(11) Scalan, M. J.; Hiller, I. H.; Davis, R. H. *J. Chem. Soc., Chem. Commun.* **1982**, 685.
(12) Scanlan, M. J.; Hiller, I. H.; McDowell, A. A. *J. Am. Chem. Soc.* **1983**, *105*, 3569.
(13) Schlegel, H. B.; Gund, P.; Fluder, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 5347.
(14) Takeuchi, Y.; Dennis, N. *Org. Magn. Reson.* **1975**, *7*, 244.
(15) Vitorge, M. C.; Chenon, M. T.; Coupry, C.; Lumbroso-Bader, N. *Org. Magn. Reson.* **1983**, *21*, 20.
(16) Fayet, J. P.; Vertut, M. C.; Cativiela, C.; Melendez, E.; Elguero, J. *Bull. Soc. Chim. Fr.* **1984**, 233.
(17) Brügel, W. *Handbook of NMR Spectral Parameters*; Heyden: London, 1979.
(18) Gil, V. M. S.; von Philipsborn, W. *Magn. Reson. Chem.* **1989**, *27*, 409.
(19) Vögeli, V.; Herz, D.; von Philipsborn, W. *Org. Magn. Reson.* **1980**, *12*, 200.
(20) Tobias, S.; Günther, H. *Tetrahedron Lett.* **1982**, *23*, 4785.
(21) Kuzuya, M.; Noguchi, A.; Okuda, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3454.
(22) Kowalewski, D. G. de; Contreras, R. H.; de los Santos, C. *J. Mol. Struct.* **1989**, *213*, 201.
(23) Boykin, D. W., Ed. *^{17}O NMR Spectroscopy in Organic Chemistry*; CRC: Boca Raton, FL, 1990.
(24) Jameson, C. G.; Mason, J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum: New York, 1987.
(25) Orendt, A. M.; Biekofsky, R. R.; Pomilio, A. B.; Contreras, R. H.; Facelli, J. C. *J. Phys. Chem.* **1991**, *95*, 6179.
(26) Hansen, A. E.; Bouman, T. D. *J. Chem. Phys.* **1985**, *82*, 5035.
(27) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavarachi, K.; Melius, C. F.; Martin, R. L.; Steward, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburg, PA, 1984.
(28) Dunning, T. H.; Hay, P. J. In *Methods in Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum: New York, 1977.
(29) Duddeck, H.; Jászbérenyi, J. C.; Lévai, A.; Timár, T.; Elgamal, M. H. *Magn. Reson. Chem.* **1989**, *27*, 170.
(30) Krivdin, L. B.; Kalabin, G. A. *Prog. NMR Spectrosc.* **1989**, *21*, 293.
(31) Krivdin, L. B.; Zinchenko, S. V.; Shcherbakov, V. V.; Kalabin, G. A.; Contreras, R. H.; Tufró, M. F.; Ruiz de Azúa, M. C.; Giribet, C. G. *J. Magn. Reson.* **1989**, *84*, 1.
(32) Facelli, J. C.; Contreras, R. H.; de Kowalewski, D. G.; Kowalewski, V. J.; Piegaia, R. N. *J. Mol. Struct.* **1983**, *94*, 163.

Anharmonic Force Field of CO_2

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A group theoretical algorithm to calculate the number of independent force constants of a molecule at any given order has been extended to treat linear molecules in a fashion analogous to nonlinear molecules. Using this algorithm to determine the independent force constants and a finite-difference formalism to obtain higher-order force constants from low-order analytic geometric derivatives of the electronic energy, the anharmonic force field of CO_2 has been determined at the ab initio TZ2P SCF and QZ2P CCSD(T) levels. It is shown that accurate sextic force fields can be calculated from only analytic first derivatives if the wave function is tightly converged and the calculated forces are highly accurate. The calculated anharmonic force fields are compared to experimentally determined sextic force fields of CO_2, and uncertainties and discrepancies in the experimental fields are discussed.

Introduction

The present paper describes, to our best knowledge, the first quantum chemical calculation of the complete sextic force field of any molecule larger than diatomic. This study complements and extends several recent investigations[1-8] which showed the unique value of ab initio calculations in the determination of molecular constants which characterize the vibration–rotation spectra of semirigid[9] molecules and the considerable accuracy of the underlying anharmonic molecular force fields. Some important results of these earlier studies are the following: (a) For most constants the self-consistent-field (SCF) cubic and quartic force fields show little variation with basis set extension; the values can be considered as converged using a basis set of triple-zeta plus double-polarization function (TZ2P) quality. (In many cases, especially for molecules not having multiple bonds, the convergence at the SCF level is nearly achieved even at the rather low double-zeta plus polarization function (DZP) level.) (b) Particularly accurate values can be obtained using methods incorporating substantial part of the electron correlation energy; the improvement is especially pronounced for the quadratic part of the force field and becomes less and less important for higher-order constants. (c) A substantial part of the discrepancy between force constants calculated at theoretical stationary points and force constants obtained from experiments comes from differences in the underlying reference geometries; shifting the theoretical reference geometry close to the true equilibrium geometry results in force constants which are in dramatically better agreement with their experimental counterparts. These and some other important results are especially well reviewed in a paper by Allen and Császár.[5] The accumulated knowledge about theoretical anharmonic force fields provided confidence that the sextic force field of a molecule like CO_2 determined using ab initio techniques should be accurate and thus can help to resolve existing uncertainties in the experimental anharmonic force fields of CO_2.[10-12]

Carbon dioxide has been thoroughly studied by several experimental groups.[10-18] It is one of those few molecules for which the complete force field through sixth order has been determined experimentally.[10,11] By comparing the available sextic (and quartic) experimental force fields (see Table III), one has to conclude that, partly due to the fact that different procedures were used to derive these force fields, deviations of unacceptable magnitude exist in these fields. It was hoped that a high-level theoretical study could result in anharmonic force constants whose accuracy allows improvement of the anharmonic force field of CO_2.

Due to its highly symmetric geometric structure and the relative simplicity of its electronic structure, CO_2 is a good candidate for theoretical studies as well. Thus, it is surprising to see that the first attempt[19] to calculate the complete anharmonic force field (through fourth order) of CO_2 by means of ab initio calculations was published only in 1990.[3] In that paper the highest-quality quartic force fields of CO_2 were determined at the TZ2P SCF and TZ2P CISD levels using the respective theoretical optimized geometries as references. The agreement between experiment and theory was impressive but may be not as good as one would like to see. Part of the deviations was thought to be connected to the choice of the reference geometry, since there were sizable differences between the theoretical and experimental r_e(C=O) bond lengths. Thus, in this study the reference geometry was elected to correspond to the best experimental estimate of r_e(C=O)[12,14] to improve the quality of the theoretical force constants.[4,5]

To calculate the sextic force field of a molecule using ab initio methods, one would desirably have a program which calculates the analytic sixth derivatives of the electronic energy with respect

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to geometry parameters. However, it is unlikely that theoretical methods of this complexity will be available even in the distant future. Analytic third- and fourth-derivative methods[6,20-26] are becoming available at the Hartree–Fock level of theory, but for more sophisticated theoretical methods, ones which calculate substantial parts of the electron correlation energy, analytic first (and maybe second) derivatives are available at most.[26] Thus, it is of special interest to investigate whether one can derive the complete sextic force field using only analytic gradients. Surface-fitting procedures proved too inaccurate to determine higher-order force constants;[4,27,28] thus, a cost-efficient finite-difference procedure has to be employed to generate all force constants up to sixth order. For a finite-difference procedure it is necessary to determine all independent force constants of the given molecule. This is possible using an elegant group theoretical approach, first described by Watson[29] and then by Zhou and Pulay.[30] This systematic procedure is modified in the next section to determine the number of independent force constants for linear molecules. Then details concerning the numerical differentiation scheme applied are given. After summary of the computational details the sextic force fields of CO_2 obtained experimentally and theoretically are compared, and important features of the calculated force fields are discussed.

A Group Theoretical Approach To Determine Independent Force Constants

For completely unsymmetrical molecules (point group C_1) the number of independent force constants in kth order can evidently be obtained according to the formula

$$\frac{1}{k!}\prod_{j=1}^{k}(n+j-1) \tag{1}$$

where $n = 3N - 6$ and N is the number of atoms in the molecule. In molecules having certain symmetry elements the number of independent force constants will be substantially less than can be determined from eq 1.

To devise a systematic, group theoretical approach for the determination of independent force constants, it is of fundamental importance to recall that all symmetry relations between molecular parameters follow from the following general principle: the vibrational–rotational Hamiltonian must be invariant (i.e., totally symmetric) under all the symmetry operations of the molecular symmetry (point) group. The Hamiltonian and the potential energy expression

$$\begin{aligned}V = V_0 + \frac{1}{2}\sum_{ij}^{3N-6} V_{ij}S_iS_j + \frac{1}{6}\sum_{ijk}^{3N-6} V_{ijk}S_iS_jS_k + \\ \frac{1}{24}\sum_{ijkl}^{3N-6} V_{ijkl}S_iS_jS_kS_l + \frac{1}{120}\sum_{ijklm}^{3N-6} V_{ijklm}S_iS_jS_kS_lS_m + \\ \frac{1}{720}\sum_{ijklmn}^{3N-6} V_{ijklmn}S_iS_jS_kS_lS_mS_n + \ldots\end{aligned} \tag{2}$$

where V_i are the forces, V_{ij}, V_{ijk}, V_{ijkl}, V_{ijklm}, and V_{ijklmn} are the quadratic, cubic, quartic, quintic, and sextic force (potential) constants, respectively, and the summations are unrestricted, must therefore contain only those terms which are totally symmetric under all symmetry operations. Consequently, to determine whether a particular force constant can appear in the potential energy expansion, one has the following simple algorithm: (a) obtain the symmetry coordinates according to well-known rules,[31] (b) calculate the necessary direct products of the symmetry species involved in the particular force constant term, and (c) only if the direct product transforms according to the totally symmetric irreducible representation of the point group will that term (force constant) appear in the potential energy expansion. Note that, as a consequence, the quadratic force constant matrix is always block-diagonal in symmetry coordinates.

As shown below, a more elegant group theoretical approach can be devised to obtain the higher-order force constants. It is based on the fact that eq 2 contains products of symmetry coordinates S_α ($\alpha = i, j, k, \ldots$) and that the constants $S_\alpha S_\beta \ldots S_\omega$ and the ones obtained by any permutation of the indices are indistinguishable. Thus, the n-member products transform according to the permutation (symmetric) group S_n[32-36] or in another, perhaps more appropriate, notation $[\Gamma^n_{vib}]$,[29] where $[\Gamma^n_{vib}]$ is the nth-order representation of the vibrational displacements of the molecule. Consequently, the number of independent force constants at any order is given by the number of times the totally symmetric representation is contained in the symmetric power of the vibrational representation at that order. In conclusion, for the determination of the independent force constants of molecules with symmetry one needs the character tables of two groups: the point group of the molecule's spatial symmetry and the permutation (symmetric) group of the order corresponding to the order of the force constants in question.

Let $\chi_n(R)$ be the character of $[\Gamma^n_{vib}]$ for the Rth symmetry operation of order n. As first shown, through fourth order, by Tisza,[37] the characters $\chi_n(R)$ of $[\Gamma^n_{vib}]$ can be obtained as follows:

$$\chi_2(R) = (1/2)[\chi(R)^2 + \chi(R^2)] \tag{3}$$

$$\chi_3(R) = (1/6)[\chi(R)^3 + 3\chi(R)\chi(R^2) + 2\chi(R^3)] \tag{4}$$

$$\begin{aligned}\chi_4(R) = (1/24) \times \\ [\chi(R)^4 + 6\chi(R)^2\chi(R^2) + 8\chi(R)\chi(R^3) + 6\chi(R^4) + 3\chi(R^2)^2]\end{aligned} \tag{5}$$

$$\begin{aligned}\chi_5(R) = (1/120)[\chi(R)^5 + 10\chi(R)^3\chi(R^2) + 20\chi(R)^2\chi(R^3) + \\ 30\chi(R)\chi(R^4) + 15\chi(R)\chi(R^2)^2 + 20\chi(R^2)\chi(R^3) + 24\chi(R^5)]\end{aligned} \tag{6}$$

$$\begin{aligned}\chi_6(R) = \\ (1/720)[\chi(R)^6 + 15\chi(R)^4\chi(R^2) + 40\chi(R)^3\chi(R^3) + \\ 90\chi(R)^2\chi(R^4) + 45\chi(R)^2\chi(R^2)^2 + 120\chi(R)\chi(R^2)\chi(R^3) + \\ 144\chi(R)\chi(R^5) + 120\chi(R^6) + 90\chi(R^2)\chi(R^4) + 15\chi(R^2)^3 + \\ 40\chi(R^3)^2]\end{aligned} \tag{7}$$

$$\begin{aligned}\chi_7(R) = \\ (1/5040)[\chi(R)^7 + 21\chi(R)^5\chi(R^2) + 70\chi(R)^4\chi(R^3) + \\ 210\chi(R)^3\chi(R^4) + 105\chi(R)^3\chi(R^2)^2 + 420\chi(R)^2\chi(R^2)\chi(R^3) + \\ 504\chi(R)^2\chi(R^5) + 840\chi(R)\chi(R^6) + 630\chi(R)\chi(R^2)\chi(R^4) + \\ 105\chi(R)\chi(R^2)^3 + 280\chi(R)\chi(R^3)^2 + 504\chi(R^2)\chi(R^5) + \\ 210\chi(R^2)^2\chi(R^3) + 420\chi(R^3)\chi(R^4) + 720\chi(R^7)]\end{aligned} \tag{8}$$

$$\begin{aligned}\chi_8(R) = \\ (1/40320)[\chi(R)^8 + 28\chi(R)^6\chi(R^2) + 112\chi(R)^5\chi(R^3) + \\ 420\chi(R)^4\chi(R^4) + 210\chi(R)^4\chi(R^2)^2 + \\ 1120\chi(R)^3\chi(R^2)\chi(R^3) + 1344\chi(R)^3\chi(R^5) + \\ 3360\chi(R)^2\chi(R^6) + 2520\chi(R)^2\chi(R^2)\chi(R^4) + \\ 420\chi(R)^2\chi(R^2)^3 + 1120\chi(R)^2\chi(R^3)^2 + \\ 4032\chi(R)\chi(R^2)\chi(R^5) + 1680\chi(R)\chi(R^2)^2\chi(R^3) + \\ 3360\chi(R)\chi(R^3)\chi(R^4) + 5760\chi(R)\chi(R^7) + 5040\chi(R^8) + \\ 1260\chi(R^4)^2 + 1260\chi(R^2)^2\chi(R^4) + 3360\chi(R^2)\chi(R^6) + \\ 1120\chi(R^2)\chi(R^3)^2 + 2688\chi(R^3)\chi(R^5) + 105\chi(R^2)^4]\end{aligned} \tag{9}$$

The above formulas were obtained at order n by applying only the information given for the classes and orders of S_n. Since permutation groups are not treated in standard chemistry textbooks, classes and orders of the permutation groups S_2 through S_8 are listed in Table I to assist the reader. The complete character tables of groups S_2 through S_{10} can be obtained from ref 32. The same formulas can be obtained using recursive formulas. A simple one, an analog of Brioschi's formula,[34] was presented by Zhou and Pulay[30] in the form

$$\chi_n(R) = \frac{1}{n}\sum_{k=1}^{n}\chi(R^k)\chi_{n-k}(R) \tag{10}$$

where $\chi_0(R) = 1$ and $\chi_1(R) = \chi(R)$.

Let us now briefly outline the group theoretical method one should use to obtain the number of independent force constants of a given molecule: (1) Determine the point group of the molecule. (2) Place a set of appropriately directed Cartesian coordinate vectors on each atom and obtain the characters of Γ_{tot}.

TABLE I: Classes and Orders of the Permutation Groups S_2 through S_8

S_2

class	order	class	order
1^2	1	2	1

S_3

class	order	class	order
1^3	1	3	2
12	3		

S_4

class	order	class	order
1^4	1	4	6
$1^2 2$	6	2^2	3
13	8		

S_5

class	order	class	order
1^5	1	12^2	15
$1^3 2$	10	23	20
$1^2 3$	20	5	24
14	30		

S_6

class	order	class	order
1^6	1	15	144
$1^4 2$	15	6	120
$1^3 3$	40	24	90
$1^2 4$	90	2^2	15
$1^2 2^2$	45	3^2	40
123	120		

S_7

class	order	class	order
1^7	1	124	630
$1^5 2$	21	12^3	105
$1^4 3$	70	13^2	280
$1^3 4$	210	25	504
$1^3 2^2$	105	$2^2 3$	210
$1^2 23$	420	34	420
$1^2 5$	504	7	720
16	840		

S_8

class	order	class	order
1^8	1	125	4032
$1^6 2$	28	$12^2 3$	1680
$1^5 3$	112	134	3360
$1^4 4$	420	17	5760
$1^4 2^2$	210	8	5040
$1^3 23$	1120	4^2	1260
$1^3 5$	1344	$2^2 4$	1260
$1^2 6$	3360	26	3360
$1^2 24$	2520	23^2	1120
$1^2 2^3$	420	35	2688
$1^2 3^2$	1120	2^4	105

(3) Obtain Γ_{vib} by subtracting those symmetry species which correspond to translational (Γ_{tr}) and rotational (Γ_{rot}) motions.[38] (4) Obtain the characters of the symmetric powers of Γ_{vib} up to the desired order using eqs 3–9 (or similar equations for higher orders). (5) Calculate, using standard methods, the number the totally symmetric irreducible representation appears in Γ_{vib} and in its higher symmetric powers.

This method can easily be used for nonlinear molecules, as shown by Watson[29] for CH_3X molecules and by Zhou and Pulay[30] for benzene. For the linear molecule CO_2, of $D_{\infty h}$ symmetry, an additional difficulty arises: during reduction of the representations infinite sums appear due to the infinite nature of the linear point groups. Sophisticated algorithms exist in the literature to circumvent this problem.[36] On the other hand, a simple, elementary solution can be proposed as follows.[39] It is known[40] in the theory of molecular vibrations that the only irreducible representations involved for point groups $C_{\infty v}$ and $D_{\infty h}$ are Σ^+, Π and Σ_g^+, Π_g, Σ_u^+, Π_u, respectively. This is an important observation since then only these few irreducible representations have to be considered for the reduction of Γ_{vib} of linear molecules. Furthermore, only characters involving symmetry operations E, σ_v and E, σ_v, i, C_2 should be considered for point groups $C_{\infty v}$ and $D_{\infty h}$, respectively; thus, one can avoid algebraic problems during the reduction. The representations and characters obtained using this approach for CO_2 are collected in Table II. Future use of this approach, providing a simple and easy way to deal with linear molecules, is recommended. As expected, CO_2 has 1 structural parameter and 3 quadratic, 3 cubic, 6 quartic, 6 quintic, and 10 sextic force constants. Symmetry classification of these force constants can be performed according to the procedure given by Watson.[29]

TABLE II: Representations of Symmetric Powers of Γ_{vib} for CO_2[a]

representation	E	σ_v	i	C_2	species ($D_{\infty h}$)
Γ_{vib}	4	2	−2	0	$\mathbf{1}\Sigma_g^+ + \Sigma_u^+ + \Pi_u$
$[\Gamma_{vib}^2]$	10	4	4	2	$\mathbf{3}\Sigma_g^+ + \ldots$
$[\Gamma_{vib}^3]$	20	6	−6	0	$\mathbf{3}\Sigma_g^+ + \ldots$
$[\Gamma_{vib}^4]$	35	9	9	3	$\mathbf{6}\Sigma_g^+ + \ldots$
$[\Gamma_{vib}^5]$	56	12	−12	0	$\mathbf{6}\Sigma_g^+ + \ldots$
$[\Gamma_{vib}^6]$	84	16	16	4	$\mathbf{10}\Sigma_g^+ + \ldots$

[a] In Cartesian coordinates. The number of structural parameters and force constants at any given order is indicated by bold numbers.

A Numerical Differentiation Scheme to Obtain Force Constants up to Sixth Order

The two basic methods for determining derivatives (in the present context forces and force constants) of functions (here electronic energy) numerically are least-squares fitting and use of finite-difference expressions. An excellent review of these numerical techniques for the calculation of theoretical force fields up to third order is provided in an article by Fogarasi and Pulay.[4] They emphasize the pitfalls associated with least-squares procedures by giving several examples. Although they state that the more accurate finite-difference formulas are less economical, the cost associated with deriving these finite-difference formulas and obtaining the necessary quantum chemical information to evaluate them is well justified by the superior numerical accuracy obtainable. Indeed, in Table 1 of ref 3 Allen and co-workers show how accurate finite-difference formulas are by comparing the complete quartic force field of HCN calculated from analytic third derivatives to the field calculated from analytic first derivatives. All the deviations observed are just a fraction of 1%; in most cases they are even comparable to the formula errors associated with obtaining the quartic constants by finite differences of analytic third derivatives.

Based on the proven success of this approach, finite-difference formulas were developed in this paper which allow obtaining the complete sextic force field of any symmetric linear XY_2 triatomic molecule from calculated analytic derivatives in symmetry coordinates at appropriately distorted geometries. Similar finite-difference formulas can be developed to obtain anharmonic force fields simply from a number of energy points, but contributions of quintic and sextic terms to the electronic energy are so small that complete sextic force fields cannot be obtained this way. The symmetry coordinates for symmetric linear XY_2 molecules are $S_1 = 2^{-1/2}(r + r')$, $S_2 = 2^{-1/2}(r - r')$, $S_3 = \alpha$, and $S_4 = \alpha'$, where r and r' in our case correspond to the two CO bond lengths (describing the stretching motions) and α and α' to the OCO angles (describing the so-called in-plane and out-of-plane linear bending motions) of CO_2. The distorted geometries are centered around the reference geometry to assure maximum accuracy with minimum number of displacements and to simplify the finite-difference formulas. It is important to point out that the formulas obtained are unique in that they allow nonzero forces at the reference geometry. This means that if the reference geometry is not a stationary point at the level of theory applied to calculate the analytic derivatives (just like in the present study), one has to be careful in transforming the directly calculated Cartesian analytic derivatives to derivatives in symmetry coordinates. This transformation is always linear for analytic first derivatives, but the general transformation is nonlinear between Cartesian and internal quadratic force constant matrices and becomes linear only when the forces at the reference geometry are zero.[5,41] For higher-order derivatives the transformation equations[5] are always nonlinear and depend explicitly on lower-order derivatives (e.g., forces at the reference geometry).

The finite-difference formulas necessary to obtain the complete sextic (or higher-order) force field can be obtained from a set of simple algebraic equations. To extract the force constants from these equations can be, however, rather involved, especially for higher-order derivatives. Consequently, the computer program (e.g., written in FORTRAN) which applies these equations can be somewhat tedious to write. On the other hand, the program package *Mathematica*[42] provides an easy and elegant solution through its ability to handle symbolic mathematics. While the computer code written by the present author in FORTRAN to calculate the sextic force field from analytic gradients is more than 1000 lines long, the code written in *Mathematica* to perform the same task is less than 100 lines long and can be extended to handle higher-order constants or molecules with different point groups much more easily than its FORTRAN counterpart. Furthermore, if one uses *Mathematica*, there is no need to solve sets of simultaneous equations explicitly; it will be all handled by the program, decreasing substantially the possibilities of human error.

To obtain all force constants up to sixth order for a symmetric linear XY_2 molecule from analytic first derivatives (forces), it is necessary to make single, double, and triple displacements along each coordinate and simultaneous displacements along two or three coordinates. If higher-order analytic derivatives are available, the number of calculations at displaced geometries decreases considerably. (For example, the complete quartic force field can be calculated from just five analytic second-derivative calculations.)

It is sometimes advantageous to transform the symmetry coordinate force constants (and forces) obtained to internal coordinates. The formulas necessary for this transformation, up to sixth order, are summarized in the Appendix.

Finally, it should be pointed out that for linear molecules, due to the presence of degenerate linear bending motions, there are some dependent force constants which have to be included in the power series expansion: the quartic constant $f_{\alpha\alpha\alpha'\alpha'}$ and the sextic constant $f_{\alpha\alpha\alpha\alpha\alpha'\alpha'}$. These constants can be obtained from the following mathematical identities

$$F_{3344} = f_{\alpha\alpha\alpha'\alpha'} = (1/3)(F_{3333} + 4F_{33}) = (1/3)(f_{\alpha\alpha\alpha\alpha} + 4f_{\alpha\alpha}) \tag{11}$$

and

$$F_{333344} = f_{\alpha\alpha\alpha\alpha\alpha'\alpha'} = (1/15)(3F_{333333} + 40F_{3333} + 112F_{33}) = (1/15)(3f_{\alpha\alpha\alpha\alpha\alpha\alpha} + 40f_{\alpha\alpha\alpha\alpha} + 112f_{\alpha\alpha}) \tag{12}$$

Computational Details

Two basis sets were chosen for this study: a triple-zeta plus double-polarization (TZ2P) and a quadruple-zeta plus double-polarization (QZ2P) quality. The TZ2P basis was chosen to be exactly the same as used in ref 3, i.e., the TZ basis is that of Huzinaga and Dunning,[43] and may be designated as (9s5p/5s3p), and the exponents of the polarization functions are as follows: $\alpha_d(C) = 0.375, 1.50$ and $\alpha_d(O) = 0.425, 1.70$. In accord with the choice of the polarization exponents the TZ2P basis is used in SCF level calculations. The QZ basis is that of Huzinaga and Dunning[44,45] and may be designated as (10s6p/5s4p). The correlation-optimized exponents of the polarization functions were taken from Dunning,[46] and they are as follows: $\alpha_d(C) = 0.318, 1.097$ and $\alpha_d(O) = 0.645, 2.314$. In all cases the polarization functions contain sets of six Cartesian d-type functions.

The reference geometry for the force field calculations was chosen to be the same as the most reasonable estimate of the true equilibrium C═O bond length, 1.1600 Å.[12,14]

Electronic wave functions were determined in this study by both the single-configuration, self-consistent-field, restricted Hartree–Fock (SCF) method and the single-reference coupled-cluster singles and doubles with a perturbational estimate of connected triple excitations (CCSD(T)) methods. In the QZ2P CCSD(T) calculations three core and three virtual orbitals were kept frozen. Analytic first[47,48] and second[49] derivatives in Cartesian coordinates with respect to geometry parameters at the SCF and analytic first derivatives at the CCSD(T)[50] levels were computed with the aid of the PSI[51] and TITAN[52] program packages, respectively. To ensure numerical accuracy, the wave functions were extremely tightly converged: convergence on the SCF density matrix was set to 10^{-14}, while during the calculation of the CCSD(T) wave function all convergence criteria were set to 10^{-12}. (For further details see the appropriate program descriptions.[51,52]) For the generation of distorted geometries and for transformation of analytic derivatives in Cartesian coordinates to derivatives in symmetry coordinates, the program INTDER[53] was employed. The displacement sizes were chosen as follows: S_1, S_2 = 0.01 Å and S_3 = 0.02 rad.

Anharmonic Force Field of CO_2

The sextic force fields of CO_2 in internal coordinates, obtained both experimentally and theoretically, are presented in Table III. There are several important observations one can make from the data of Table III as detailed below.

It is striking to observe that the higher the order of the force constants is, the larger the range of the experimental values[10–12] for any individual constant becomes. The quadratic force constants obtained by the different experimental procedures agree with each other excellently; the deviations between the largest and smallest experimental values for the force constants are 0.3% for f_{rr}, 2.3% for $f_{rr'}$, and 0.9% for $f_{\alpha\alpha}$; i.e., the average deviation is only 1%. For the cubic constants these values are 2.5% for f_{rrr}, 58% for $f_{rrr'}$, and 2.0% for $f_{r\alpha\alpha}$, the average being 21%. For the quartic constants, except for f_{rrrr}, the experimental studies[10–12] yielded substantially different values; for example, the value of $f_{rrr'r'}$ varies between 0.8^{10} and 122^{11} aJ Å^{-4}. For the quintic and sextic constants, which give very little contribution to the total energy of the system, the discrepancies are even larger; in most cases even the sign of the force constant is different in the two studies available.[10,11]

In clear contrast to these sizable variations, theory results in constants which agree considerably better with each other. Variations in the TZ2P SCF//TZ2P SCF, TZ2P SCF//expt, and QZ2P CCSD(T)//expt force constants are never disturbingly large, confirming the known trend that most force constants for most closed-shell molecules can be calculated with considerable precision at the SCF level of theory. As expected, changing the reference C═O bond length from the shorter TZ2P SCF optimized value (1.1349 Å) to the longer experimental one (1.1600 Å) decreases the appropriate TZ2P SCF force constants and thus improves agreement between SCF theory and experiment substantially. For example, the deviation between SCF theory and the experimental constants of Chēdin[10] decreases for f_{rr}, f_{rrr}, and f_{rrrr} from 19% to −3%, from 19% to 4%, and from 10% to −6%, respectively. Most off-diagonal force constants change rather little as a result of the change in the reference geometry, again in accord with expectations. Note also that for $f_{rr'}$ change in the reference geometry did not improve substantially the large discrepancy between SCF theory and experiment: the TZ2P SCF//expt constant, 2.21 aJ Å^{-2}, is still almost twice as large as the well-established experimental constant, 1.25 aJ Å^{-2}. In ref 3 it was shown that including electron correlation by the configuration interaction with all single and double substitutions (CISD) approach changed $f_{rr'}$ only moderately; the TZ2P CISD//TZ2P CISD value is still too high at 1.75 aJ Å^{-2}. The QZ2P CCSD(T)//expt $f_{rr'}$ constant, 1.27 aJ Å^{-2}, calculated in the present study is finally very close to the available experimental values. Although the calculated constant might still be a little too high, its deviation from the experimental values is only about as large as the variation among the experimental constants. This and the substantial improvement observed for the value of $f_{\alpha\alpha}$ suggest above all that the QZ2P CCSD(T) force field derived in this study has

TABLE III: Complete Sextic Force Fields for CO_2 in Internal Coordinates[a]

	theory			experiment		
constant	TZ2P SCF//TZ2P SCF[b]	TZ2P SCF/expt[c,d]	QZ2P CCSD(T)//expt[c]	Lacy[11]	Suzuki[12]	Chêdin[10]
f_r	0.000	0.49256 (0)	−0.10101			
f_{rr}	19.067	15.754 (0)	16.224	15.976	16.022	16.017
$f_{rr'}$	2.342	2.205 (0)	1.272	1.232	1.261	1.253
$f_{\alpha\alpha}$	0.977	0.917 (0)	0.754	0.778	0.785	0.783
f_{rrr}	−138.6	−120.89 (0)	−116.4	−116.8	−113.9	−116.1
$f_{rrr'}$	−2.917	−2.560 (0)	−2.534	−2.48	−3.909	−2.913
$f_{r\alpha\alpha}$	−1.232	−1.159 (0)	−1.246	−1.218	−1.218	−1.194
f_{rrrr}	750.1	641.2 (0)	693.2	638.9	630.0	656.1
$f_{rrrr'}$	4.125	4.284 (0)	3.975	75.24	22.06	8.332
$f_{rrr'r'}$	10.086	9.938 (0)	2.368	122.2	12.09	0.835
$f_{rr\alpha\alpha}$	0.066	−0.111 (0)	1.176	0.92	2.015	0.975
$f_{rr'\alpha\alpha}$	3.047	2.808 (0)	0.305	−0.72	3.740	2.816
$f_{\alpha\alpha\alpha\alpha}$	2.422	2.176 (0)	1.707	2.16	1.106	1.356
f_{rrrrr}		−3967 (1)		−110.4		−2315.8
$f_{rrrrr'}$		2.322 (40)		−253.7		70.08
$f_{rrrr'r'}$		−2.240 (53)		372.8		−276.9
$f_{rrr\alpha\alpha}$		−1.989 (52)		−22.4		−3.950
$f_{rrr'\alpha\alpha}$		−2.132 (3)		−24.0		−1.218
$f_{r\alpha\alpha\alpha\alpha}$		−4.713 (59)		6.2		−3.113
f_{rrrrrr}		27947 (10)		39406		−48871
$f_{rrrrrr'}$		−590 (17)		−34188		5756.0
$f_{rrrrr'r'}$		48.4 (12)		−88739		9283.3
$f_{rrrr'r'r'}$		14.5 (43)		−58921		5530.1
$f_{rrrr\alpha\alpha}$		3.3 (76)		293		−454.8
$f_{rrrr'\alpha\alpha}$		21.9 (30)		−31.0		−361.9
$f_{rrr'r'\alpha\alpha}$		14.1 (8)		−1011.7		−326.9
$f_{rr\alpha\alpha\alpha\alpha}$		−0.5 (44)		40.8		−6.84
$f_{rr'\alpha\alpha\alpha\alpha}$		22.0 (69)		250.1		−2.90
$f_{\alpha\alpha\alpha\alpha\alpha\alpha}$		−29.9 (1)		−68		20.0

[a] Units for the force constants are consistent with energy measured in attojoules, stretching coordinates (r and r') in angstroms, and bending coordinates (α) in radians. The designation // means "at the geometry of". [b] Reference 3. [c] This study. The abbreviation "expt" means that the force field was calculated at the experimental geometry of r_{CO} = 1.1600 Å. Therefore, nonzero theoretical forces (f_r) remain at the reference geometry. [d] The values given in parentheses at the TZ2P SCF/expt level of theory are deviations of the results obtained using analytic first derivatives from the results obtained using analytic second derivatives.

an accuracy unprecedented in previous studies and that similar (or higher) levels of theory can result in quantitatively accurate anharmonic force fields. The values determined for the quartic force field of CO_2 at the QZ2P CCSD(T) level of theory clearly support most experimental anharmonic force constants. If one needs to make a choice among the three experimental studies available, the QZ2P CCSD(T) constants seem to be in closest agreement with the constants obtained by Chêdin:[10] the average deviation is only 2.1% and 5.8% for the quadratic and cubic constants, respectively.

To ascertain the accuracy of the sextic force field of CO_2 derived from analytic first derivatives, the complete force field was determined also from analytic second derivatives at the TZ2P SCF level. As can be seen from Table III, the deviations between the force constants determined from analytic first and second derivatives is negligible up to fourth order. Noticeable deviations can be observed for some quintic and sextic constants, but the discrepancies between the two sets of results are still acceptably small for all force constants but $f_{rrrr\alpha\alpha}$ and $f_{rr\alpha\alpha\alpha\alpha}$ for which one should accept the values obtained from the more accurate analytic second-derivative calculations. This result suggests that accurate sextic force fields can be derived from only analytic first derivatives if great care is exercised in converging the wave function and calculating its first geometric derivatives.

The TZ2P SCF quintic and sextic force constants do not clearly support the studies of either Lacy[11] or Chêdin.[10] All quintic constants, except f_{rrrrr}, are predicted to be rather small, which is in basic agreement with the results of Chêdin. Since the TZ2P SCF level of theory provides reasonably accurate off-diagonal stretch–stretch interaction constants up to fourth order (up to this order the values can be compared to accurate QZ2P CCSD(T) values), it is expected that $f_{rrrrr'}$ should also be predicted with considerable accuracy and that consequently it is overestimated by Chêdin. The sextic diagonal stretching constant, f_{rrrrrr}, is predicted to be a large positive number by theory, as one would expect. Chêdin obtained an unexpected negative value for this constant. In the light of the present theoretical data this result might need to be reevaluated. Similarly to the quintic constants, most sextic constants are also calculated to be rather small, whereas both Lacy and Chêdin calculate sizable sextic stretch–stretch interaction constants (although their magnitude and sign is rather different in the two studies). Again, it would probably be beneficial to redetermine these constants experimentally to see whether their values are not indeed much smaller. The sextic bending constant, $f_{\alpha\alpha\alpha\alpha\alpha\alpha}$, is calculated to be a negative value (−29.9 aJ rad^{-6}) at the TZ2P SCF level of theory, supporting the sign obtained by Lacy and not that of Chêdin. For the other constants no meaningful comparison can be made between theory and experiment because of the considerable deviations between the two available experimental studies.

Conclusions

The several conclusions of this study can be summarized as follows:

1. It is shown that a group theoretical procedure, given first by Watson,[29] then by Zhou and Pulay[30] and reformulated here again, can be modified using an elementary approach so that it can handle linear molecules in a fashion analogous to nonlinear molecules. In this approach, to avoid algebraic difficulties associated with the infinite nature of the linear point groups, only characters involving symmetry operations E and σ_v, and E, σ_v, i, and C_2 should be considered for point groups $C_{\infty v}$ and $D_{\infty h}$, respectively, to determine the characters of the symmetric powers of Γ_{vib} and during their reduction.

2. It is found that finite-difference formulas are exceptionally well suited for programming in *Mathematica*,[42] since using the symbolic mathematical capabilities of this package tedious explicit solutions of sets of linear equations can be avoided. Thus, use of *Mathematica* is highly recommended for all similar studies in the future.

3. Although sextic force fields cannot be derived simply from energy points, accurate anharmonic force fields (up to sixth order)

can be derived from only analytic first derivatives if the wave function is tightly converged and if its first geometric derivatives are calculated with high accuracy.

4. It is shown again that by simply changing the reference geometry from the theoretical optimum to the experimental one one can obtain considerably improved force constants even at the SCF level of theory. Improvements are especially pronounced for the stretching constants affected most by the change in the underlying reference geometry.

5. The QZ2P CCSD(T) quartic force field, obtained as part of this study, reproduces the corresponding experimental force fields with great accuracy, the deviations are 2% and 6% at the quadratic and cubic force constant levels, respectively. This suggests that quantitative accuracy can be achieved for anharmonic force field studies at a computational level which can be made affordable for considerably larger systems than CO_2 in the near future. The force constants obtained at the QZ2P CCSD(T) level seem to be in closest agreement with the force field of CO_2 obtained by Chêdin.[10]

Appendix

Transformation Formulas between Internal and Symmetry Coordinate Sextic Force Constants for Symmetric Linear XY_2 Molecules. In the presentation of the formulas below the following notation is adopted: symmetry coordinate force constants are denoted by F_{ijk} (such as F_{112233}, based on symmetry coordinate definitions $S_1 = 2^{-1/2}(r + r')$, $S_2 = 2^{-1/2}(r - r')$, $S_3 = \alpha$, and $S_4 = \alpha'$, where r and r' describe the individual stretching motions and α and α' the so-called in-plane and out-of-plane linear bending motions), while internal coordinate force constants (employing individual stretches r and r' as opposed to their linear combinations) are denoted by $f_{\alpha\beta\tau}$ (e.g., $f_{rr'\alpha\alpha}$).

$$f_r = (2^{1/2}/2)F_1; \quad f_{rr} = \tfrac{1}{2}(F_{11} + F_{22}); \quad f_{rr'} = \tfrac{1}{2}(F_{11} - F_{22}); \quad f_{\alpha\alpha} = F_{33};$$

$$f_{rrr} = (2^{1/2}/4)(F_{111} + 3F_{122}); \quad f_{rrr'} = (2^{1/2}/4)(F_{111} - F_{122}); \quad f_{r\alpha\alpha} = (2^{1/2}/2)F_{133};$$

$$f_{rrrr} = \tfrac{1}{4}(F_{1111} + F_{2222} + 6F_{1122}); \quad f_{rrrr'} = \tfrac{1}{4}(F_{1111} - F_{2222});$$

$$f_{rrr'r'} = \tfrac{1}{4}(F_{1111} + F_{2222} - 2F_{1122}); \quad f_{rr\alpha\alpha} = \tfrac{1}{2}(F_{1133} + F_{2233});$$

$$f_{rr'\alpha\alpha} = \tfrac{1}{2}(F_{1133} - F_{2233}); \quad f_{\alpha\alpha\alpha\alpha} = F_{3333};$$

$$f_{rrrrr} = (2^{1/2}/8)(F_{11111} + 10F_{11122} + 5F_{12222});$$

$$f_{rrrrr'} = (2^{1/2}/8)(F_{11111} + 2F_{11122} - 3F_{12222});$$

$$f_{rrrr'r'} = (2^{1/2}/8)(F_{11111} - 2F_{11122} + F_{12222}); \quad f_{rrr\alpha\alpha} = (2^{1/2}/4)(F_{11133} + 3F_{12233});$$

$$f_{rrr'\alpha\alpha} = (2^{1/2}/8)(F_{11133} - F_{12233}); \quad f_{r\alpha\alpha\alpha\alpha} = (\tfrac{1}{2}^{112})F_{13333};$$

$$f_{rrrrrr} = (\tfrac{1}{8})(F_{111111} + 15F_{111122} + 15F_{112222} + F_{222222});$$

$$f_{rrrrrr'} = (\tfrac{1}{8})(F_{111111} + 5F_{111122} - 5F_{112222} - F_{222222});$$

$$f_{rrrrr'r'} = (\tfrac{1}{8})(F_{111111} - F_{111122} - F_{112222} + F_{222222});$$

$$f_{rrrr'r'r'} = (\tfrac{1}{12})(F_{111111} - 3F_{111122} + 3F_{112222} - F_{222222});$$

$$f_{rrrr\alpha\alpha} = \tfrac{1}{4}(F_{111133} + 6F_{112233} + F_{222233});$$

$$f_{rrr'r'\alpha\alpha} = \tfrac{1}{4}(F_{111133} - 2F_{112233} + F_{222233});$$

$$f_{rrrr'\alpha\alpha} = \tfrac{1}{4}(F_{111133} - F_{222233}); \quad f_{rr\alpha\alpha\alpha\alpha} = \tfrac{1}{2}(F_{113333} + F_{223333});$$

$$f_{rr'\alpha\alpha\alpha\alpha} = \tfrac{1}{2}(F_{113333} - F_{223333}); \quad f_{\alpha\alpha\alpha\alpha\alpha\alpha} = F_{333333}$$

References and Notes

(1) (a) Pulay, P.; Lee, J.-G.; Boggs, J. E. *J. Chem. Phys.* **1983**, *79*, 3382. (b) Dunn, K. M.; Boggs, J. E.; Pulay, P. *J. Chem. Phys.* **1986**, *85*, 5838. (c) Dunn, K. M.; Boggs, J. E.; Pulay, P. *J. Chem. Phys.* **1987**, *86*, 5088. (d) Dunn, K. M. *Chem. Phys. Lett.* **1987**, *139*, 165.

(2) Clabo, D. A., Jr.; Allen, W. D.; Remington, R. B.; Yamaguchi, Y.; Schaefer, H. F. III *Chem. Phys.* **1988**, *123*, 187.

(3) Allen, W. D.; Yamaguchi, Y.; Császár, A. G.; Clabo, D. A., Jr.; Remington, R. B.; Schaefer, H. F. III *Chem. Phys.* **1990**, *145*, 427.

(4) Fogarasi, G.; Pulay, P. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: Amsterdam, 1985; Vol. 14, pp 125–219.

(5) Allen, W. D.; Császár, A. G. *J. Chem. Phys.*, submitted for publication.

(6) (a) Gaw, J. F.; Handy, N. C. *Chem. Phys. Lett.* **1985**, *121*, 321. (b) Gaw, J. F.; Handy, N. C. *Chem. Phys. Lett.* **1986**, *128*, 182. (c) Handy, N. C.; Gaw, J. F.; Simandiras, E. D. *J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 1577. (d) Simandiras, E. D.; Gaw, J. F.; Handy, N. C. *Chem. Phys. Lett.* **1987**, *141*, 166. (e) Amos, R. D.; Gaw, J. F.; Handy, N. C.; Carter, S. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 1247. (f) Lee, T. J.; Willets, A.; Gaw, J. F.; Handy, N. C. *J. Chem. Phys.* **1989**, *90*, 4330. (g) Green, W. H.; Jayatilaka, D.; Willets, A.; Amos, R. D.; Handy, N. C. *J. Chem. Phys.* **1990**, *93*, 4965.

(7) (a) Botschwina, P.; Zilch, A.; Rosmus, P.; Werner, H.-J.; Reinsch, E.-A. *J. Chem. Phys.* **1986**, *84*, 1683. (b) Botschwina, P.; Zilch, A.; Werner, H.-J.; Rosmus, P.; Reinsch, E.-A. *J. Chem. Phys.* **1986**, *85*, 5107. (c) Botschwina, P. *J. Chem. Phys.* **1989**, *90*, 4301.

(8) (a) Xie, Y.; Boggs, J. E. *J. Chem. Phys.* **1989**, *90*, 4320. (b) Xie, Y.; Boggs, J. E. *J. Chem. Phys.* **1989**, *91*, 1066.

(9) Aliev, M. R.; Watson, J. K. G. In *Molecular Spectroscopy: Modern Research*; Rao, K. N., Ed.; Academic Press: New York, 1985; Vol. 3, pp 1–67.

(10) Chêdin, A. *J. Mol. Spectrosc.* **1979**, *76*, 430.

(11) Lacy, M. *Mol. Phys.* **1982**, *45*, 253.

(12) Suzuki, I. *J. Mol. Spectrosc.* **1968**, *25*, 479.

(13) Fermi, E. *Z. Phys. (Munich)* **1931**, *71*, 250.

(14) Gershikov, A. G.; Spiridonov, V. P. *J. Mol. Struct.* **1982**, *96*, 141.

(15) Wattson, R. B.; Rothman, L. S. *J. Mol. Spectrosc.* **1986**, *119*, 83.

(16) Smith, M. A. H.; Rinsland, C. P.; Fridovich, B.; Narahari Rao, K. In *Molecular Spectroscopy: Modern Research*; Rao, K. N., Ed.; Academic Press: New York, 1985; Vol. 3.

(17) Bailly, D.; Farrenq, R.; Guelachvili, G.; Rossetti, C. *J. Mol. Spectrosc.* **1981**, *90*, 74.

(18) Chêdin, A.; Teffo, J.-L. *J. Mol. Spectrosc.* **1984**, *107*, 333.

(19) Note that Steele et al. published in 1981 (Steele, D.; Person, W. B.; Brown, K. G. *J. Phys. Chem.* **1981**, *85*, 2007) a paper in which part of the quartic force field of CO_2 was determined at the 4-31G SCF level.

(20) Pulay, P. *J. Chem. Phys.* **1983**, *78*, 5043.

(21) Gaw, J. F.; Yamaguchi, Y.; Schaefer, H. F. III *J. Chem. Phys.* **1984**, *81*, 6395.

(22) Gaw, J. F.; Yamaguchi, Y.; Schaefer, H. F. III, Handy, N. C. *J. Chem. Phys.* **1986**, *85*, 5132.

(23) Gaw, J. F.; Yamaguchi, Y.; Remington, R. B.; Osamura, Y.; Schaefer, H. F. III *Chem. Phys.* **1986**, *109*, 237.

(24) Duran, M.; Yamaguchi, Y.; Osamura, Y.; Schaefer, H. F. III *J. Mol. Struct.* **1988**, *163*, 389.

(25) Colwell, S. M.; Jayatilaka, D.; Maslen, P. E.; Amos, R. D.; Handy, N. C. *Int. J. Quantum Chem.* **1991**, *40*, 179.

(26) Jørgensen, P., Simons, J., Eds. *Geometrical Derivatives of Energy Surfaces and Molecular Properties*; Reidel: Dordrecht, 1986.

(27) (a) Bartlett, R. J.; Shavitt, I.; Purvis, G. D. III *J. Chem. Phys.* **1979**, *71*, 281. (b) Kraemer, W. P.; Roos, B. O.; Siegbahn, P. E. M. *Chem. Phys.* **1982**, *69*, 305.

(28) Meyer, W.; Rosmus, P. *J. Chem. Phys.* **1975**, *63*, 2356.

(29) Watson, J. K. G. *J. Mol. Spectrosc.* **1972**, *41*, 229.

(30) Zhou, X-F.; Pulay, P. *J. Comput. Chem.* **1989**, *10*, 935.

(31) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; Dover: New York, 1980.

(32) Littlewood, D. E. *The Theory of Group Characters*, 2nd ed.; Oxford Press: Oxford, 1958.

(33) Hamermesh, M. *Group Theory and Its Applications to Physical Problems*; Addison-Wesley: Reading, MA, 1964.

(34) Lederman, W. *Introduction to Group Characters*; Cambridge University Press: Cambridge, 1987; p 123.

(35) Chen, J.-Q. *Group Representation Theory for Physicists*; World Scientific: Singapore, 1989.

(36) Wigner, E. P. *Group Theory*; Academic Press: New York, 1959.

(37) Tisza, L. *Z. Phys. (Munich)* **1933**, *82*, 48.

(38) Evidently, the number the totally symmetric irreducable representation appears in Γ_{vib} is equal to the number of independent geometry parameters of the molecule, since only combinations of displacements along the totally symmetric coordinates are allowed in structural variations.[29]

(39) The author thanks Prof. Pêter Pulay for initiating this solution.

(40) (a) Henry, L.; Amat, G. *J. Mol. Spectrosc.* **1965**, *15*, 168. (b) Schäfer, L.; Cyvin, S. *J. Chem. Educ.* **1971**, *48*, 295.

(41) Pulay, P. In *Modern Theoretical Chemistry*; Schaefer, H. F. III, Ed.; Plenum: New York, 1977; Vol. 4, pp 153–185.

(42) (a) Wolfram, S. *Mathematica: A System for Doing Mathematics by Computer*, 2nd ed.; Addison-Wesley: Redwood City, 1991. (b) Mathematica Version 2.0.2, Wolfram Research, Inc., 1991.

(43) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. (b) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823. (c) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F. III, Ed.; Plenum: New York, 1977; Vol. 3, pp 1–27.

(44) Huzinaga, S. *Approximate Atomic Functions*, Department of Chemistry Report: University of Alberta, 1971; Vol. 2.

(45) Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716.

(46) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(47) Pulay, P. *Mol. Phys.* **1969**, *17*, 197; **1970**, *18*, 473.

(48) (a) Saxe, P.; Yamaguchi, Y.; Schaefer, H. F. III *J. Chem. Phys.* **1982,** *77,* 5647. (b) Osamura, Y.; Yamaguchi, Y.; Saxe, P.; Vincent, M. A.; Gaw, J. F.; Schaefer, H. F. III *Chem. Phys.* **1982,** *72,* 131.

(49) (a) Osamura, Y.; Yamaguchi, Y.; Saxe, P.; Fox, D. J.; Vincent, M. A.; Schaefer, H. F. *J. Mol. Struct.* **1983,** *103,* 183. (b) Handy, N. C.; Schaefer, H. F. *J. Chem. Phys.* **1984,** *81,* 5031.

(50) (a) Rendell, A. P.; Lee, T. J. *J. Chem. Phys.* **1991,** *94,* 6219. (b) Lee, T. J.; Rendell, A. P. *J. Chem. Phys.* **1991,** *94,* 6229.

(51) PSI 1.0, 1989, PSITECH, Inc., Watkinsville, GA.

(52) TITAN is a set of electronic structure programs written by T. J. Lee, A. P. Rendell, and J. E. Rice.

(53) Allen, W. D. Program INTDER, Stanford University, Stanford, CA.

Radiationless Decay of the S_2 States of Azulene and Related Compounds: Solvent Dependence and the Energy Gap Law

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The UV-visible absorption spectra, S_2 lifetimes, and $S_2 \rightarrow S_0$ fluorescence quantum yields of azulene, azulene-d_8, 1,3-dichloroazulene, 1,3-dibromoazulene, 4,6,8-trimethylazulene, and 1,4-dimethyl-7-isopropylazulene (guaiazulene) have each been measured accurately in six solvents. The S_2–S_1 electronic energy spacings of each solute vary by ca. 500 cm^{-1} in these solvents. The variations in the S_2 nonradiative relaxation rates with electronic energy spacing are interpreted within the framework of the energy gap law of radiationless transition theory. $S_2 \rightsquigarrow S_1$ internal conversion dominates the nonradiative decay in azulene and azulene-d_8, but intersystem crossing (likely $S_2 \rightsquigarrow T_1$) is important in the halogenated derivatives. The alkyl-substituted compounds exhibit anomalous behavior and demonstrate that factors other than the electronic energy spacing are involved in determining the rates of their radiationless relaxation. Previous energy gap law correlations based on data from a series of structurally different compounds must be reinterpreted.

Introduction

Azulene is the first-discovered and best-known example of a closed-shell polyatomic molecule which exhibits "anomalous" $S_2 \rightarrow S_0$ fluorescence in condensed media.[1-9] Although the number of compounds which are known to radiate efficiently and react chemically from upper electronic excited states is now rather large,[10-12] azulene and its derivatives continue to be the focus of considerable attention and to be quoted as the "classical examples".[13-15]

In preparation for studies of the dynamic behavior of the short-lived S_1 states of azulene and other compounds in condensed media by two-photon, pump-probe methods,[16] we conducted a thorough review of the literature on this subject. To our surprise, we discovered that there is a remarkable degree of disagreement on the values of the quantum yields of $S_2 \rightarrow S_0$ fluorescence and the lifetimes of the S_2 states of azulene, azulene-d_8, and its closely related derivatives in various condensed media. Moreover, although azulene and other nonalternant hydrocarbons and their derivatives clearly exhibit "slow" S_2 nonradiative decay rates owing to their large S_2–S_1 (or perhaps S_2–T_n) electronic energy spacings, none of the previous attempts[4-9] to measure and correlate these rates quantitatively within the framework of the energy gap law[17] of radiationless transition theory has been completely successful.

Murata et al.[4,5] measured the quantum yields of $S_2 \rightarrow S_0$ fluorescence, ϕ_f, of azulene and thirteen of its derivatives but did not measure the S_2 lifetimes directly. Instead they calculated the radiative rate constants, k_r, from the absorption spectra using the Strickler–Berg formalism,[18] calculated the lifetimes via $\tau = \phi_f/k_r$, and then obtained the nonradiative rate constants from $\sum k_{nr} = (1 - \phi_f)/\tau$. A linear relationship between log ($\sum k_{nr}$) and $\Delta E(S_2 - S_1)$ for the 14 compounds led them to conclude that $S_2 \rightsquigarrow S_1$ internal conversion constituted the major S_2 radiationless decay process. Later Eber et al.[6] measured both ϕ_f and τ but adopted Murata et al.'s[4,5] value of $\phi_f = 0.031$ for azulene in ethanol as a secondary fluorescence standard. (Neither group applied the required "n^2" refractive index correction in the measurement of the quantum yields.[19]) Eber et al. concluded that log ($\sum k_{nr}$) was not a linear function of $\Delta E(S_2 - S_1)$, that the brominated and chlorinated derivatives exhibited a "heavy atom" effect,[20] and that intersystem crossing played an important role in S_2's radiationless decay. However, Gillespie and Lim[7] reevaluated the data from the previous two studies in terms of Siebrand's extended theory of radiationless transitions[21] and concluded that intersystem crossing from S_2 to T_n was not significant. Most recently Griesser and Wild[8,9] measured $\tau(S_2)$ of azulene, azulene-d_8, and four derivatives in both 3-methylpentane and ethanol at 77 K. They obtained $\sum k_{nr}$ by subtracting k_r from τ^{-1} but calculated k_r from the room temperature solution-phase absorption spectrum using the Strickler–Berg relationship,[18] assuming that k_r was independent of both temperature and solvent. Use of the latter procedure does not introduce very large errors into $\sum k_{nr}$ even though the values of k_r so obtained may not be particularly accurate. The largest experimental error in Griesser and Wild's data is therefore associated with their measurements of τ. However, their use of a wide variety of azulene derivatives to test the energy gap law of S_2 radiationless decay mechanism remains problematic because the structural changes used to vary the electronic energy spacing (Cl, Br, and alkyl substitution) will also change (i) the magnitudes of the matrix elements coupling S_2 to all lower states, and (ii) the numbers and/or energies of all vibrational modes in the molecule.

We have accurately remeasured the $S_2 \rightarrow S_0$ fluorescence quantum yields and the S_2 lifetimes of azulene, azulene-d_8, and four of its derivatives using current standards of experimental practice. Variations in the electronic energy gaps of each compound have been introduced by changing only the nature of the solvent. The results of these measurements and attempted correlations of the S_2 nonradiative decay rates with electronic energy gap are presented in this paper.

Experimental Section

Azulene (AZ) and guaiazulene (GAZ, 1,4-dimethyl-7-isopropylazulene), both from Aldrich, were used a received. Samples of highly purified AZ and azulene-d_8 were kindly supplied by Dr. B. Nickel. 1,3-Dichloroazulene (DCAZ) and 1,3-dibromoazulene

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