

VIBRATIONAL CONTRIBUTION TO DIPOLE POLARIZABILITY AND FIRST HYPERPOLARIZABILITY OF LiH

Marcello F. Costa*

Universidade Estadual do Oeste do Paraná, Campus Toledo, Rua da Faculdade, 2550, 85903-000 Toledo - PR, Brasil

Mauro C. C. Ribeiro

Instituto de Química, Universidade de São Paulo, CP 26077, 05513-970 São Paulo - SP, Brasil

Recebido em 6/2/06; aceito em 9/3/06; publicado na web em 11/8/06

The role played by electron correlation and vibrational correction on the polarizability of the LiH molecule is demonstrated. We present results for the dipole moment, polarizability and first hyperpolarizability of the LiH molecule obtained through many-body perturbation-theory, coupled-cluster and quadratic configuration interaction methods. Our best result for the dipole polarizability, obtained using the QCISD(T) scheme, indicates that the vibrational contribution is appreciable, amounting to *ca.* 10% of the total polarizability. Regarding the first hyperpolarizability, the vibrational contribution is even more important and has opposite sign in comparison with the electronic contribution.

Keywords: *ab initio*; polarizability; hyperpolarizability.

INTRODUCTION

The important role played by polarizability to understand a large variety of physical phenomena has already been stressed in a number of previous articles¹⁻³. The well-known experimental difficulties to obtain reliable results of polarizabilities, justifies the need for accurate theoretical results. In some cases, these results are the only source of information regarding polarizabilities. It has been shown that in order to get accurate results for electrical properties, calculations must take into account a careful choice of the function basis set and an appropriate inclusion of electronic correlation effects. In addition to these well-established precautions, another important aspect, which will be considered in this work, is the inclusion of vibrational corrections.

The finite field method^{4,5} is usually employed to calculate electrical properties. According to this scheme, the energy of the system is calculated in absence and in the presence of an external electric field, and the properties of interest are obtained by means of numerical differentiations of the energy. A common feature of previous works is the use of the same geometry both in the presence and in the absence of the field. This clearly constitutes a risky procedure when dealing with ionic system, as the positive ions are driven in the direction of the applied field while the negative ions are pulled in the opposite direction. The repositioning of the ions in the presence of the electric field changes the framework and is responsible, as we are going to show in the sequence, for a relevant contribution to the polarizabilities. The effect of nuclear motion in the calculation of electric properties has already been studied using the finite perturbation theory (FTP) by Cohen *et al.*⁶ and Bishop and Kirtman^{7,8} using their perturbation theory method. The FTP approach has been employed by Papadopoulos *et al.*⁹ in evaluating vibrational contributions to polarizability and hyperpolarizability of LiH. However, Papadopoulos *et al.*⁹ did not include electronic correlation. The purpose of this article is to evaluate the importance of simultaneous inclusion of electronic correlation effects and geometry relaxation in the calculation of polarizabilities and hyperpolarizabilities. We choose LiH as a test molecule due to its pronounced ionic character. Furthermore, we obtained new optimized exponents for the basis sets of Li and H based on the convergence of calculated hyperpolarizability.

COMPUTATIONAL DETAILS

Methods

Recent calculations^{10,11} showed that in order to obtain reliable results for electrical properties it is necessary to use a careful built basis set and include electronic correlation at high order. In this work, we first performed calculations at Hartree-Fock level, and then we included electronic correlation effects through the following methods: configuration interaction (CI), which is variational but not size consistent¹², many-body perturbation theory (MBPT), and coupled-cluster (CC), which are size consistent but not variational^{13,14}. As these methods adopt different approaches, the comparison of results will allow useful and interesting analysis of electronic correlation effects. As the size consistency is usually considered more important than provision of an energy upper bound in the calculation of electric properties, the MBPT and CC methods are frequently preferred in this type of calculation. In particular, when compared to MBPT, coupled-cluster has the advantage of including higher order contributions of some substitutions. An interesting scheme is the coupled-cluster with double substitutions (CCD)^{13,14} which includes all the contributions within the space of double and quadruple substitutions, up to fourth-order in perturbation theory [DQ-MBPT(4)], and some selected high order contributions. The CCD+ST(CCD) scheme¹⁵ includes single and triple substitutions contributions in the way done by MBPT(4), except that the coefficients of the double substitutions are taken from a previous CCD calculation. It has been stressed in the literature that this scheme treats the electronic correlation more properly than MBPT(4)^{15,16}. An alternative approach is the use of the so called quadratic configuration interaction (QCI) method^{17,18}. This approach includes some quadratic terms in the CI expansion aiming to restore the size consistency, at the cost of losing the variational character of the CI method. In this work, we have employed the quadratic configuration interaction method, with single and double substitutions (QCISD), adding the contribution of triple substitutions through the QCISD(T) approximation^{17,18}. Both the QCISD(T) and the CCD-ST(CCD) approaches are manageable approximations to the more sophisticated but more expensive CCSD(T) scheme (coupled cluster with single, double and triple substitutions).

*e-mail: mcosta@iq.usp.br

Basis sets

Alkali metal hydrides (LiH, NaH and KH) are the subject of a comprehensive study¹¹⁻¹⁸ and that treats the electronic and vibrational contributions to dipole moment, polarizability and hyperpolarizabilities. This work is intended to provide a benchmark study for these molecules and we discuss it here to exemplify the kind of results obtainable or the static response functions of small molecule using current state of the art methods.

As important as the correct treatment of the correlation problem, is the care in selecting the basis set¹¹⁻²⁰. Bad choice of the basis set does not compensate for the most sophisticated treatment of electronic correlation. Bearing this in mind, we have chosen at the substrate basis set the (6s4p/3s2p) contraction proposed by Sadlej¹⁹ for H and the (10s6p4d/5s3p2d) contraction from Sadlej and Urban²¹ for Li. This set has been successfully applied in the calculation of dipole moment and polarizability of LiH. In our calculations, it has been supplemented by including diffuse and polarization functions in order to ensure a proper behavior of the hyperpolarizability. In the case of LiH there are a number of high level calculations in the literature with which these calculations can be compared and it is of interest at this point to examine how well they have converged on settled values. For the computation of accurate hyperpolarizabilities, one needs a method for the satisfactory calculation of the contribution of the electron correlation and an adequate basis set, which will allow the physically correct polarization of the molecule in the presence of an electric field. It is well documented that the first demand is properly answered, in general, by fourth-order Möller Plesset perturbation theory. As for the design of appropriate basis sets, various rules and strategies have been proposed.

Our option was to use some basis sets for Li and H which we have recently published and which gave good results for the polarizabilities and hyperpolarizabilities of Li⁺ and H⁺.⁹ The exponents ζ_i of the polarization and diffuse functions are defined by

$$\zeta_i = ab^i$$

where a and b are parameters optimized to reproduce energy and i takes the values 0, ± 1 , ± 2 , In our calculations, it has been supplemented by including diffuse and polarization functions in order to ensure a proper behavior of the hyperpolarizability.

The procedure adopted was a continue adding of new exponents until a modification of no more than 2% was achieved in the first hyperpolarizability at the CISD level. Table I shows the obtained extra exponents. Inclusion of f -type functions has no influence on results. The complete set comprises a total of 86 basis functions, in comparison with *ca.* 40 of Sadlej and Urban²¹. Finally, it is worth mentioning that all orbitals, occupied and virtuals, were employed in our calculations including electronic correlation.

Table 1. The extra exponents in the basis sets for H and Li

| H | Li |
|---------------|----------------|
| $s = 0.0102$ | $p = 0.002601$ |
| $s = 0.0032$ | $d = 4.15340$ |
| $p = 14.6596$ | $d = 1.16944$ |
| $p = 4.1216$ | $d = 0.002061$ |
| $p = 0.0102$ | |
| $p = 0.0032$ | |
| $d = 0.357$ | |

Electric properties

It is well known that the energy of a molecule in an applied field can be expressed as an expansion involving coefficients identified as permanent multipole moments and polarizabilities. Following McLean and Yoshimine²², when a linear molecule is placed in the presence of an external electric field, its energy is modified according to the expression

$$\varepsilon = -\mu E_z - \frac{1}{2}\alpha_{zz}E_z^2 - \frac{1}{2}\alpha_{xx}E_x^2 - \frac{1}{6}\beta_{zzz}E_z^3 - \frac{1}{2}\beta_{xxz}E_x^2E_z - \dots$$

where E_z and E_x represents, respectively, the parallel and perpendicular components of the applied field, μ is the permanent dipole moment, α_{zz} and α_{xx} are the parallel and perpendicular components of the polarizabilities, and β_{zzz} and β_{xxz} are the independent components of the first dipole hyperpolarizability. According to the finite field method, the multipole moments and polarizabilities are obtained as numerical differentiation of the energy calculated in the presence of different values of the applied electric field. In this work, we started by calculating polarizabilities and hyperpolarizabilities of LiH with no change in molecular geometry due to the presence of the field. This is what we call the electronic contribution. The second contribution to the calculated properties, due to the repositioning of the ions, is called here the vibrational contribution.

RESULTS AND DISCUSSION

We first optimized the internuclear distance in the absence of an electrical field at all levels of calculations. Keeping unaltered the optimized geometry of the free molecule, with different magnitude the energy has been calculated in the presence of applied electric fields of different magnitude. As this procedure does not take into account the nuclear motion, the calculated properties incorporate only the electronic contribution. This has been the procedure usually adopted, which excludes the vibrational contribution. These calculations were performed by using the Gaussian94 package²³. We then optimized the internuclear distance for each value of the applied field. For this purpose, we have performed several independent single-point energy calculations. Following this procedure, we present the molecular reorientation when an electric field is applied perpendicularly to the molecular axis.

In order to calculate the electronic contribution to μ , α_{zz} , α_{xx} and β_{zzz} we used different values of field: $E_z = \pm 0.001$, ± 0.002 , ± 0.003 and $E_x = \pm 0.002$ a.u.. To obtain β_{xxz} , we performed an extra calculation applying a field with components $E_x = \pm 0.002$ and $E_z = \pm 0.002$ a.u.. These selected values were chosen as a compromise of achieving the desired numerical accuracy, but not disturbing appreciably the electronic density. An eight-degree polynomial was employed to obtain the fitting of the energy as function of the electric field. To obtain α_{xx} we performed calculations applying two different values of the electric field: $E_x = 0.001$ and 0.002 a.u.. The fitting of the energy curve was obtained using a four-degree polynomial.

Table 2 shows the calculated electronic contributions for μ , α and β .

Calculated dipole moment at different levels of theory are very similar, indicating that no sophisticated treatment is needed in order to have a reliable estimative of this property. The difference between the SCF result and the best level of correlation, QCISD(T), is only 2%. These results are in very good agreement with those of Roos and Sadlej²⁴, Papadopoulos *et al.*⁹ and Rothstein²⁵.

Concerning parallel and perpendicular components of dipole polarizability, Table 2 shows that electronic correlation effects are

Table 2. Calculated electronic contribution for dipole moment, polarizability and first hyperpolarizability of LiH (in *a.u.*)

| Method | μ | α_{zz}^e | α_{xx}^e | β_{zzz}^e | β_{xxx}^e |
|-------------|-------|-----------------|-----------------|-----------------|-----------------|
| SCF | 2.37 | 22.02 | 25.45 | 315 | 173 |
| MBPT(2) | 2.34 | 23.52 | 27.21 | 438 | 230 |
| MBPT(3) | 2.33 | 24.31 | 28.27 | 479 | 252 |
| DQ-MBPT(4) | 2.32 | 24.83 | 28.87 | 513 | 265 |
| SDQ-MBPT(4) | 2.32 | 24.93 | 28.96 | 524 | 271 |
| MBPT(4) | 2.32 | 24.95 | 28.97 | 526 | 271 |
| CID | 2.32 | 24.94 | 29.03 | 517 | 269 |
| CISD | 2.32 | 25.57 | 29.56 | 593 | 301 |
| QCISD | 2.31 | 26.00 | 30.01 | 693 | 307 |
| QCISD(T) | 2.31 | 26.06 | 30.04 | 700 | 309 |
| CCD | 2.32 | 25.17 | 29.30 | 534 | 275 |
| CCD+ST(CCD) | 2.32 | 25.56 | 29.66 | 577 | 293 |

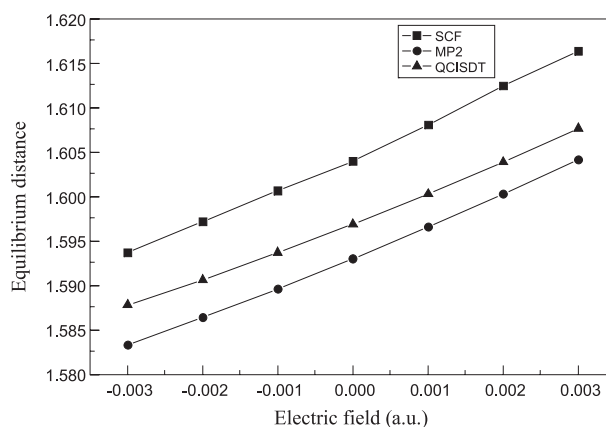
Ref. 21. $\mu = 2.29$; Ref. 24. $\mu = 2.31$; Ref. 25. $\alpha_{xx}^e = 21.9$; Ref. 27. $\alpha_{zz}^e = 26.99$; $\alpha_{xx}^e = 25.29$

not negligible for this property. The difference between SCF and QCISD(T) results amounts to 15% for both components. Our results are again in good agreement with those of Sadlej and Urban²¹, McCullough²⁶, Papadopoulos *et al.*⁹, and Lazzarotti *et al.*²⁷.

One finds in the literature a number of calculated first hyperpolarizability at SCF level, which are not in agreement with them^{9,26}. Our SCF results for β_{zzz}^e and β_{xxx}^e are in good agreement with Lazzarotti *et al.*²⁷ results. The accuracy of our results is supported by the use of an extensive basis set which has been carefully selected. Correlation effects are of fundamental importance for the calculation of β , as SCF results are *ca.* half of QCISD(T) results. This finding has been also obtained by Papadopoulos *et al.*⁹, indicating that electronic correlation contribution is increasingly more important for higher order coefficients in the energy expansion. It is clear that contributions from triple substitutions are negligible by comparing SDQ-MBPT(4) and MBPT(4) or QCISD and QCISD(T) values. Conversely, single substitutions are relevant. As single substitutions are more appropriately included in the QCISD method than in the CCD+ST(CCD) one, we consider that results obtained within the QCISD(T) approximation are our best values for the properties studied here. The small difference between DQ-MBPT(4), CCD, and CID results indicates that contributions beyond fourth-order, arising from double substitutions, do not affect significantly these properties. Finally, it is worth mentioning that contrary to dipole polarizabilities, the perpendicular component of the first hyperpolarizability is smaller than the parallel component. In fact, the β_{xxx}^e value is *ca.* 50% of the β_{zzz}^e value.

Table 3. Calculated polarizability and first hyperpolarizability of LiH (in *a.u.*) together with electronic and vibrational contributions

| Method | α_{zz}^e | α_{zz}^v | α_{zz} | β_{zzz}^e | β_{zzz}^v | β_{zzz} | β_{xxx}^e | β_{xxx}^v | β_{xxx} |
|-------------|-----------------|-----------------|---------------|-----------------|-----------------|---------------|-----------------|-----------------|---------------|
| SCF | 22.02 | 3.61 | 25.63 | 315 | -250 | 65 | 173 | -55 | 118 |
| MBPT(2) | 23.52 | 3.08 | 26.60 | 438 | -346 | 92 | 230 | -52 | 178 |
| MBPT(3) | 24.31 | 2.95 | 27.26 | 479 | -348 | 131 | 252 | -52 | 200 |
| DQ-MBPT(4) | 24.83 | 2.89 | 27.72 | 513 | -353 | 160 | 265 | -52 | 213 |
| MBPT(4) | 24.95 | 2.88 | 27.81 | 526 | -353 | 173 | 271 | -54 | 217 |
| CID | 24.94 | 2.87 | 27.84 | 517 | -354 | 163 | 269 | -54 | 215 |
| CISD | 25.57 | 2.77 | 28.34 | 593 | -358 | 237 | 301 | -56 | 245 |
| QCISD | 26.00 | 2.73 | 28.73 | 693 | -364 | 329 | 307 | -56 | 251 |
| QCISD(T) | 26.06 | 2.71 | 28.77 | 700 | -363 | 337 | 309 | -56 | 253 |
| CCD | 25.17 | 2.87 | 28.04 | 534 | -361 | 173 | 275 | -52 | 223 |
| CCD+ST(CCD) | 25.56 | 2.80 | 28.36 | 577 | -361 | 216 | 293 | -56 | 237 |

**Figure 1.** Equilibrium distance of the LiH molecules versus electric field calculated at different levels of theory

We now turn the discussion to the vibrational contribution on the calculated properties, which is the main purpose of this work. In order to calculate the vibrational contribution, the equilibrium geometry was optimized at all levels of calculation and for each value of the applied electric field. In order to illustrate the changes in the geometry, Fig.1 shows the optimized geometry versus E_z at SCF, MBPT(2), and QCISD(T) levels of theory. As expected, test calculations indicated that the geometry is not affected by the presence of an electric field in the perpendicular direction. The results for the vibrational contribution, the previously calculated electronic contribution (for comparison), and the total values of α_{zz} , β_{zzz} and β_{xxx} are listed in Table 3, in which the superscript “e” and “v” stand for the electronic and the vibrational contributions, respectively. The absence of superscripts means the total value.

It is clear from Table 3 that the vibrational contribution for dipole moment and α_{xx} component of the polarizability are null. For the parallel component of dipole polarizability, the vibrational contribution decreases with the inclusion of electronic correlation, whereas the electronic contribution increases. In this way, the relative importance of the vibrational contribution for the total polarizability diminishes with the inclusion of electronic correlation. At the SCF level, this contribution is 14%, whereas it is *ca.*10% at the QCISD(T) level. Table 3 shows that the vibrational contribution for the first dipole hyperpolarizability is of fundamental importance at all levels of calculation. It should be noted that vibrational contribution have opposite sign to electronic contribution, for both components. Concerning the β_{zzz} component, it can be seen that both contributions increase with the inclusion of electronic correlation, but the rate of increase is less remarkable for the vibrational contribution. For the electronic contribution, the SCF value

Table 4. Total and the electronic contribution of the mean and anisotropic polarizabilities of LiH (in a.u.)

| Method | $\bar{\alpha}^e$ | $\bar{\alpha}$ | $\Delta\alpha^e$ | $\Delta\alpha$ | $\bar{\beta}^e$ | $\bar{\beta}$ | $\Delta\beta^e$ | $\Delta\beta$ |
|-------------|------------------|----------------|------------------|----------------|-----------------|---------------|-----------------|---------------|
| SCF | 24.31 | 25.51 | -3.43 | 0.18 | 397 | 181 | -204 | -289 |
| MBPT(2) | 25.98 | 27.01 | -3.69 | -0.61 | 539 | 269 | -252 | -442 |
| MBPT(3) | 26.95 | 27.93 | -3.96 | -1.01 | 590 | 319 | -277 | -469 |
| MBPT(4) | 27.63 | 28.58 | -4.02 | -0.16 | 641 | 364 | -287 | -678 |
| CID | 25.67 | 28.62 | -4.09 | -1.22 | 633 | 356 | -290 | -482 |
| CISD | 28.23 | 29.15 | -3.99 | -1.22 | 717 | 436 | -310 | -498 |
| QCISD | 28.67 | 29.58 | -4.01 | -1.28 | 784 | 499 | -228 | -424 |
| QCISD(T) | 28.71 | 29.62 | -3.98 | -1.27 | 791 | 506 | -227 | -422 |
| CCD+ST(CCD) | 28.29 | 29.23 | -4.10 | -1.30 | 698 | 414 | -302 | -495 |

corresponds to only 45% of our best value obtained at the QCISD(T) level, while the MBPT(2) value corresponds to 63%. For the vibrational contribution, the SCF value corresponds to 69% while the MBPT(2) value corresponds to 95% of the QCISD(T) value. For the β_{xxz} component, our results show that the vibrational contribution is practically independent of the level of approximation.

In addition to α_{zz} , α_{xx} , β_{zzz} and β_{xxz} components of polarizabilities, we show in Table 4 the mean polarizabilities, given by:

$$\bar{\alpha} = \frac{1}{3}(\alpha_{zz} + 2\alpha_{xx})$$

$$\bar{\beta} = \frac{3}{5}(\beta_{zzz} + 2\beta_{xxz})$$

and the anisotropies, defined as

$$\Delta\alpha = \alpha_{zz} - \alpha_{xx}$$

$$\Delta\beta = \beta_{zzz} - 3\beta_{xxz}$$

Interestingly, Table 4 shows that inclusion of vibrational contribution decreases the magnitude of anisotropy of the dipole polarizability.

CONCLUSIONS

The results obtained in this work indicate that inclusion of the effect of nuclear repositioning due to the presence of an applied electric field, called in this paper the vibrational contribution, turn to be of fundamental importance to the calculation of dipole polarizability and hyperpolarizability of the LiH molecule. The same conclusion should stand for any molecule which has ionic character. In case of LiH, inclusion of electronic correlation changes significantly calculated values of α_{zz}^v , β_{zzz}^v and β_{xxz}^v . Convergence of calculated values for vibrational contributions, with respect to different levels of approximation, is more systematic than for the corresponding electronic values.

The results obtained for the electronic contribution show small differences between the QCISD, QCISD(T) and CCD+ST(CCD) values, which demonstrate that the quadratic configuration interaction (QCI) scheme provides an appropriate description of single and double substitutions for this system and that near-degeneracy effects are negligible. Considering that the contributions of the triple substitutions are relatively small, specially when calculated by means of the QCI scheme, we expect, even in the absence of experimental results for comparison, that the values obtained using the QCISD(T) approach should be in close agreement with the exact figure.

Finally this paper confirm the statement that an appropriate treatment of the electron correlation is of fundamental importance in order to obtain accurate estimates for the electronic contributions to dipole moments, polarizabilities and hyperpolarizabilities by the molecule ionic character. Our results allow us to state, in addition, that the electron correlation effects are also essential to the evaluation of the vibrational corrections.

ACKNOWLEDGMENTS

This work was supported by CNPq and Fapesp. The computational facilities of LCCA-USP is acknowledged.

REFERENCES

- Buckingham, A. D.; *Adv. Chem. Phys.* **1967**, *12*, 107.
- Archibong, E. F.; Thakkar, A. J.; *Phys. Rev. A: At., Mol., Opt. Phys.* **1991**, *44*, 5478.
- Castro, M. A.; Canuto, S.; *J. Phys. B: At., Mol. Opt. Phys.* **1993**, *26*, 4301.
- Urban, M.; Cernusak, I.; Kello, V.; Noga, J. In *Methods in Computational Chemistry*; Wilson, S., ed.; Plenum New York, 1987, vol. 1.
- Dykstra, C. E.; *Ab Initio Calculations of the Structure of Properties of Molecules*, Elsevier: Amsterdam, 1988.
- Cohen, M. J.; Willets, A.; Amos, R. D.; Handy, N. C.; *J. Chem. Phys.* **1994**, *100*, 4467.
- Kirtman, B.; Bishop, D. M.; *Chem. Phys. Lett.* **1990**, *175*, 601.
- Bishop, D. M.; Kirtman, B.; *J. Chem. Phys.* **1992**, *97*, 5255.
- Papadopoulos, M. G.; Willets, A.; Handy, N. C.; Underhill, A. E.; *Mol. Phys.* **1996**, *88*, 1063.
- Maroulis, G.; *J. Phys. Chem.* **1996**, *100*, 13466.
- Medeiros, R.; Castro, M. A.; Amaral, O. A. V.; *Phys. Rev. A: At., Mol., Opt. Phys.* **1996**, *45*, 3661.
- Szabo, A.; Ostlund, N. S.; *Modern Quantum Chemistry*, Macmillan: New York, 1984.
- Bartlett, R. J.; *Annu. Rev. Phys. Chem.* **1981**, *32*, 359.
- Jørgensen, P.; Simons, J., *Second Quantization-Based Methods in quantum Chemistry*, Academic Press: New York, 1981.
- Raghavashari, K.; *J. Chem. Phys.* **1995**, *82*, 4607.
- Raghavashari, K.; *J. Chem. Phys.* **1995**, *82*, 4142.
- Pople, J. A.; Head-Gordon, M.; Raghavashari, K.; *J. Chem. Phys.* **1990**, *87*, 5968.
- Lee, T. J.; Rendell, A. P.; Taylor, P. R.; *J. Phys. Chem.* **1995**, *94*, 5463.
- Sadlej, A. J.; *Collect. Czech. Chem. Commun.* **1998**, *53*, 1995.
- Chong, D. P.; Langhoff, S. R.; *J. Phys. Chem.* **1990**, *93*, 570.
- Sadlej, A. J.; Urban, M.; *J. Mol. Struct.* **1990**, *234*, 147.
- MacLean, A. D.; Yoshimine, M.; *J. Chem. Phys.* **1967**, *47*, 1927.
- Gaussian 94*; Frisch, M. J.; et al.; Gaussian, Inc., Pittsburgh PA, 1995.
- Rothstein, E.; *J. Chem. Phys.* **1969**, *50*, 1899.
- Roos, B. O.; Sadlej, A. J.; *Chem. Phys.* **1991**, *94*, 43.
- McCullough, E. A.; *J. Chem. Phys.* **1975**, *63*, 5050.
- Lazzeretti, P.; Rossi, E.; Zanasi, R.; *J. Phys. B: At., Mol. Opt. Phys.* **1982**, *15*, 521.