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Electrooptical Properties and Molecular Polarization of Iodine, I_2

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Experimental and theoretical efforts are combined to determine a reliable value of the static dipole polarizability of I_2. The experimental estimate of the mean dipole polarizability is $\alpha = 69.7 \pm 1.8 e^2a_0^2E_h^{-1}$. The polarizability of the iodine atom has also been deduced from experimental measurements and is estimated at $32.9 \pm 1.3 e^2a_0^2E_h^{-1}$. Accurate ab initio calculations predict $\alpha = 70.9 \pm 1.4 e^2a_0^2E_h^{-1}$ and for the anisotropy $\Delta\alpha = 41.2 \pm 0.8 e^2a_0^2E_h^{-1}$. The deformation of the iodine molecule in the presence of general static fields has been studied and analyzed.

Introduction

Electric multipole moments and polarizabilities are fundamental properties of atoms and molecules. The accurate description of the polarization of a molecule interacting with an electric field represents the cornerstone of the rational approach to a wide range of phenomena. These include nonlinear optical phenomena,[1,2] various phenomena induced by intermolecular interactions[3,4] and electron scattering.[5] The knowledge of accurate electric moments and polarizabilities is presently highly desirable as they find application in various models predicting the structure and properties of weakly bonded van der Waals molecules.[6,7] One should emphasize the importance of polarizability in various fields of interest for general chemistry: in studies of relative gas-phase acidities and basicities,[8,9] the study of hardness/softness,[10] the relationship between atomic polarizability and electronegativity,[11] the relationship of hardness with polarizability and the dipole moment[12] and the study of hydrogen-bonding capabilities in peptides.[13] Last, the study of molecular polarizability supports actively the efforts directed toward the synthesis of new molecules with enhanced nonlinear optical properties.[14,15] Understandably, the determination of electric moments and polarizabilities constitutes a very active research field.[16−20]

There is currently a renewed interest in the physicochemical behavior of iodine. Recent efforts include a study of the I_2−Ne van der Waals system,[21] the study of I_2 in solid Kr,[22] and I_2 in rare-gas solvents[23] as well as detailed spectroscopic investigations of I_2[24] which are helpful for realizing frequency standards. Moreover, the study of the collisional shift and broadening of iodine spectral lines in air by Fletcher and McDaniel[25] brought forth the need for accurate dipole polarizability values for this molecules. In this work we combine experimental and theoretical efforts to obtain an accurate estimate of the static mean dipole polarizability. Our efforts extend to the description of the polarizability curve around the experimental equilibrium bond length and the study of the molecular polarization in the presence of a general static electric field.

Experimental Work and Results

The interferometric experiments are performed with an evacuated Michelson twin interferometer, which has been used before for the determination of the electrooptical properties of NO_2/N_2O_4,[26] Zn,[27] Cd,[28] and Hg.[29] We measured the complex refractive index $\hat{n}(\sigma,p,T) = n(\sigma) - ia(\sigma)/(4\pi\sigma)$ ($\sigma = 1/\lambda =$ wavenumber, $a(\sigma) =$ absorption coefficient of Lambert−Beer's law) at three discrete wavenumbers $\sigma_1 = 15\,798.0$ cm^{-1}, $\sigma_2 = 16\,832.3$ cm^{-1}, and $\sigma_3 = 30\,756.9$ cm^{-1}, using laser as radiation sources. Additionally, we have applied dispersive Fourier transform spectroscopy in order to obtain $\hat{n}(\sigma,p,T)$ in the wavenumber range between 11 500 and 17 500 cm^{-1} with a resolution of about 7 cm^{-1}, using a 100 W halogen lamp as white-light source.

$\hat{n}(\sigma,p,T)$ is analyzed according to the complex Lorenz−Lorentz formula,[30] yielding the frequency-dependent polarizability $\alpha(\sigma)$ as well as the absorption coefficent $a(\sigma)$. $a(\sigma)$ is in very good accordance with an absorption spectrum of similar resolution given by Capelle and Broida,[31] and the vibrational structure of the B $^3\Pi_u^+ \leftarrow$ X $^1\Sigma_g^+$ transition is exactly reproduced. The main purpose, however, is the determination of $\alpha(\sigma)$, where our measurements yield $\alpha(\sigma_1) = 86.8 \pm 2.2$, $\alpha(\sigma_2) = 93.6 \pm 3.4$, and $\alpha(\sigma_3) = 95.3 \pm 1.9$ (all in au).

The quasi-continuous spectrum of $\alpha(\sigma)$ of I_2 in the experimentally accessible σ-range is shown in Figure 1 (full curve). One can recognize the vibrational energy spacing of the B state of iodine in this *polarizability* spectrum, too. This feature has never been observed experimentally up to now in a broad wavenumber range. To obtain the static value of the dipole polarizability, $\alpha(0)$, we have fitted the global shape of our recorded polarizability spectrum to a two-term Kramers−Heisenberg dispersion relation, which disregards the vibrational fine-structure measured in our $\alpha(\sigma)$ spectrum. However, we make allowance for the strong absorption in the visible by including radiation damping:

$$\alpha(\sigma) = \left(\frac{E_h}{hc}\right)^2 \left[\frac{f_1({\sigma_{01}}^2 - \sigma^2)}{({\sigma_{01}}^2 - \sigma^2)^2 + (\Gamma_1\sigma)^2} + \frac{f_2}{{\sigma_{02}}^2 - \sigma^2}\right] \quad (1)$$

h and *c* are Planck's constant and the speed of light in vacuum, respectively. A nonlinear fit yields the effective transition

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TABLE 1: All-Electron, Self-Consistent Field Electric Moments and Dipole Polarizability for I_2 at the Equilibrium Internuclear Separation of $R_e = 2.6663$ (z Is the Molecular Axis, All Values in au)

basis	description	CGTF	Θ	Φ	α_{zz}	α_{xx}	α	$\Delta\alpha$
B1.0	[6s5p3d]	72	5.7116	269.1395	98.059	52.779	67.872	45.280
B1.1	[6s5p4d]	82	5.7463	267.0947	95.185	51.988	66.387	43.197
B1.2	[6s5p4d1f]	96	4.9700	238.0947	97.550	52.000	67.183	45.550
B1.3	[6s5p4d2f]	110	4.6148	230.4760	97.281	52.288	67.286	44.993
B1.4	[7s6p5d3f]	142	4.6001	227.3421	98.503	53.183	68.290	45.320
B2.0	[11s9p5d]	126	5.6479	270.8061	100.859	54.113	69.695	46.746
B2.1	[11s9p6d]	136	5.5905	272.7717	98.990	54.491	69.324	44.499
B2.2	[11s9p6d2f]	164	4.5897	233.5639	99.737	54.206	69.383	45.531
B2.3	[12s10p7d3f]	196	4.6111	236.4921	100.169	54.861	69.964	45.308
B3.0	[20s15p12d]	250	5.1435	267.3543	100.202	54.916	70.011	45.287
B3.1	[20s15p12d4f]	306	4.5502	243.3477	100.040	55.020	70.027	45.020
B3.2	[21s16p13d5f]	338	4.5498	243.7242	100.063	55.049	70.054	45.013

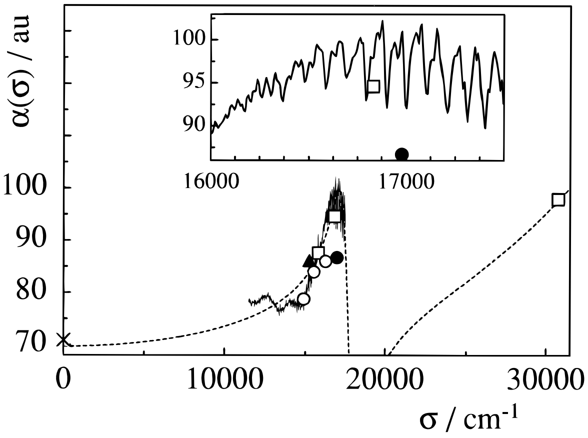

Figure 1. Experimentally determined dispersion of $\alpha(\sigma)$ of I_2 (full curve and □, this work; ○, ref 52; ●, ref 53; ▲, ref 51). The dashed curve is fitted according to eq 1. × best ab initio value, this work. The insert shows the vibrational structure of the polarizability due to the B ${}^3\Pi_u^+ \leftarrow X\ {}^1\Sigma_g^+$ transition in more detail.

wavenumbers $\sigma_{01} = 1.7680 \pm 0.0021$ and $\sigma_{02} = 5.379 \pm 0.046$ (both in 10^4 cm^{-1}), the corresponding oscillator strengths $f_1 = 0.020\,00 \pm 0.000\,88$ and $f_2 = 4.003 \pm 0.087$, and the radiation damping constant $\Gamma_1 = (1.111 \pm 0.046) \times 10^3$ cm^{-1}. Interestingly, σ_{01} corresponds very well to the absorption maximum in the visible, whereas σ_{02} is located in between the continuous absorption band of the $D\ {}^1\Sigma_u^+ \leftarrow X\ {}^1\Sigma_g^+$ transition of iodine (Cordes bands[32,33]). However, f_1 is about twice the value given by Mulliken[33] (0.0121). Equation 1 gives a static limit of $\alpha = \alpha(\sigma \rightarrow 0) = 69.7 \pm 1.8$ au, which can considered to be the first experimentally determined static dipole polarizability of molecular iodine.

Theory and ab Initio Calculations

For a linear centrosymmetric molecule, as I_2, all electric moments have only one independent component (with z as the molecular axis, these are chosen to be Θ_{zz} and Φ_{zzzz} or just Θ (quadrupole moment) and Φ (hexadecapole moment) hereafter) and the dipole polarizability tensor $\alpha_{\alpha\beta}$ is specified by α_{xx} and α_{zz}.[34] The mean dipole polarizability and the anisotropy are then defined as $\alpha = (\alpha_{zz} + 2\alpha_{xx})/3$ and $\Delta\alpha = \alpha_{zz} - \alpha_{xx}$. We have used three groups of basis sets of Gaussian-type functions (GTF) in the ab initio study presented in this work (see Table 1): B1,[35] B2,[35] and B3.[36] The largest basis set is B3.2 or [21s16p13d5f] in contracted form, consisting of 338 GTF and yielding a self-consistent field (SCF) energy of $-13835.999827E_h$. All SCF values are given in Table 1, in atomic units[37] (au). We expect these values to have converged closer than 1% to the Hartree−Fock limit for all properties.

Electron correlation effects on the dipole polarizability were obtained via many-body perturbation theory (MP)[38] and coupled cluster theory (CCSD, or single and double excitations CC and CCSD(T) which includes an estimate of connected triple excitations by a perturbational treatment).[39] CCSD(T) calculations were performed with basis B1.1 at the equilibrium geometry,[40] R_e, MP2 calculations with B2.2 at R_e and eight other bond lengths around R_e. All calculations were performed with the GAUSSIAN 92 set of programs.[41] The results are in Table 2. We have also obtained the shape of the polarizability curves around R_e from MP2 calculations with basis B2.2. The mean and anisotropy were found to vary as

TABLE 2: Electron Correlation Effects on the Dipole Polarizability of I_2 at R_e (in au)

method	α_{zz}	α_{xx}	α	$\Delta\alpha$
	Basis set **B1.1** [6s5p4d][a]			
SCF	95.19	51.99	66.39	43.20
MP2	94.47	53.15	66.93	41.32
MP3	93.92	53.18	66.76	40.74
MP4	94.17	53.55	67.09	40.62
CCSD	94.22	53.28	66.93	40.93
CCSD(T)	94.22	53.60	67.14	40.63
	Basis set **B2.3** [11s9p6d2f][b]			
SCF	99.74	54.21	69.38	45.53
MP2	98.11	55.79	69.90	42.32

[a] The 36 innermost orbitals were kept frozen in electron correlation calculations. [b] In the MP2 calculations the 36 innermost orbitals were kept frozen and exctitations were not allowed to the 28 highest virtual ones.

$$\alpha(R) = 69.90 + 11.64(R - R_e) + 1.95(R - R_e)^2 - 1.45(R - R_e)^3 - 0.45(R - R_e)^4$$

$$\Delta\alpha(R) = 42.35 + 21.09(R - R_e) + 6.80(R - R_e)^2 - 3.52(R - R_e)^3 - 1.66(R - R_e)^4$$

From these curves and experimental spectroscopic constants[40] we obtained α, $\Delta\alpha$, in the vJ rovibrational state[42] as

$$(vJ|\alpha|vJ) = 69.90 + 0.1371(v + {}^1/_2) + 0.000007J(J + 1)$$

$$(vJ|\Delta\alpha|vJ) = 42.35 + 0.2774(v + {}^1/_2) + 0.000013J(J + 1)$$

We combine all the aforementioned data to estimate the static limit of α and $\Delta\alpha$ at the ground vibrational state. The electron correlation correction to α is small. Comparing the MP2 values for B1.1 and B2.3 we see that 0.8 au is a very conservative estimate of the correction. The zero-point vibrational correction for α is 0.07 au. Our best SCF value (B3.2) is 70.054 au. In total, adding the above corrections, we advance a theoretical estimate of $\alpha = 70.9 \pm 1.4$ au (an uncertainty of 2%). We follow a similar line of reasoning for $\Delta\alpha$. For B1.1 the CCSD-

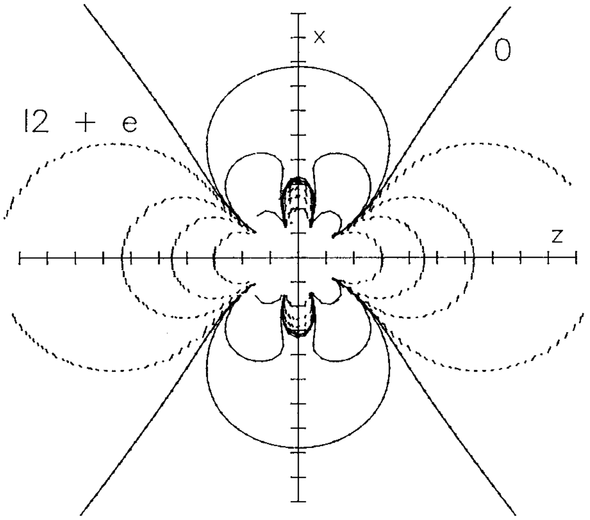

Figure 2. Electrostatic interaction energy between an electron and I_2 (the molecule on the z axis).The zero contour is explicitly marked. The solid contours correspond to interaction energies of 0.0005, 0.002, and $0.05E_h$ in increasing distance from the molecule. The dashed contours correspond to −0.05, −0.01, −0.003, and −0.0005 E_h in order of increasing z distance from the origin. The unit of length is $2a_0$ on either axis.

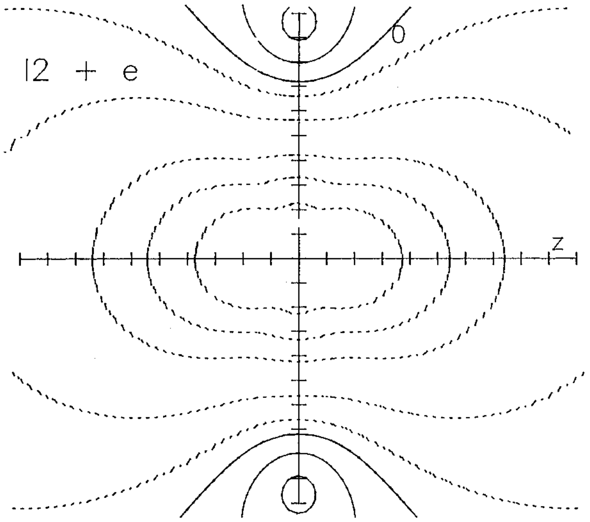

Figure 3. Total interaction energy between an electron and I_2 (the molecule on the z axis).The zero contour is explicitly marked. The solid contours correspond to interaction energies of 0.00006 and $0.000085E_h$ in order of increaing x distance. The dashed contours correspond to −0.05, −0.01, −0.003, −0.0005, and −0.0001 E_h in order of increasing x distance from the origin. The unit of length is $2a_0$ on either axis.

(T) value for this property is 0.7 au lower than the MP2 one. This means that given the B2.3 correction of −3.2 au, we should expect the true effect to be ≈−4.0 au. Adding this and vibrational correction of 0.14 au to the SCF B2.3 value of 45.013 au, we obtained $\Delta\alpha = 41.2 \pm 0.8$ au (an uncertainty of 2%).

Molecular Polarization. We relied on the present SCF values of Θ, Φ, α_{zz}, and α_{xx} and higher polarizabilities from previous work[43] to obtain polarization maps of I_2 interacting with the general static electric field of an electron or a proton.[44] The interaction energy ΔE is decomposed into an electrostatic (E_{est}, due to the electric moments) and an inductive (E_{ind}, due to the electric polarizability) part, $\Delta E = E_{\mathrm{est}} + E_{\mathrm{ind}}$. These 2D maps[45] provide valuable information about the distribution of electronic charge in the molecule. In Figure 2 shows the electrostatic interaction of I_2 with an electron. Figures 3 and 4 show the total interaction for $I_2 \cdots e^-$ and $I_2 \cdots H^+$. As iodine is a very soft molecule, the $I_2 \cdots e^-$ interaction is attractive in a large area around I_2 and becomes repulsive at distances $>14a_0$ on the x axis. The $I_2 \cdots H^+$ interaction becomes repulsive for the proton around the z axis, at distances $>10a_0$ with a maximum at $\approx 14a_0$.

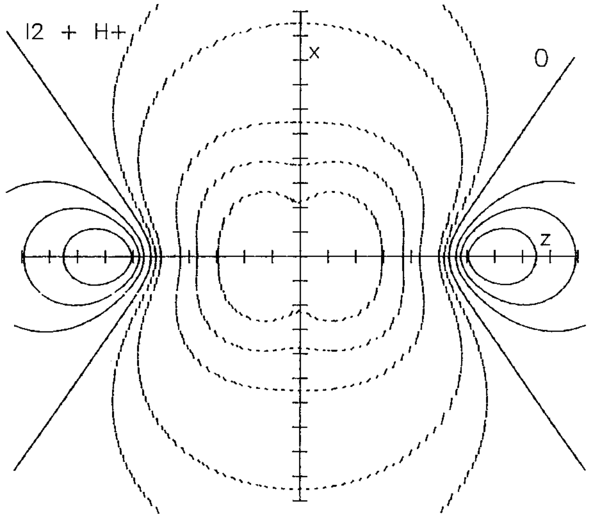

Figure 4. Total interaction energy between a proton and I_2 (the molecule on the z axis).The zero contour is explicitly marked. The solid contours correspond to interaction energies of 0.0002, 0.0003, and $0.0004E_h$ in order of increaing z distance. The dashed contours correspond to −0.05, −0.01, −0.003, −0.0005, and $-0.0002E_h$ in order of increasing z distance from the origin. The unit of length is $2a_0$ on either axis.

TABLE 3: Comparison of Theory and Experiment

method	α /au	$\Delta\alpha$ /au
	Theory	
SDQ-MP4[a]	69.33	42.10
MP2[b]	69.81	42.15
present estimate	70.9 ± 1.4	41.2 ± 0.8
	Experiment	
	69.7 ± 1.8[c]	45.1 ± 2.3[d]

[a] MP4 with single, double, and quadruple excitations.[43] [b] Reference 46. [c] Present investigation, see text. [d] Reference 47.

Discussion

Experiment and theory are compared in Table 3. The present experimental value (static limit) of $\alpha = 69.7 \pm 1.8$ au is quite close to the theoretical estimate of 70.9 ± 1.4 au. Our theoretical values agree well with previous efforts. It appears now that theory predicts $\Delta\alpha$ systematically lower than the only available experimental value.[47] The conservative uncertainty of the latter 45.1 ± 2.3 au, if taken into account, bridges the discrepancy with the present estimate of 41.2 ± 0.8 au.

It should be mentioned that we have not considered relativistic effects. Kellö and Sadlej[48] found that the relativistic correction lowers the value of α_{zz} of HI from 38.15 to 37.84 au. The same property is reduced from 69.0 to 68.2 au for ICN.[49] In both cases the effect is smaller than the uncertainty, admittedly a conservative one, adopted here.

An estimate of the polarizability of atomic iodine shall conclude the discussion. We have observed the linear relationship $D/\mathrm{J\ mol^{-1}} = (561 \pm 25) \times 10^3 + (1.06 \pm 0.37) \times 10^5 \delta\alpha$ between the bond dissociation energy D and the change in polarizability $\delta\alpha = \sum_P \alpha_P - \alpha_R$ (in au) in the course of a chemical reaction[50] like $A_mB_n \rightarrow mA + nB$. Here, α_P denotes the polarizability of the products A or B, respectively, whereas α_R is the polarizability of the reactant A_mB_n. Using our experimentally determined polarizability of $\alpha_{I_2}(0) = 69.7 \pm 1.8$

au and the bond dissociation energy of iodine of $D = 152.532$ kJ mol^{-1}, a polarizability of atomic iodine of $\alpha_I(0) = 32.9 \pm 1.3$ au is obtained. This is in very good accordance with an approximation based on experimental results given by Braun and Hölemann[51] of $\alpha_I(0) = 33.4$ au.

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References and Notes

(1) Hanna, D. C; Yuratich, M. A.; Cotter, D. *Nonlinear optics of atoms and molecules*; Springer: Berlin, 1979.

(2) Shen, Y. R. *Principles of nonlinear optics*; Wiley: New York, 1984.

(3) Birnbaum, G., Ed. *Phenomena induced by intermolecular interactions*; Plenum: New York, 1985.

(4) Tabisz, G., Neumann, M. N., Eds. *Collision- and Interaction-Induced Spectroscopy*; Kluwer: Dordrecht, 1995.

(5) Lane, N. F. *Rev. Mod. Phys.* **1980**, *52*, 29.

(6) Dykstra, C. E. *J. Am. Chem. Soc.* **1990**, *112*, 7540.

(7) Dykstra, C. E. *Chem. Rev.* **1993**, *93*, 2339.

(8) Hehre, W. J.; Pau, C. F.; Headley, A. D.; Taft, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 1711.

(9) Headley, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 2347.

(10) Vela, A.; Gázquez, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 1490.

(11) Nagle, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 4741.

(12) Pal, S; Chandra, A. K. *J. Phys. Chem.* **1995**, *99*, 13865.

(13) Nilar, S. H.; Pluta, T. S. *J. Am. Chem. Soc.* **1996**, *117*, 12603.

(14) Lecours, S. M.; Guan, H. W.; Dimagno, S. G.; Wang, C. H.; Therien, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 1497.

(15) Priyadarshy, S.; Therien, M. J.; Beratan, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 1504.

(16) Gierke, T. D.; Tigelaar, H. L.; Flygare, W. H. *J. Am. Chem. Soc.* **1972**, *94*, 330.

(17) Miller, K. J. *J. Am. Chem. Soc.* **1990**, *112*, 8533.

(18) Miller, K. J. *J. Am. Chem. Soc.* **1990**, *112*, 8543.

(19) Stout, J. M.; Dykstra, C. E. *J. Am. Chem. Soc.* **1995**, *117*, 5129.

(20) Liu, S. Y.; Dykstra, C. E. *J. Phys. Chem.* **1987**, *91*, 1749.

(21) Garcia-Vela, A. *J. Chem. Phys.* **1996**, *104*, 1047.

(22) Sterling, M.; Zadoyan, R.; Apkarian, V. A. *J. Chem. Phys.* **1996**, *104*, 6497.

(23) Ben-Nun, M.; Levine, R. D. *Chem. Phys.* **1995**, *201*, 163.

(24) Appadoo, D. R. T.; LeRoy, R. J.; Bernath, P. F.; Gerstenkorn, S.; Luc, P.; Verges, J.; Sinzelle, J.; Chevillard, J.; D'Aignaux, Y. *J. Chem. Phys.* **1996**, *104*, 903.

(25) Fletcher, D. G.; McDaniel, J. C. *J. Quant. Spectrosc. Radiat. Transfer* **1995**, *54*, 837.

(26) Goebel, D.; Hohm, U.; Kerl, K.; Trümper, U.; Maroulis, G. *J. Phys. Chem.* **1994**, *98*, 13123.

(27) Goebel, D.; Hohm, U.; Maroulis, G. *Phys. Rev. A* **1996**, *54*, 1973.

(28) Goebel, D.; Hohm, U. *Phys. Rev. A* **1995**, *52*, 3691.

(29) Goebel, D.; Hohm, U. *J. Phys. Chem.* **1996**, *100*, 7710.

(30) Born, M. *Optik*; Springer: New York, 1985; p 479.

(31) Capelle, G. A.; Broida, H. P. *J. Chem. Phys.* **1973**, *58*, 4212.

(32) Okabe, H. *Photochemistry of Small Molecules*; John Wiley & Sons: New York, 1979; p 187.

(33) Mulliken, R. S. *J. Chem.Phys.* **1971**, *55*, 288.

(34) Buckingham, A. D. *Adv. Chem. Phys.* **1967**, *12*, 107.

(35) From: Poirier, R.; Kari, R.; Csizmadia, I. G. *Handbook of Gaussian basis sets*; Elsevier: Amsterdam, 1985. The B1 group is built upon the 53.3.1 basis of the collection or [5s4p2d] augmented with diffuse 1s1p-GTF and one d-GTF with exponent chosen to maximize the mean polarizability α. The B2 group is built upon the 53.1.1 set or [10s8p4d] + 1s1p-GTF (diffuse) and one d-GTF with the exponent chosen in the same way. The B2.3 set contains additional 1s1p1d-GTF (diffuse). Further details available from the authors.

(36) Partridge, H.; Faegri, K., Jr. *High quality Guassian basis sets for fourth-row atoms*; NASA Technical Memorandum 103918, March 1992. An intial primitive basis (24s19p13d) contracted to [19s14p10d] and augmented by 1s1p2d-GTF (diffuse) gave B3.0. The final B3.2 contains additional diffuse 1s1p1d-GTF. Further details available from the authors.

(37) Conversion factors to SI units: energy, $1E_h = 4.359\,748\,2 \times 10^{-18}$ J, length, $1a_0 = 0.529\,177\,249 \times 10^{-10}$ m, Θ, $1ea_0{}^2 = 4.486\,554 \times 10^{-40}$ C m^2, Φ, $1ea_0{}^4 = 1.256\,363 \times 10^{-60}$ C m^4 and α, $1e^2a_0{}^2E_h{}^{-1} = 1.648\,778 \times 10^{-41}$ C^2 m^2 J^{-1}.

(38) Urban, M.; Cernusak, I.; Kellö, V.; Noga, *J. Methods Comput. Chem.* **1987**, *1*, 117 where the definition of the various orders MPn is also to be found.

(39) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1987**, *157*, 479.

(40) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure IV*; Van Nostrand-Reinhold: New York, 1979.

(41) Frisch,M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B,; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92 (Revision C)*, Carnegie-Mellon Quantum Chemistry Publishing Unit, 1992.

(42) Buckingham, A. D. *J. Chem. Phys.* **1962**, *36*, 3096.

(43) Maroulis, G.; Thakkar, A. J. *Mol. Phys.* **1991**, *73*, 1235.

(44) Bishop, D. M.; Maroulis, G. *J. Chem. Phys.* **1985**, *82*, 2380.

(45) Giannopoulos, G.; Haritos, C.; Maroulis, G. *MOL-Q (Version 1.5) A program for the study and graphical presentation of the interaction of molecules with electric charges*; Department of Chemistry, University of Patras, 1992.

(46) Dougherty, J.; Spackman, M. A. *Mol. Phys* **1994**, *82*, 193.

(47) Callahan, D. W.; Jokozeki, A.; Muenter, J. S. *J. Chem. Phys.* **1980**, *72*, 4791.

(48) Kellö, V.; Sadlej, A. J. *J. Chem. Phys.* **1990**, *93*, 8122.

(49) Kellö, V.; Sadlej, A. J. *Mol. Phys.* **1992**, *75*, 209.

(50) Hohm, U. *J. Chem. Phys.* **1994**, *101*, 6362.

(51) Braun, A.; Hölemann, P. *Z. Phys. Chem.* **1936**, *B 34*, 357.

(52) Cuthbertson, C; Cuthbertson, M. *Proc. R. Soc. London* **1910**, *A88*, 13.

(53) Larsson, R.; Folkensson, B. *J. Electron. Spectrosc. Relat. Phenom.* **1990**, *50*, 251.