                               | 0.1049649 | 0.0971929         | 0.0941847         | 0.1396                                      |         | -0.0375           | -0.0713           | -0.0577           |
| 3.04178          | 0.1428636                               | 0.1187246 | 0.1091516         | 0.1054139         | 0.1539                                      |         | -0.0666           | -0.1073           | -0.1027           |
| 3.18093          | 0.1597767                               | 0.1319730 | 0.1202886         | 0.1157004         | 0.1688                                      |         | -0.1027           | -0.1527           | -0.1623           |

<sup>a</sup> All values in atomic units and relative to the equilibrium values; absolute values may be found in Tables 1 and 10. Basis set (O: 11s, 6p, 2d, 1f/H: 5s, 2p, 1d<sub>g</sub>).

<sup>b</sup>  $r_e$  and turning points of the classical motion, from the RKR curve of Ref. [13].

<sup>c</sup> Ref. [13].

<sup>d</sup> Ref. [26];  $\mu = \mu'_e(r + 0.036r^2 - 0.129r^3 - 0.543r^4 + 0.441r^5 - 0.246(e^{2.32r} - 1))$ ,  $r = r^{\text{OH}} - r_e^{\text{OH}}$  in Å,  $\mu'_e$  is undetermined by intensity ratios, it is put here at 1 D/Å.

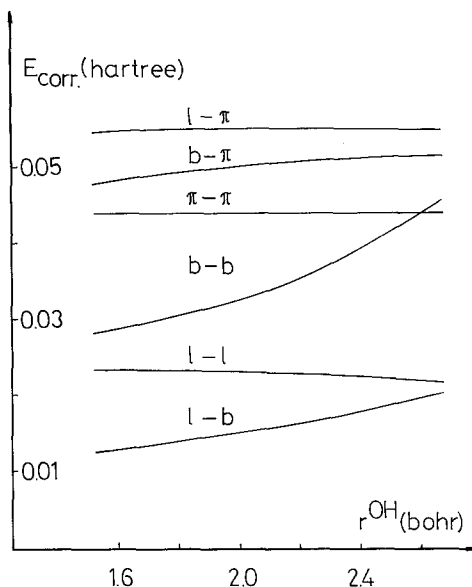


Fig. 1. Pair correlation energies for OH ( ${}^2\Pi$ ) ( $b$ : localized bond pair;  $l$ : lone pair)

Figure 1 shows the behaviour of pair correlation energies referring to partially localized orbitals ( $2\sigma$  and  $3\sigma$  are transformed into a bond orbital ( $b$ ) and a lone orbital ( $l$ ), the  $\pi$  orbitals are unchanged). Not surprisingly, the main increase of correlation with distance is due to the  $b$ - $b$  intraorbital pair. In addition, there is a rather strong increase of the  $b$ - $l$  interorbital correlation which is also due to the increasing left-right mobility of the  $b$  electrons. Somewhat unexpectedly, there is no corresponding increase in  $b$ - $\pi$  correlation, probably because of little left-right flexibility of the  $\pi$  electrons and the decreasing penetration of the  $b$  and the  $\pi$  charge clouds. Whereas the  $\pi$ - $\pi$  correlation and the  $l$ - $\pi$  correlation seem completely unaffected, there is a slight decrease in the  $l$ - $l$  intraorbital pair energy. This effect is sufficiently small however that a partial CI treating only the  $b$ - $b$  pair and the  $b$ -other pairs would probably give a reasonable near-equilibrium surface. This is important in view of the possibility of local investigations of larger molecules. Such a partial CI would amount to calculating an 'independent pair potential' as introduced by Mehler [15].

Using the same basis set as described above, we have also calculated energy curves and dipole moment curves for the first excited state of OH,  $2\Sigma^+$ , and the ground state of its cation,  $\text{OH}^+$  ( ${}^3\Sigma^-$ ) (Tables 3 and 4; in order to save computing time, the classical turning points of the OH ground state were used again for inter-nuclear distances).

Spectroscopic constants as calculated from the given curves are compared with observed values in Table 5. Since  $\omega_e$  and  $\omega_e x_e$  depend on the way the observed vibrational frequencies are fitted (literature values for  $\omega_e x_e$  of the ground state range from  $82.81 \text{ cm}^{-1}$  to  $86.35 \text{ cm}^{-1}$  [16], we compare these frequencies directly with those obtained from solving the vibrational Schrodinger equation for the theoretical potential energy curves (Table 6). The way we have treated the potential curves in order to obtain the spectroscopic constants will

Table 3. Total energies and dipole moments of OH ( ${}^2\Sigma^+$ ) in atomic units

| Distance | Total energy + 75.00 |           |           | Dipole moment |        |
|----------|----------------------|-----------|-----------|---------------|--------|
|          | HF                   | PNO-CI    | CEPA      | HF            | CEPA   |
| 1.43377  | -0.184720            | -0.394003 | -0.403648 | 0.4309        | 0.4107 |
| 1.46789  | -0.199482            | -0.409092 | -0.418828 | 0.4554        | 0.4334 |
| 1.51106  | -0.215105            | -0.425123 | -0.434977 | 0.4869        | 0.4625 |
| 1.57021  | -0.231791            | -0.442356 | -0.452370 | 0.5307        | 0.5030 |
| 1.66972  | -0.250121            | -0.461547 | -0.471834 | 0.6063        | 0.5728 |
| 1.75000  | -0.258207            | -0.470260 | -0.480768 | 0.6678        | 0.6296 |
| 1.83485  | -0.262054            | -0.474687 | -0.485430 | 0.7320        | 0.6891 |
| 1.93000  | -0.262232            | -0.475401 | -0.486410 | 0.8018        | 0.7541 |
| 2.04234  | -0.258644            | -0.472256 | -0.483581 | 0.8768        | 0.8261 |
| 2.22809  | -0.247739            | -0.461537 | -0.473405 | 0.9728        | 0.9273 |
| 2.37704  | -0.237309            | -0.450619 | -0.462977 | 1.0078        | 0.9833 |
| 2.51367  | -0.227941            | -0.440156 | -0.453127 | 0.9947        | 1.0058 |
| 2.64535  | -0.219831            | -0.430319 | -0.444170 | 0.9398        | 0.9959 |
| 2.77577  | -0.213019            | -0.421243 | -0.436237 | 0.8556        | 0.9513 |
| 2.90720  | -0.207426            | -0.413016 | -0.429356 | 0.7550        | 0.8914 |

Table 4. Total energies and dipole moments of OH ( ${}^3\Sigma^-$ ) in atomic units

| Distance | Total energy + 75.00 |           |           | Dipole moment <sup>a</sup> |        |
|----------|----------------------|-----------|-----------|----------------------------|--------|
|          | HF                   | PNO-CI    | CEPA      | HF                         | CEPA   |
| 1.46789  | -0.930579            | -0.088984 | -0.093604 | 0.7869                     | 0.7728 |
| 1.51106  | -0.947009            | -0.106033 | -0.110835 | 0.8076                     | 0.7920 |
| 1.57021  | -0.964729            | -0.124605 | -0.129554 | 0.8370                     | 0.8191 |
| 1.66972  | -0.984577            | -0.145898 | -0.151108 | 0.8893                     | 0.8665 |
| 1.75000  | -0.993661            | -0.156147 | -0.161585 | 0.9342                     | 0.9064 |
| 1.83485  | -0.998318            | -0.162029 | -0.167722 | 0.9844                     | 0.9501 |
| 1.93000  | -0.999083            | -0.164152 | -0.170153 | 1.0439                     | 1.0009 |
| 2.04234  | -0.995713            | -0.162353 | -0.168746 | 1.1190                     | 1.0630 |
| 2.22809  | -0.983916            | -0.153039 | -0.160149 | 1.2547                     | 1.1702 |
| 2.37704  | -0.971478            | -0.142407 | -0.150153 | 1.3740                     | 1.2593 |
| 2.51367  | -0.959103            | -0.131580 | -0.139963 | 1.4915                     | 1.3417 |

<sup>a</sup> referring to the position of 0.

be fully described in a forthcoming paper where we present similar calculations for the Hydrodes from LiH to HCl [17]. The nearly perfect agreement between the observed data for the ground state and the equilibrium distance and vibrational frequencies calculated by CEPA is somewhat fortuitous. In Ref. [17] we obtain typical deviations of the frequencies of around  $20\text{ cm}^{-1}$  and about  $0.003\text{ \AA}$  for the distances in first row hydrodes. In view of that the frequencies calculated for the state  ${}^2\Sigma^+$  are not quite satisfactory.

We may note however that in Ref. [17] we obtain also relatively large deviations for BeH and MgH which have the same structure of  $\sigma$  electrons in the valence shell: the unpaired  $\sigma$  electron is a lone electron at the heavy nucleus for



Table 5. Spectroscopic constants for OH ( ${}^2\Pi$ ), OH ( ${}^2\Sigma^+$ ), OH $^+$  ( ${}^3\Sigma^-$ )

| State                      | Method            | $r_e$<br>bohr | $\omega_e$<br>$\text{cm}^{-1}$ | $\omega_e x_e$<br>$\text{cm}^{-1}$ | $B_e$<br>$\text{cm}^{-1}$ | $\alpha_e$<br>$\text{cm}^{-1}$ | $D_e$<br>eV                   |
|----------------------------|-------------------|---------------|--------------------------------|------------------------------------|---------------------------|--------------------------------|-------------------------------|
| OH( ${}^2\Pi_-$ )          | HF                | 1.7961        | 4054                           | 74.0                               | 19.69                     | 0.656                          | 2.99                          |
|                            | PNO-CI            | 1.8254        | 3841                           | 80.2                               | 19.06                     | 0.695                          | 4.22                          |
|                            | CEPA              | 1.8353        | 3742                           | 85.3                               | 18.85                     | 0.727                          | 4.35                          |
|                            | Exp. <sup>a</sup> | 1.8342        | 3740 <sup>b</sup>              | 86.4 <sup>b</sup>                  | 18.87                     | 0.714                          | 4.63                          |
| OH( ${}^2\Sigma^+$ )       | HF                | 1.8857        | 3323                           | 112.0                              | 17.86                     | 0.890                          | 0.91                          |
|                            | PNO-CI            | 1.8996        | 3295                           | 97.8                               | 17.60                     | 0.816                          | 2.10                          |
|                            | CEPA              | 1.9070        | 3248                           | 96.9                               | 17.46                     | 0.819                          | 2.23                          |
|                            | Exp. <sup>a</sup> | 1.9133        | 3181                           | 95.9                               | 17.35                     | 0.807                          | 2.49                          |
| OH $^+$ ( ${}^3\Sigma^-$ ) | HF                | 1.8998        | 3297                           | 81.3                               | 17.60                     | 0.711                          | 5.17                          |
|                            | PNO-CI            | 1.9335        | 3188                           | 81.0                               | 16.94                     | 0.724                          | 5.23                          |
|                            | CEPA              | 1.9432        | 3124                           | 84.7                               | 16.77                     | 0.737                          | 5.24                          |
|                            | Exp. <sup>a</sup> | 1.9421        | (3123) <sup>c</sup>            |                                    | 16.79                     | 0.732                          | (4.85 $\pm$ 0.2) <sup>d</sup> |

<sup>a</sup> Ref. [30].<sup>b</sup> Ref. [16].<sup>c</sup> From the observed fundamental frequency of 2955  $\text{cm}^{-1}$  and an assumed anharmonicity of 84.0  $\text{cm}^{-1}$ .<sup>d</sup> From the IP of OH given in Ref. [11].Table 6. Calculated and observed vibrational frequencies in  $\text{cm}^{-1}$ 

|                       | HF   | PNO-CI | CEPA | Obs. <sup>a</sup> |
|-----------------------|------|--------|------|-------------------|
| OH ( ${}^2\Pi$ )      | 3907 | 3675   | 3572 | 3570              |
|                       | 3765 | 3522   | 3405 | 3404              |
|                       | 3628 | 3372   | 3240 | 3240              |
|                       | 3494 | 3228   | 3079 | 3077              |
|                       | 3368 | 3087   | 2918 | 2916              |
| OH ( ${}^2\Sigma^+$ ) | 3088 | 3104   | 3050 | 2989              |
|                       | 2840 | 2906   | 2837 | 2793              |
|                       | 2578 | 2705   | 2615 | 2593              |
| OH ( ${}^3\Sigma^-$ ) | 3235 | 3031   | 2958 | 2955              |
|                       | 3077 | 2878   | 2800 |                   |
|                       | 2923 | 2730   | 2647 |                   |

<sup>a</sup> Ref. [13].

distances around the equilibrium, then gradually moves through the region of the other electrons and becomes completely attached to the proton for large distances. Therefore the correlation energy shows a maximum not far outside of  $r_e$ , and it looks like we have not been able to fully account for the curvature in that region.

The dissociation energies calculated for the ground state and the first excited state of OH are below the observed values by 0.28 eV and 0.26 eV, respectively.

The differences between the observed dissociation energies and the HF values are 1.64 eV and 1.58 eV, respectively. That means we have accounted for 83% of the correlation contribution to the dissociation energy which is in gratifying agreement with the fraction of the total correlation recovered. We consider this relation as plausible and take our results as indicating the possibility of rather reliable estimates for dissociation energies based on what we may call the CEPA-limit. Given some experience with particular types of basis sets and corresponding threshold values, a fair assessment of this limit seems to be well possible (e.g. compare the fractions of correlation recovered for H<sub>2</sub>O [1], CH<sub>4</sub> [2], and OH).

The system OH<sup>+</sup> dissociates into O + H<sup>+</sup>, i.e. the dissociation energy is a proton affinity which usually involve only very small correlation contributions. We therefore attribute rather high accuracy to the value of 5.24 eV. This would mean that the experimental value for the ionization potential of OH quoted in Ref. [11] is too large by about 0.4 eV and should be put at 13.0 eV. We shall come back to this in Section 5.

### 5. Ionization Potential, Excitation Energy and Electron Affinity for OH

The potential curves presented in the previous section yield theoretical values for the ionization potential and the lowest excitation energy of OH. We have also calculated the ground state of OH<sup>-</sup> at the equilibrium distance of OH. Cade [18] has shown that there is practically no change in the internuclear distance and the harmonic frequency due to the electron attachment, and that has also been verified experimentally [19]. The calculated energy difference may therefore be compared directly with the observed electron affinity. In order to account for the more diffuse electron distribution in OH<sup>-</sup>, the basis set described above has been augmented by a set of *s*- and *p*-type functions with small exponents.

An analysis of the changes in correlation accompanying the three transition processes is given in Table 7 in the following terms [2, 20]: change in all-external

Table 7. Correlation contributions to vertical ionization, electron attachment, and excitation of OH (<sup>2</sup>Π)

| Type <sup>a</sup>                      | OH <sup>+</sup> ( <sup>3</sup> Σ <sup>-</sup> ) | OH <sup>-</sup> ( <sup>1</sup> Σ <sup>+</sup> ) | OH ( <sup>2</sup> Σ <sup>+</sup> ) |
|----------------------------------------|-------------------------------------------------|-------------------------------------------------|------------------------------------|
| <i>E</i> <sup>scf</sup>                | 0.42101                                         | 0.00500                                         | 0.15680                            |
| <i>E</i> <sup>c</sup> <sub>xx,xi</sub> | 0.06256                                         | -0.07371                                        | 0.00312                            |
| <i>E</i> <sup>c</sup> <sub>p</sub>     | -0.00997                                        | 0.01077                                         | -0.00281                           |
| <i>E</i> <sup>c</sup> <sub>sl</sub>    | -0.00930                                        | 0.01198                                         | -0.00351                           |
| <i>DE</i> <sup>c</sup> <sub>xa</sub>   | 0.00285                                         | -0.00497                                        | -0.00048                           |
| <i>DE</i> <sup>c</sup> <sub>ab</sub>   | 0.00179                                         | -0.00269                                        | -0.00067                           |
| total                                  | 0.46895                                         | -0.05362                                        | 0.15245                            |
| observed                               | (0.495 ± 0.01) <sup>b</sup>                     | -0.067 <sup>c</sup>                             | 0.151 <sup>d</sup>                 |

<sup>a</sup> See text.

<sup>b</sup> From adiab. IP of Ref. [11] corrected for vibration, 0.481 seems more likely according to *D<sub>e</sub>*(OH<sup>+</sup>).

<sup>c</sup> Ref. [21].

<sup>d</sup> Ref. [13], from *v*<sub>00</sub> corrected to vertical transition.

correlation due to the change in the occupancy of orbital  $x$  ( $E_{xx,ax}^c$ ), change in polarization-type ( $Ep$ ) and semi-internal correlation ( $E_{SI}^c$ ) which is due to reduction or enlargement of the correlation space, and finally change in correlation due to the deformation of the orbitals ( $DE_{xa}^c$  and  $DE_{ab}^c$ ).

For the ionization potential as well as for the electron affinity, the dominant contribution is the change in external correlation but one third of this effect is cancelled by polarization-type and semi-internal contributions. The orbital deformation has effects in opposite direction for ionization and electron attachment and is particularly pronounced in the latter case reflecting the spreading of the charge distribution in a negative ion. The calculated CEPA ionization energy of 12.78 eV differs from the observed value quoted in Ref. [11], 13.36 eV, by 4% which is more than twice the error previously obtained for ionization potentials of  $H_2O$  [1] and  $CH_4$  [2]. By scaling the external contribution from 86% to 100% (only this type of contribution should be affected by basis set deficiencies) we estimate a CEPA-limit of 13.02 eV, which is in nice agreement with the value deduced from the calculated dissociation energy of  $OH^+$ .

The electron affinity is calculated as  $-0.136$  eV,  $1.265$  eV,  $1.460$  eV, and  $1.510$  eV from HF, PNO-CI, CEPA<sub>1</sub> and CEPA<sub>2</sub>, respectively. In the same way as for the ionization potential we may estimate the CEPA limit to be about  $1.76$  eV as compared to the observed value of  $1.83 \pm 0.04$  eV [21]. This result indicates the possibility of quite reliable predictions for electron affinities which are often not well known experimentally.

The excitation into the  $^2\Sigma^+$  state involves just small changes in correlation. The slight decrease of external correlation is outweighed by a small increase of semi-internal and polarization correlation yielding a net decrease of the HF excitation energy by only 3%. Using the vibrational energies obtained in the previous section,  $\nu_{00}$  is calculated as  $32690$   $cm^{-1}$  as compared to the observed value of  $32440$   $cm^{-1}$  [13].

## 6. Repulsive Curves for $OH(^4\Sigma^-)$ and $OH(^4\Pi)$ and the Predissociation of $OH(^2\Sigma^+)$

Anusual intensity distributions in the violet bands ( $^2\Sigma^+ \leftrightarrow ^2\Pi$ ) of OH have been interpreted as caused by predissociation of the  $^2\Sigma^+$  state due to curve crossing with one of the three excited states that may be formed from  $O(^3P)$  and  $H(^2S)$ ,  $^4\Sigma^-$ ,  $^4\Pi$ , and  $^2\Sigma^-$  [22]. The crossing point has been determined by Naegeli and Palmer [23] to be outside of the minimum and very close to the  $v=2$  level of  $^2\Sigma^+$ , i.e. at about  $1.36$  Å and  $7620$   $cm^{-1}$  above the energy minimum of  $^2\Sigma^+$ . Michel and Harris [6] have investigated all possibly involved curves by minimum basis CI calculations. They found the ordering of the repulsive states as given above and obtained – by adjusting the curves to the experimental dissociation limits – the lowest crossing point at about  $1.4$  Å and  $9900$   $cm^{-1}$ .

We have calculated a few points of the repulsive states around the crossing region. The energies are collected in Table 7. For these states, the basis set has been augmented by a few  $\sigma$ -type functions with small exponents. The crossing points resulting from our various methods are compared with the observed crossing in Table 8.

Table 8. Calculated total energies for repulsive states dissociating into  $O(^3P) + H(^1S)^a$  (a.u.)

| $r_{OH}$ | $^4\Sigma^-$ |          | $^4\Pi$  |          | $^2\Sigma^-$ |
|----------|--------------|----------|----------|----------|--------------|
|          | HF           | CEPA     | HF       | CEPA     | HF           |
| 2.377    | -0.24289     | -0.42269 | -0.17937 | -0.34888 |              |
| 2.514    | -0.25337     | -0.43291 | -0.20219 | -0.37108 | -0.22847     |
| 2.645    | -0.26213     | -0.44044 | -0.22090 | -0.38923 | -0.21617     |
| 2.776    | -0.26958     | -0.46695 | -0.23650 | -0.40445 |              |
| 3.5      | -0.29475     | -0.46559 |          |          |              |
| $\infty$ | -0.30961     | -0.47690 | -0.30961 | -0.47690 | -0.30961     |

<sup>a</sup> Energy values relative to  $-75$  Hartree.

Considering the well known defect of an HF wavefunction in representing the  $^1D-^3P$  splitting of oxygen, it is not surprising that the HF crossing point is shifted towards shorter distance and lower energy with respect to the  $^2\Sigma^+$  minimum. It is rather unexpected however that CEPA appears as over-correcting the HF error: The OH distance is now too long by  $0.05 \text{ \AA}$  and the crossing energy is too high by  $1530 \text{ cm}^{-1}$ . The source of this discrepancy is revealed when the dissociation limits are taken as reference energy (Table 9, Column 3). At the position of the crossing deduced from the intensity data,  $1.36 \text{ \AA}$ , the  $^4\Sigma^-$  repulsive curve has risen to  $11540 \text{ cm}^{-1}$  according to HF, to  $8780 \text{ cm}^{-1}$  according to CEPA, but only to  $2950 \text{ cm}^{-1}$  according to experiment. We are unable to explain this disturbing discrepancy, particularly since our HF curve virtually agrees with another near-HF curve [24].

## 7. Dipole Moment Function and IR Transition Probabilities

The dipole moment as a function of the internuclear distance is directly linked to the IR intensities and is therefore of considerable interest. It is rather difficult however to deduce a dipole moment function from observed intensity ratios, and it has apparently been possible in only a few cases. On the other hand, the dipole moment function provides a very sensitive check on the quality of a wavefunction

Table 9. Crossing point of the states  $^2\Sigma^+$  and  $^4\Sigma^-$ 

| Method              | $r_{OH}(\text{\AA})$ | $E - E_e(^2\Sigma^+)(\text{cm}^{-1})$ | $E - E(O(^3P) + H)$ |
|---------------------|----------------------|---------------------------------------|---------------------|
| HF                  | 1.246                | 4970                                  | 15257               |
| PNO-CI              | 1.385                | 8888                                  | 8780                |
| CEPA                | 1.412                | 9147                                  | 7050                |
| Exper. <sup>a</sup> | 1.36                 | 7620                                  | 2955 <sup>b</sup>   |

<sup>a</sup> Ref. [23].

<sup>b</sup> Assuming a dissociation energy for  $OH(^2\Pi)$  of  $4.63 \text{ eV}$  [30].

Table 10. Dipole moment expectation values for lower vibrational states of OH ( ${}^2\Pi$ ) in D

|                  | HF     | PNO-CI | CEPA   | Exper.            |
|------------------|--------|--------|--------|-------------------|
| $\mu(r_e^{exp})$ | 1.784  | 1.705  | 1.683  |                   |
| $\mu_0$          | 1.7783 | 1.7079 | 1.6865 | 1.66 <sup>a</sup> |
| $\mu_1$          | 1.7995 | 1.7182 | 1.6911 |                   |
| $\mu_2$          | 1.8204 | 1.7274 | 1.6926 |                   |

<sup>a</sup> Ref. [32].

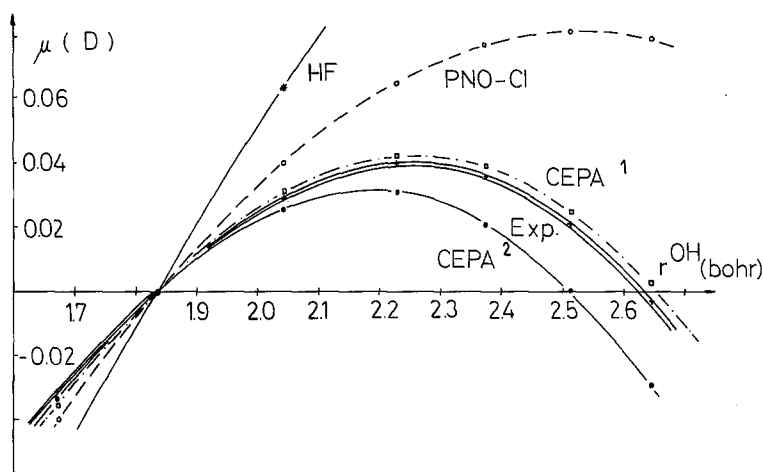


Fig. 2. Calculated and experimental dipole moment function of OH ( ${}^2\Pi$ )

when sufficient experimental data are available. OH is such a fortunate case. Intensity data for  $\Delta v=2$  transitions have been used to deduce a fifth-degree polynomial expression for  $\mu(r)$  by using a Morse potential and its vibrational wavefunctions [25]. The solution is claimed to reproduce the experimental data to within 5–15% but it is obvious that such an expansion can only be valid in a limited region around the minimum. Some recently measured intensity ratios involving  $\Delta v=1$  transitions have then been used to fix an otherwise arbitrary additive Morse-type expression [26]. The resulting dipole moment function, which is somewhat dependent on the validity of the Morse approximation, is given analytically as a footnote in Table 2.

For comparison with the experimental curve, our calculated values are given in Table 2 also with reference to  $\mu_e$  which itself may be found in Table 10 together with some vibrational expectation values  $\mu_v$ . The equilibrium dipole moments calculated from the correlated wavefunctions are significantly better than the HF value though still too large by about 0.05 debye for PNO-CI and 0.03 debye for CEPA, respectively. We find a similar systematic deviation for

Table 11. Observed and calculated ratios of Einstein transition probabilities for OH ( ${}^2\Pi$ )

| Transitions   | HF   | PNO-CI | CEPA | RKR <sup>a</sup> / $\mu_{\text{exp}}$ <sup>b</sup> | Obs. <sup>b</sup> |
|---------------|------|--------|------|----------------------------------------------------|-------------------|
| $A_0^2/A_1^2$ | 0.09 | 0.27   | 0.62 | 0.53 (0.40)                                        | $0.44 \pm 0.0$    |
| $A_1^3/A_2^3$ | 0.18 | 0.60   | 1.90 | 1.76 (1.21)                                        | $1.15 \pm 0.0$    |
| $A_2^4/A_3^4$ | 0.28 | 1.05   | 5.35 | 5.80 (3.28)                                        | $3.3 \pm 0.7$     |

<sup>a</sup> Ref. [13].

<sup>b</sup> Ref. [26], see footnote of Table 2. Numbers in brackets: in  $\mu_{\text{exp}}$  the expression  $-0.246(e^{2.32r} - 1)$  is replaced by  $-0.260(e^{2.158r} - 1)$ . The morse exponent 2.32 is improper for OH.

other diatomic hydrides [17] and further investigations are under way to clarify the reasons for that. More significant however are the shapes of the curves as shown in Fig. 2. The rather large deviation of the PNO-CI curve reveals the importance of the higher-order substitutions, but their effects are apparently taken care of by the CEPA in a reasonable way. The differences between the two versions of CEPA become evident at larger distances. Version 1 seems to be preferable although the virtually complete coincidence of its curve with the experimental one is certainly somewhat fortuitous.

In Table 11 we compare some observed ratios of Einstein coefficients with theoretical values. These numbers are very sensitive with respect to the shape of the dipole moment curve, and even with the "experimental" curve and the RKR potential we can not accurately reproduce the observed ratios which indicates some shortcomings in the curve deduced in Ref. [26].

We have also calculated dipole moment curves for OH ( ${}^2\Sigma^+$ ) and OH<sup>+</sup> ( ${}^3\Sigma^-$ ); they are given in Tables 3 and 4. It may be noted that the correlation correction to the HF values changes its sign near the maximum of the curve at about 2.4 bohr. The computed dipole moment at equilibrium distance is 1.88D as compared to the CI value of 1.83 obtained by Green [27] and experimental values of  $1.98 \pm 0.08\text{D}$  from the Stark effect for OH [28], and  $1.72 \pm 0.1\text{D}$  from microwave measurements on OD [29].

## 8. Concluding Remarks

The results just presented make evident that the CEPA method is superior to any variational CI based on double substitutions of the leading configuration. It apparently provides a rather simple scheme for calculating near-equilibrium surfaces with high accuracy. There is no arbitrariness with respect to configuration selection and no complications arise when the method is applied to polyatomic molecules. There are only minor differences between the results of the two versions of CEPA. Version 1, which we think is preferable by theoretical reasons [2], seems to do better with respect to dipole moment curves. Version 2 yields better energy results probably because the somewhat

larger cluster contributions compensate for other shortcomings of our limited CI expansion. The present results have encouraged us to undertake a systematic study of the diatomic hydrides from LiH to HCl in order to establish the degree of reliability of CEPA potential curves. This will be published in a forthcoming paper.

After the manuscript had been completed we learned that a ground state potential curve of high quality has been obtained by the MC-SCF method [31]. The self-consistency allows to apply this method to larger distances without loss of accuracy. Particularly the dipole moment curve is probably more reliable than ours if all relevant configurations have indeed been selected.

*Acknowledgement.* I would like to thank the Max-Planck-Institut für Astrophysik, Munich, for providing their computing facilities. I am also indebted to the IBM Research Laboratories, San Jose, where these computations have been started during a visit in 1971.

## References

1. Meyer, W.: Intern. J. Quantum Chem. S **5**, 341 (1971)
2. Meyer, W.: J. Chem. Phys. **58**, 1017 (1973)
3. Das, G., Wahl, A. C.: J. Chem. Phys. **44**, 87 (1966)  
Wahl, A. C., Das, G.: Advan. Quantum Chem. **5**, 261 (1970)  
Das, G., Wahl, A. C.: J. Chem. Phys. **56**, 1769 (1971)
4. Hinze, J. A., Roothaan, C. C.: Progr. Theoret. Phys. **40**, 37 (1967)  
Levy, B.: Intern. J. Quantum Chem. **4**, 297 (1970)
5. Harris, F. E., Michels, H. H.: Intern. J. Quantum Chem. S **1**, 329 (1967)
6. Michels, H. H., Harris, F. E.: Chem. Phys. Letters **3**, 441 (1969)
7. Schaefer, H. F.: J. Chem. Phys. **54**, 2207 (1971)  
Pearson, P. K., Bender, C. F., Schaefer, H. F., III: J. Chem. Phys. **55**, 5235 (1971)  
O'Neil, S. V., Schaefer, H. F.: J. Chem. Phys. **55**, 394 (1971)
8. Bondybey, V., Pearson, P. K., Schaefer, H. F.: J. Chem. Phys. **57**, 1123 (1972)
9. Kelly, H. P.: Phys. Rev. **134A**, 1450 (1964); **136B**, 896 (1964)
10. Goldstone, J.: Proc. Roy. Soc. (London) A **239**, 267 (1957)
11. Cade, P. E., Huo, W. M.: J. Chem. Phys. **47**, 614 (1967)
12. Huzinaga, S.: J. Chem. Phys. **42**, 1293 (1965)
13. Fallon, R. J., Tobias, I., Vanderslice, J. T.: J. Chem. Phys. **34**, 167 (1961)  
Schäfer, J.: Private communication
14. Bender, C. F., Davidson, E. R.: Phys. Rev. **138**, 23 (1969)
15. Mehler, E.: Theoret. chim. Acta (Berl.) **35**, 17 (1974)
16. Chamberlain, J. W., Roessler, F. L.: Phys. Rev. **58**, 541 (1954)
17. Meyer, W., Rosmus, P.: To be published
18. Cade, P. E.: J. Chem. Phys. **47**, 2390 (1967)
19. Siebert, H.: Anwendungen der Schwingungsspektroskopie. Wien: Springer 1966
20. Silverstone, H. J., Sinanoğlu, O.: J. Chem. Phys. **44**, 1898, 3608 (1966)
21. Brandscamb, L. M.: Phys. Rev. **148** (1966)
22. Gaydon, A. G., Wolfhard, H. G.: Proc. Roy. Soc. A **208**, 63 (1951)
23. Naegeli, D. W., Palmer, H. B.: J. Mol. Spectr. **23**, 44 (1967)
24. Mulder, J.: Unpublished results
25. Ferguson, F., Parkinson, D.: Planet. Space Sci. **11**, 149 (1963)
26. Murphy, R. E.: J. Chem. Phys. **54**, 4852 (1971)
27. Green, S.: J. Chem. Phys. **58**, 4327 (1972)

28. Scarl, E. A., Dalby, F. W.: *Can. Phys. Soc.* **49**, 2825 (1971)
29. Weinstock, E. M., Zare, R. N.: *J. Chem. Phys.* **58**, 4319 (1972)
30. Herzberg, G.: *Spectra of diatomic molecules*. Princeton: Van Nostrand 1950
31. Karo, A., Krauss, M., Wahl, A. C.: *Intern. J. Quantum Chem. S* **7**, 143 (1973)
32. Powell, F. X., Lide, D. R.: *J. Chem. Phys.* **42**, 4201 (1965)

Prof. Dr. W. Meyer  
Institut für Phys. Chemie III  
der Johannes Gutenberg Universität  
D-6500 Mainz  
Jakob Welder-Weg 26  
Federal Republic of Germany