

DIPOLE MOMENTS AND ELECTRIC FIELD GRADIENTS FOR CORRELATED WAVEFUNCTIONS OF NO: THE X²Π, A²Σ⁺, AND D²Σ⁺ STATES*

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Received 10 February 1975

Recent experiments by Bergeman and Zare led to a dipole moment of $|\mu| = 1.10 \pm 0.03$ D for the $\nu = 3$ vibrational level of the A²Σ⁺ state of NO, whereas configuration interaction (CI) studies by Green led to $\mu = 0.39$ D (N⁺O⁻), a serious discrepancy. We report herein ab initio generalized valence bond (GVB) and GVB CI calculations resulting in a dipole moment of +1.36 at R_e for the A²Σ⁺ state; considering the expected decrease of μ for increasing ν , this is in reasonable agreement with experiment. Theoretical values of the dipole moment, electric field gradient, and excitation energies are reported for the X²Π, A²Σ⁺, and D²Σ⁺ states of NO.

1. Introduction

Recently Bergeman and Zare [1] reported the first experiments determining the dipole moment of a Rydberg state of a molecule. They found the dipole moment for the $\nu = 3$ vibrational level of the A²Σ⁺ state of NO to be

$$|\mu| = 1.10 \pm 0.03 \text{ debye,}$$

where the quoted uncertainty was estimated as three standard deviations. They pointed out that this value differs quite significantly from that determined by Green [2] from configuration interaction (CI) calculations:

$$\mu = 0.47 \pm 0.03 \text{ debye (N}^+\text{O}^-)$$

for $R = 1.06 a_0$ and an estimated value [based on the variation of μ with R for the Hartree-Fock (HF) wavefunction] of

$$\mu = 0.39 \pm 0.10 \text{ debye}$$

for the $\nu = 3$ level. Bergeman and Zare suggested two

possible explanations for the difficulty: (1) An R -dependent "dipole borrowing" from the D state that would come in differently with CI than for HF and (2) nonadiabatic coupling of the A and D states. They analyzed the second effect and found the correction to be small.

We felt that the theoretical results deserved re-evaluation and carried out extensive generalized valence bond [3] (GVB) and GVB CI calculations on the X state at R_e (2.1747 bohr) and the A and D states at R_e (2.0101 bohr). The results for the dipole moment are (all CI wavefunctions)

$$\begin{aligned} \mu &= -0.10 \text{ debye for X}^2\Pi, \\ \mu &= +1.36 \text{ debye for A}^2\Sigma, \\ \mu &= -2.21 \text{ debye for D}^2\Sigma. \end{aligned}$$

The value for the ground state is in good agreement with the experimental value $|\mu| = 0.16$ D [4] and the value for the A state is in reasonable agreement with the value obtained by Bergeman and Zare (especially considering that our value for μ should decrease in magnitude when averaged over the $\nu = 3$ vibrational level).

We find that the Hartree-Fock wavefunctions lead to a significant error (-0.67 D) in the dipole moment. The reason is as follows: (1) due to the doubly-occupied orbital restrictions of HF the π orbitals of the NO⁺ core

* Partially supported by a grant (GP-40783X) from the National Science Foundation.

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[†] Contribution No. 5018.

tend to concentrate too much on the oxygen; (2) as a result the Rydberg orbital polarizes toward the N; however the resulting relatively small changes in the Rydberg orbital lead to large changes in the dipole moment. Correlating the NO bonds as in GVB removes this problem. The CI calculations of Green were based on HF wavefunctions and apparently sufficiently high orders of excitation to overcome the deficiencies of HF were not included.

Thus there is no reason to presume particularly large nonadiabatic corrections in the dipole moments for Rydberg excited states of molecules.

2. Theoretical details

We used three basis sets for these calculations. The first (32 basis functions) consisted of the "double zeta" (DZ) set of contracted cartesian gaussian functions of Dunning and Huzinaga [5], augmented by a set of d functions on the N and O (orbital exponents $\alpha_N = 0.80$ and $\alpha_O = 1.04$). This is the type of basis (denoted DZd) we would normally use for describing potential curves of valence states and it was used for the $X^2\Pi$ state. In order to describe the Rydberg states ($A^2\Sigma^+$ and $D^2\Sigma^+$), the DZd basis was augmented by diffuse s and p σ functions on the N and O (N exponents: $\alpha_s = 0.0650$ and 0.0198 , $\alpha_p = 0.0515$ and 0.0160 ; O exponents: $\alpha_s = 0.0862$ and 0.0261 , $\alpha_p = 0.0637$ and 0.0190). (The exponents for the diffuse functions were obtained by scaling down from the exponents of the valence primitives, a procedure that has worked well for the Rydberg states of a number of molecules [6-8].) This leads to a total of 40 basis functions for this second basis set (denoted as DZdR). As a check on the validity of our results for the A state we also carried out calculations using a more extensive basis set (denoted as Big) in which the (9s5p1d) primitive basis set was contracted to [5s, 3p, 1d] [5], and in addition to the diffuse functions of the DZdR set we added more diffuse s and p $_z$ functions (N exponents $\alpha_s = 0.0060$ and $\alpha_p = 0.0050$; O exponents $\alpha_s = 0.0079$ and $\alpha_p = 0.0057$) and diffuse d functions ($2d_{z^2} - d_{x^2} - d_{y^2}$; N exponent $\alpha = 0.03$ and O exponent $\alpha = 0.04$). The Big basis involves 58 basis functions.

For each state we carried out self-consistent generalized valence bond (GVB) calculations followed by appropriate CI calculations. For the $A^2\Sigma$ state the

GVB wavefunction differs from the HF wavefunction by having the σ bond and each of the π bonds correlated [referred to as GVB(3/PP)]. Thus we solve for 11 orbitals self-consistently rather than eight as in HF. Since the orbitals are optimized for the dominant correlation effects, one can account for most of the residual correlation effects remaining in the GVB wavefunction by including other configurations involving the 11 GVB orbitals, rather than using the full basis (40 basis functions). To describe the D state we also included the 3p-like orbital obtained as the lowest variational orbital from the GVB variational solution of the $A^2\Sigma^+$ state (this leads to the optimum excited orbital for the D state within the restriction that the NO^+ core orbitals from the $A^2\Sigma^+$ state are not readjusted).

For the ground state wavefunction we carried out GVB(2/PP) calculations (splitting the σ and π_y bonds, with a singly-occupied π_x orbital in addition to the π_x bond pair) using the DZd basis. This procedure leads to different orbitals in the x and y directions. To generate an equivalent set for the CI calculations, we rotated the π_y correlating orbital and orthogonalized to the first two π_x orbitals. The resulting three orbitals were then used in both directions.

In the CI calculations we initially allowed only configurations involving excitations among the GVB orbitals. However, after preliminary calculations we found that a good description of the $^2\Pi$ state required additional configurations involving excitation from the GVB π orbitals into the remaining virtual orbitals of the π space. (These configurations were more important for the X state than for the excited states.) We also allowed up to double excitations from the GVB π orbitals into the four virtual orbitals of delta symmetry. This procedure yielded 202 spatial configurations (483 spin eigenfunctions or 908 determinants) for the $X^2\Pi$ state and 190 spatial configurations (532 spin eigenfunctions or 939 determinants) for the $^2\Sigma^+$ states (A and D).

The GVB calculations used the Bobrowicz-Wadt-Goddard program incorporating the full variational treatment of open shell systems [9] and the GVB variational methods [10]. The Caltech CI program (Bobrowicz, Winter, Ladner, Goddard, Hay, Moss, Walch, and Harding) was used for the CI calculations. The CI properties were evaluated with a program written by Walch and Dunning using the NYU (Moskowitz)

Table 1

Calculated and experimental properties for X, A, and D states of NO (in the DZd basis for X $^2\Pi$ and the DZdR basis for $^2\Sigma^+$ unless noted otherwise)

		X $^2\Pi$	A $^2\Sigma^+$	D $^2\Sigma^+$
Excitation energy (eV)				
	HF ^{a)}	0.0	5.45	(6.59) ^{f)}
	GVB	0.0	4.60 ^{b)}	(5.69) ^{g)}
	CI	0.0	5.05 ^{d)}	6.39 ^{d)}
	ref. [2]	0.0	3.92	-
	exper.	0.0	5.42 ^{c,d)}	6.55 ^{c,d)}
Dipole moment (D)				
	HF	+0.36	+0.66	(-2.10)
	this work	+0.36	+0.74 ^{h)}	-
	ref. [2]	+0.26	+0.63	-
	GVB	0.0	1.36	(-2.20)
	this work	0.0	+1.41	-2.21
	CI	-0.10	+1.36	-
	ref. [2]	-0.25	+0.39	-
	exper.	± 0.16 [4]	$\pm 1.10 \pm 0.03$ ^{e)}	-
Quadrupole coupling constants at N (MHz)				
eQ_Nq_N	HF	-1.79	-6.35	(-4.49)
	this work	-1.79	-5.29 ⁱ⁾	-
	GVB	-1.20	5.25	(-4.23)
	this work	-1.20	-4.27	-4.38
	CI	-1.10	-4.36	-
	ref. [2]	-1.63	-5.62	-
	exper.	-1.876 ± 0.008 [4]	-2.88 ± 0.17 ^{e)}	-
$eQ_N\bar{q}_N$	HF	29.35		
	this work	29.35		
	ref. [2]	21.03		
	GVB	21.75		
	CI	26.76		
	exper.	23.04 ± 0.05 [4]		

- a) The calculated total energies for the X $^2\Pi$ state are -129.26934 H, -129.32614 H, and -129.43055 H for HF, GVB, and CI, respectively.
- b) The Big basis leads to a drop in the energy of 0.206 eV for HF and 0.218 eV for GVB. This basis would also lead to a similar drop for $^2\Pi$ and hence little change in the excitation energy is expected.
- c) Includes a correction of 0.03 eV for the difference in zero-point energies for the ground and Rydberg states. Excitation energies are taken from ref. [11].
- d) The calculated oscillator strength (f) for A \leftrightarrow D is 0.324, the experimental value [13] is 0.18.
- e) Ref. [1], this is for the $\nu = 3$ vibrational level.
- f) Parentheses for an HF quantity indicate that the HF wavefunction was obtained by deleting the second natural orbitals of the GVB wavefunction.
- g) Parentheses for a GVB quantity for the D state indicate that the core orbitals were restricted to be those of the A state.
- h) Using the GVB wavefunction and the approximate HF-type wavefunction described in footnote f leads to +1.54 D.
- i) Using the GVB wavefunction and the approximate HF-type wavefunction described in footnote f leads to -4.33 MHz.

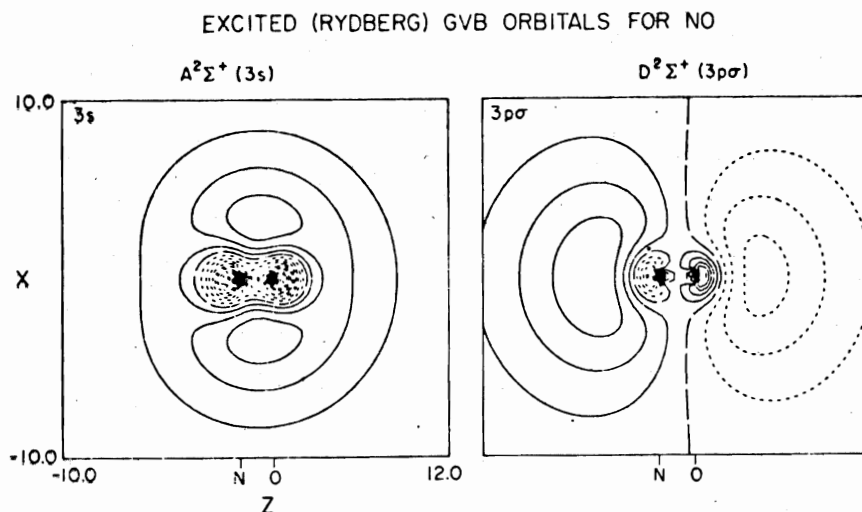


Fig. 1. The Rydberg orbitals from GVB wavefunctions of the $A^2\Sigma^+$ and $D^2\Sigma^+$ states of NO. The long dashes indicate nodal planes. Solid and dotted lines indicate positive and negative amplitudes. Contour intervals are 0.01 au.

integrals program. The molecular integrals were evaluated with a version of the POLYATOM (Basch and Snyder) integrals program.

3. Results and comparison with experiment

The calculated energies and properties are compared with experiment in table 1. The shapes of the excited orbitals for the A and D states of NO are shown in fig. 1 (using the DZdR basis). As expected, these orbitals have basically the character of $3s$ and $3p\sigma$ orbitals, respectively, and are well described as Rydberg orbitals. For simplicity we will refer to these self-consistent GVB orbitals as $3s$ and $3p\sigma$.

3.1. Energies and oscillator strength

The calculated excitation energies (CI) are 5.05 eV for $A \leftarrow X$ and 6.39 eV for $D \leftarrow X$, which are 0.37 eV and 0.18 eV lower, respectively, than the experimental values [11] (errors of 7% and 3%, respectively).

The calculated bond dissociation energy $D_e(\text{NO})$ is 6.41 eV which is 97% of the experimental value[†] of 6.60 eV.

[†] We have taken the energies of the separated atoms as $O(^3P) = -74.80087$ H from a DZd HF calculation [12] and that for $N(^4S)$ as -54.39439 H [5] from a DZ HF calculation. [For the $N(^4S)$ state the d functions do not mix into the HF wavefunction.] The experimental dissociation energy $D(\text{NO})$ was corrected for the zero-point vibrational energy $\frac{1}{2}h\nu_0$ for comparison with the calculated value.

We calculated the oscillator strength, f , only for $D \leftrightarrow A$. The result is $f = 0.324$ which is 80% larger than the experimental value of 0.18 from the $D^2\Sigma^+ \rightarrow A^2\Sigma^+$ 0-0 emission band [13].

3.2. Dipole moment

For the $X^2\Pi$ ground state, the calculated dipole moment is $\mu = -0.10$ D, whereas the experimental value [4] is $|\mu| = 0.159$ D. Thus, just as for CO [14], the ground state of NO has the electron charge distribution distorted slightly from the oxygen to the more electropositive element.

Using the DZdR basis we calculated a dipole moment for the $A^2\Sigma^+$ state of $\mu = 1.41$ D with GVB and $\mu = 1.36$ D with GVB CI while the Big basis yields $\mu = 1.36$ D for GVB. Thus our best estimate of the theoretical μ is

$$\mu = 1.31 \text{ D.}$$

The experimental value is $|\mu| = 1.10 \pm 0.03$ D for $v = 3$ [1]. The dipole moment is expected to decrease in magnitude for larger R and hence should decrease for larger v . Thus the calculated value is in reasonable agreement with experiment.

We find that the $D^2\Sigma^+$ state leads to $\mu = -2.21$ D, even larger in magnitude than for the A state but directed in the opposite direction. The reason for this oscillation is understood as follows.

From the GVB(3/PP) wavefunction for the $A^2\Sigma^+$ state, we find that the dipole moment of the NO^+ core (evaluated about the nitrogen) is +0.999 au (N^+O^+). Thus if the 3s or $3p\sigma$ orbitals of the Rydberg state were centered at +0.999 au (50% of the bond length) from the N (toward the O), the dipole moment would be zero. In fact the GVB 3s orbital is pulled significantly toward the O, leading to a total μ of 1.41 D (N^+O^-) [this corresponds to a centering of the 3s orbital at 1.553 a_0 (77% of the bond length) with respect to the N]. Since the GVB Rydberg orbital for the A state has a component of $3p\sigma$ character pushing it toward the O

$$\phi_{3s} + \lambda\phi_{3p\sigma},$$

the GVB Rydberg orbital for the D state is expected (and observed) to be pushed toward the N (see fig. 1)

$$\phi_{3p\sigma} - \lambda\phi_{3s}.$$

The center of charge of the GVB $3p\sigma$ orbital is at +0.119 a_0 (6% of the bond length) relative to the N, leading to a large dipole moment in the opposite direction (N^-O^+). This effect leads to wildly different dipole moments for alternate Rydberg states. Similar results were found earlier by Hunt and Goddard for H_2O [6] and can be expected to be general.

3.3. Quadrupole coupling constants

The experimental quadrupole coupling constant (at the nitrogen), denoted as eQ_Nq_N , is a measure of both the nuclear quadrupole moment, Q_N , and the electric field gradient,

$$q_N = 2\xi_0/R^3 - \langle \sum_i \{ (3z_i^2 - r_i^2)/r_i^5 \} \rangle_N \equiv F_{zz}$$

(coordinates centered at the N) where ξ_0 and R are the oxygen atom nuclear charge and NO bond distance, respectively. For the $^2\Pi$ state there is also a second (perpendicular) component $eQ\bar{q}_N$ where

$$\bar{q}_N = 9 \langle \sum_i \{ (x_i^2 - y_i^2)/r_i^5 \} \rangle \equiv 3(F_{xx} - F_{yy}).$$

Since only the product of Q and q is experimentally accessible, the values of Q must be obtained by comparison of calculated electric field gradients q and measured values of eQq . We chose $Q_N = 1.56 \times 10^{-26} \text{ cm}^2$, the value suggested by O'Konski and Ha [15] based on a comparison of HF values for q and experimental eQq

for a number of molecules. Using this value for Q , one atomic unit of field gradient results in an eQq of 3.6657 MHz.

The calculated CI values of eQq for the X and A states are off by -41% and +51% from the experimental values and the calculated $eQ\bar{q}$ of the X state is off by +16%. These are much larger errors than for the other properties (our value for eQq for the A state is somewhat better than the value obtained by Green, 95% error). One should bear in mind here that the basis set used was designed solely on the basis of energy considerations. This basis is, we believe, quite adequate for global properties such as the dipole moment but may be deficient for describing properties at the nucleus. For example, one should include high exponent d functions (and perhaps high exponent p functions) to describe polarization of the N 1s pair and in addition f functions could lead to changes in the field gradients due to the p-like orbitals.

4. Comparison of theoretical results

4.1. Energies

The energy of the $X^2\Pi$ and $A^2\Sigma$ states drops 1.55 eV and 2.45 eV, respectively, in going from HF to GVB and drops an additional 2.84 and 2.39 eV, respectively, in going to the CI wavefunction. The net result is that the HF excitation energy is 0.03 eV above the experimental value while the CI result is 0.37 eV below experiment. We believe that the good result obtained here for HF is accidental.

Generally for excitation of a doubly-occupied valence orbital to a Rydberg orbital, HF leads to an excitation energy too small by ≈ 1 eV, corresponding to the correlation error of a valence pair. In NO the $A \leftrightarrow X$ excitation is out of a singly-occupied orbital and the above argument does not apply. However relaxing the spin restriction on the HF wavefunction of the $^2\Pi$ state leads to a decrease in the energy of 0.41 eV hence an increase in the excitation energy to 5.91 eV. Such a value, larger than experiment, is reasonable since the correlation error in the π_x pair is expected to be greater in the $^2\Sigma$ state than in the $^2\Pi_x$ states (where there is also a singly-occupied $2\pi_x$ orbital). The GVB(PP) wavefunction leads then to too small a value because this pair is still uncorrelated in the $^2\Pi$ state although correlated in the $^2\Sigma$ state.

Green obtained an HF excitation energy of 5.23 eV in reasonable agreement with our value; however, his CI wavefunctions led to an excitation energy 1.50 eV lower than experiment and 1.13 eV lower than for our wavefunction. As expected, we find that the A state has more correlation energy than the X state (4.84 eV and 4.39 eV, respectively, within the restriction that the 1s and 2s pairs remain uncorrelated). However in our CI for the X state, 25 configurations produce CI lowerings greater than 0.001 H, whereas for the A state only nine do. Thus the correlation energy for the X state is more difficult to describe in the CI and we suspect that the low excitation energy obtained by Green may be a result of using too restrictive a set of configurations.

4.2. Dipole moment

For the X state the dipole moments for the HF, GVB, and CI wavefunctions are +0.36 D, 0.00 D, and -0.10 D. Thus just as for CO the HF wavefunction leads to a dipole moment with the extra charge on the more electro-negative member while the CI wavefunctions reverse the sign. For NO the principal effect of electron correlation on the dipole moment is a decrease in the contribution of the π_y pair (-0.592 debye) partially balanced by an increased contribution due to the three electrons in the π_x orbitals (+0.183 debye).

For the A state the HF, GVB, and CI wavefunctions lead to $\mu = +0.74$ D, +1.41 D, and +1.36 D, respectively, for the DZdR basis and $\mu = 0.66$ D and +1.36 D for the HF and GVB wavefunctions with the Big basis. Thus the HF wavefunction leads to a small dipole moment in agreement with the value reported by Green (0.63 D with optimized exponents). However, when simple correlation effects are included within the positive ion core, we find significant changes, resulting in a calculated dipole moment in reasonable agreement with the experimental value.

As expected, the primary effect of correlation is a decrease in the ionic character of the core (NO^+) orbitals. (The dipole moment contribution of the core decreases by 0.398 D.) However, the resultant flow of charge from O to N in the core results in a large shift of the Rydberg orbital toward O, leading to an increased contribution for the Rydberg orbital of 1.098 D. Thus the HF wavefunction, which neglects these important correlation effects, leads to a low dipole moment.

For the GVB wavefunction, since the orbitals are solved for with the dominant correlation effects already present, only a small CI necessary to account for the remaining small effects and the CI dipole moment is little changed from the GVB value. On the other hand, for the HF wavefunction a rather extensive CI is necessary to allow correlation of the core orbitals and simultaneous reoptimization of the Rydberg orbital.

Green carried out restricted Hartree-Fock calculations, constructed a limited CI expansion, and carried out iterative natural orbital calculations to obtain the optimum orbitals. Since Green reports that the dipole moment *decreased* with CI, it would appear that the configurations selected described the correlation of the core, but were not sufficiently flexible to allow simultaneous readjustment of the 3s orbitals.

As a further check on the validity of our results for the A state, we repeated the HF and GVB calculations with the more extensive Big basis set. With the Big basis we obtain $\mu = +0.66$ D and +1.36 D for the HF and GVB(3/PP) wavefunctions, respectively, in good agreement with the results for the smaller basis (and in slightly better agreement with experiment).

4.3. The electric field gradients

For the ground state we find a large change in the electric field gradient between HF and GVB while the GVB and CI values are similar. The change of this property upon correlation is essentially related to the shift of the π_y pair toward the N (which also led to a significant decrease in the dipole moment).

Our value for q of the A state is closer to experiment than Green's values (41% error as compared with 95%). For the X state properties our values are in poorer agreement with experiment. It is likely that high exponent d functions are needed to obtain a good description of the field gradients [16].

5. Conclusion

We find that the GVB procedure of solving for the optimum orbitals with the dominant correlation terms present allows a good description of the energies and properties of both the valence and Rydberg states of NO. As a result the additional correlation effects are

small and the properties of the states can be interpreted in terms of the simple orbital description of GVB.

Acknowledgement

We thank Professor R.N. Zare for bringing to our attention the disagreement between the theoretical and experimental values of μ for the A state of NO.

References

- [1] T. Bergeman and R.N. Zare, *J. Chem. Phys.*, to be published.
- [2] S. Green, *Chem. Phys. Letters* 13 (1972) 552; 23 (1973) 115.
- [3] W.A. Goddard III, T.H. Dunning Jr., W.J. Hunt and P.J. Hay, *Accounts Chem. Res.* 6 (1973) 368, and references therein.
- [4] R.M. Neumann, *Astrophys. J.* 161 (1970) 779.
- [5] T.H. Dunning Jr., *J. Chem. Phys.* 53 (1970) 2823.
- [6] W.J. Hunt and W.A. Goddard III, *Chem. Phys. Letters* 3 (1969) 414; W.A. Goddard III and W.J. Hunt, *Chem. Phys. Letters* 24 (1974) 464.
- [7] D.C. Cartwright, W.J. Hunt, W. Williams, S. Trajmar and W.A. Goddard III, *Phys. Rev. A* 8 (1973) 2436.
- [8] W.J. Hunt, Ph.D. Thesis, California Institute of Technology, September 1971.
- [9] W.J. Hunt, W.A. Goddard III and T.H. Dunning Jr., *Chem. Phys. Letters* 6 (1970) 147.
- [10] W.J. Hunt, P.J. Hay and W.A. Goddard III, *J. Chem. Phys.* 57 (1972) 738.
- [11] B. Rosen, in: *Tables of constants and numerical data*, ed. S. Bourcier (Pergamon Press, London, 1970).
- [12] W.A. Goddard III, P.J. Hay and T.H. Dunning Jr., *J. Am. Chem. Soc.*, submitted for publication.
- [13] K.L. Wray, *J. Quant. Spectry. Radiative Transfer* 9 (1969) 255.
- [14] F. Grimaldi, A. Lecourt and C. Moser, *Intern. J. Quantum Chem.* 1S (1967) 153.
- [15] C.T. O'Konski and T.-K. Ha, *J. Chem. Phys.* 49 (1968) 5354.
- [16] P.J. Hay and W.A. Goddard III, *Chem. Phys. Letters* 9 (1971) 356.