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Vibrational Stark Spectroscopy 3. Accurate Benchmark ab Initio and Density Functional Calculations for CO and CN$^-$

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A new Stark-type experimental technique known as *electroabsorption spectroscopy* has been developed in S. G. Boxer's laboratories which offers the ability to measure the responses of isotropic solvated molecules to an applied electric field. It is applicable to a wide range of molecules and environments. We present benchmark ab initio and density-functional calculations employing 14 methods and double-ζ to penta-ζ augmented basis sets for the vibrational frequencies, dipole moment, polarizability, hyperpolarizability profiles, Stark shift, and other electroabsorption properties of two important (gas-phase) molecules, CO and CN$^-$, for which a range of high-precision experimental data is available. The results show excellent agreement with these data, verify the earlier conclusion that the transition-moment polarizability rather than the polarizability change dominates the first-derivative response in the electroabsorption spectroscopy of these systems, and convergence with respect to the treatment of electron correlation, basis set, geometrical integration, and finite-field differentiation. For large molecules, B3LYP calculations with small (eg., aug-cc-pVDZ) basis sets are predicted to offer optimum performance per computational cost.

1. Introduction

The perturbation of vibrational properties of molecules by electric fields is clearly a subject of wide-ranging importance, particularly in inorganic and biological contexts. Interest in the theoretical description of such processes has been rekindled in recent years through the development of new experimental techniques by S. G. Boxer and co-workers[1,2] which have made Stark-type spectroscopy available to a much wider range of systems and access a wider range of molecular properties. The first quantum-chemical analyses of Stark effects on molecular vibrational properties were made over 25 years ago by Hush and Williams[3] and by Gready, Bacskay, and Hush.[4−8] In those works, finite electric field theory in which the Hamiltonian **H** is expressed as

$$\mathbf{H} = \mathbf{H_0} - \boldsymbol{\mu}\cdot\mathbf{F} \qquad (1)$$

where $\mathbf{H_0}$ is the field-free Hamiltonian for the molecule considered, $\boldsymbol{\mu}$ is its dipole moment, and **F** is the uniform applied electric field, was employed to determine molecular vibrational response functions including polarizabilities and hyperpolarizabilities.[9−12] In particular, the response of molecular vibration frequencies to the applied field is usually expressed using perturbation theory in terms of the *vibrational dipole moment* change $\boldsymbol{\Delta\mu}$ and *vibrational polarizability* change $\boldsymbol{\Delta\alpha}$ respectively, i.e.,

$$h\Delta\nu = h\nu(\mathbf{F}) - h\nu(\mathbf{0}) = -\boldsymbol{\Delta\mu}\cdot\mathbf{F} - \frac{1}{2}\mathbf{F}\cdot\boldsymbol{\Delta\alpha}\cdot\mathbf{F} \qquad (2)$$

where h is Planck's constant. This language is slightly misleading, however, as $\boldsymbol{\Delta\mu}$ and $\boldsymbol{\Delta\alpha}$ are not exactly equal to the changes in the expectation values of the dipole and polarizability operators induced by the vibrational transition, $\boldsymbol{\Delta\mu}$, e.g., being equivalent only at the harmonic level of approximation.[13] The first term, $-\boldsymbol{\Delta\mu}$, is often called the "Stark tuning rate"; it is a quantity which has been measured directly for orientated CO and CN$^-$, for example, at interfaces, either physisorbed (as, e.g., in zeolites) or chemisorbed (as, e.g., on Au or Pt surfaces at the vacuum/metal or metal/electrolyte interface). Calculations of the Stark tuning rate for the free molecule can readily be used in discussing observed shifts in the former case. For example, the Stark shifts of CO physisorbed in X- and Y-zeolites were found to correlate well with a reasonable estimate of the field strength variation at the point of attachment[3]. Also, $\boldsymbol{\Delta\mu}$ can be determined indirectly from gas-phase spectroscopic data,[13−15] and values are available[15,16] for both CO and CN$^-$. The recent literature in this field is quite extensive (see, e.g., refs 15, 17−23), and we have recently[13] reviewed key relevant experiments and calculations for CO.

Special interest in particular arises concerning the Stark effect on CN vibrations as the CN stretch lies in a window in the infrared spectrum, allowing for the possibility that probe molecules containing the CN group could be used to measure local electric field properties in chemical and biochemical systems. To this end, Boxer et al. have studied Stark effects on benzonitrile and acetonitrile,[1] and we have calculated properties for hydrogen cyanide and acetonitrile.[24] For acetonitrile, the calculated gas-phase and observed condensed-phase Stark tuning rates differed by a factor of 4, an event which we postulated to be caused by solvation effects,[24] and indeed we went on to study the solvation of acetonitrile in great detail.[25]

Here we investigate, using a wide range of ab initio and density-functional computational methods, the responses of CO and CN$^-$ to an applied electric field. These are clearly two important compounds, and, indeed, experiments are currently under way in Boxer's laboratories to, for the first time, directly

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measure the Stark tuning rate for CO in an inert solvent. A variety of problems remain to be solved with the interpretation of experiments such as these; however, the most important of which is the effect of the solvent in distorting and amplifying the local electric field that the chromophore experiences, and it is common practice[1,26,27] to state experimentally derived molecular properties to an accuracy of only 30%. Despite this limitation, electroabsorption spectroscopy has been very useful as it can readily discriminate between different models of chemical structure, and typically it is the only available technique for the measurement of the properties in question. Our aim is to complement this experimental technique with a theoretical one which, for large systems, could predict results of comparable or significantly improved accuracy. These are benchmark calculations, making use of the large range of available, accurate experimental data. They also provide computed values for a wide range of electroabsorption and other properties of these molecules which, to date, remain unobserved.

2. Basic Theory

The basic theory for the interpretation of the electric-field dependence of the absorption spectroscopy of isotropic chromophores has been developed by Liptay.[28,29] We have adapted this theory specifically to describe electric field effects on vibrational spectra, extending earlier work in this area (see, e.g., refs 14, 30, 31) and determining many analytical relationships.[13] Along with the effect of the electric field on the vibration frequency (eq 1), it is necessary to determine the effect of the electric field on the vibrational transition moment **M**. This we express as

$$\mathbf{M}(\mathbf{F}) = \mathbf{M} + \mathbf{A}\cdot\mathbf{F} + \mathbf{F}\cdot\mathbf{B}\cdot\mathbf{F} \tag{3}$$

where **A** and **B** are, respectively, the transition polarizability (second-rank) and transition hyperpolarizability (third-rank) tensors. For a diatomic molecule, we assume that the only component of each tensor which is important is the one which is purely in the direction of the bond and hence replace $\boldsymbol{\Delta\mu}$, $\boldsymbol{\Delta\alpha}$, **M**, **A**, and **B** with their scalar components $\Delta\mu$, $\Delta\alpha$, M, A, and B, respectively. For a molecule AB, this direction is taken to be that from A to B thus establishing a sign convention for M, A, and μ. The Liptay equations for the change in the absorption coefficient ϵ at frequency ν of an isotropic sample as a function of the magnitude of the electric field strength F is then expressed through

$$\frac{1}{F^2R(\chi)}\left[\frac{\epsilon}{\nu}(F) - \frac{\epsilon}{\nu}(0)\right] = D_e\frac{\epsilon}{\nu}(0) + F_e\frac{\mathrm{d}}{h\mathrm{d}\nu}\frac{\epsilon}{\nu}(0) + H_e\frac{\mathrm{d}^2}{2h^2\mathrm{d}\nu^2}\frac{\epsilon}{\nu}(0) \tag{4}$$

where $R(\chi)$ is a known[1,2,28,29] function which depends on the relative orientations of the light polarization and the electric field vector, and the three primary experimental observables are expressed as

$$D_e = \frac{A^2}{M^2} + \frac{2B}{M},\ F_e = \frac{2A\Delta\mu}{M} + \frac{\Delta\alpha}{2},\ \text{and } H_e = (\Delta\mu)^2. \tag{5}$$

These coefficients represent contributions to the electroabsorption signal whose shapes are proportional to the absorption band contour (ϵ/ν) and its first and second frequency derivatives, respectively. These functions have been illustrated in a variety of places.[1,2,13,24,26,32] Usually, the transition moment M can be determined from the zero-field absorption spectrum and so eq 5 essentially expresses the three experimental observables D_e, F_e, and H_e in terms of four fundamental molecular parameters $\Delta\mu$, $\Delta\alpha$, A/M, and B/M. The first term, D_e, has the shape of the unperturbed absorption envelope; as in the corresponding perturbation of an electronic transition, this is referred to as the "constant" term. If the transition moment hyperpolarizability B is zero but the transition moment polarizability is finite ($A \neq 0$), the constant term is positive (proportional to the square of the ratio of transition polarizability to transition moment). However, when $B \neq 0$, the constant term may be either positive or negative. The second term in the perturbation, F_e, has the shape of the first derivative of the unperturbed absorption envelope. If the change of dipole moment $\Delta\mu$ accompanying excitation is zero, this term may be either positive or negative, and is a measure of the polarizability change $\Delta\alpha$; examples of both positive and negative $\Delta\alpha$ are found in the electric field perturbation of charge-transfer transitions in metal complexes.[2,26,27,32,33] For vibrational transitions, we anticipate that $\Delta\alpha$ would typically be swamped by $2A\Delta\mu/M$, however. The third term, H_e, has the shape of the second derivative of the absorption spectrum, and is simply proportional to $(\Delta\mu)^2$; it thus yields unambiguously the absolute value of $\Delta\mu$. Unfortunately, no general unique solution for the other three molecular properties, $\Delta\alpha$, A, and B is available from the remaining two experimental observables, D_e and F_e. Another technical problem associated with this approach is that the electric field strength F appearing in eq 4 is the field strength at the molecule which can differ significantly from the field strength actually applied to the sample.[1,2,26,34]

Herein we evaluate from first principles $\Delta\mu$, $\Delta\alpha$, A/M, and B/M and thence D_e, F_e, and H_e. First, we evaluate $\Delta\alpha$ and $\Delta\mu$ directly from eq 2. The potential energy surface is evaluated at seven internuclear separations r (the calculated MP2/cc-pVDZ bond length displaced by 0, ±1, ±2, and ±4 units of zero-point vibration) using five values for the applied field strength $F = 0$, ± 0.01, and ± 0.02 au (1 au = 5142.57 MV cm^{-1}). At each field strength, the potential energy surface is interpolated and the vibration frequency $\nu(F)$ determined variationally; it is then differentiated numerically with respect to the field strength in order to extract $\Delta\alpha$ and $\Delta\mu$. The dipole moment is also evaluated at the same data points, and the results similarly interpolated as a function of r to facilitate the variational determination of the $0 \rightarrow 1$ transition moment M. Finally, M is numerically differentiated as a function of the applied field strength to yield A and B via eq 3. If the dipole moment cannot be determined directly from the wave function, it is obtained by numerically differentiating the energy with respect to the field strength.

An alternative analytical approach is possible in which the electroabsorption response properties are evaluated from more fundamental molecular quantities which have been directly computed. For this, it is possible to use expressions derived from either harmonic[13,14,31,35] or first-order corrected[13] vibrational wave functions. At the harmonic level these are[13]

$$\Delta\mu_H = \frac{h\nu_H}{4{a_1}^2}(2m_2a_1 - 3m_1a_2) \tag{6}$$

$$\Delta\alpha_H = \Delta\alpha'_H + \Delta\alpha''_H$$

where

$$\Delta\alpha'_H = \frac{3h\nu_H}{16{a_1}^4}(3a_2m_1 - 2a_1m_2)^2 \text{ and}$$

$$\Delta\alpha''_H = \frac{h\nu_H}{4{a_1}^2}(2a_1\alpha_2 - 3a_2\alpha_1 - 2{m_2}^2 + 6m_1m_3) \quad (7)$$

$$\frac{M_H}{\gamma} = m_1 \quad (8)$$

$$\frac{A_H}{\gamma} = \alpha_1 + \frac{5m_1m_2}{4a_1} - \frac{3{m_1}^2a_2}{8{a_1}^2} \quad (9)$$

and

$$\frac{B_H}{\gamma} = \frac{\beta_1}{2} + \frac{m_1}{128{a_1}^4}(9m_1a_2 - 14m_2a_1)^2 + \frac{m_1}{16{a_1}^2}(18\alpha_2a_1 - 9\alpha_1a_2 + 18m_1m_3 - 2{m_2}^2) + \frac{3m_2\alpha_1}{4a_1} \quad (10)$$

where the subscript H indicates at the harmonic level of approximation, the constant prefactor γ is defined as

$$\gamma = \left(\frac{h\nu_H}{4a_1}\right)^{1/2} \quad (11)$$

and the molecular property derivatives are defined through

$$V = V_0 + a_1(r - r_e)^2 + a_2(r - r_e)^3 + a_3(r - r_e)^4$$

$$\mu = m_0 + m_1(r - r_e) + m_2(r - r_e)^2 + m_3(r - r_e)^3$$

$$\alpha = \alpha_0 + \alpha_1(r - r_e) + \alpha_2(r - r_e)^2 + \alpha_3(r - r_e)^3$$

$$\beta = \beta_0 + \beta_1(r - r_e) + \beta_2(r - r_e)^2 + \beta_3(r - r_e)^3 \quad (12)$$

where V is the potential energy, μ is the dipole moment, α is the polarizability, and β is the hyperpolarizability. These quantities are related through the expansions

$$V(F) = V - \mu F - \alpha F^2/2 - \beta F^3/6$$

$$\mu(F) = \mu + \alpha F + \beta F^2/2$$

$$\alpha(F) = \alpha + \beta F \quad (13)$$

Usually the major contribution to $\Delta\alpha$ is that involving $2a_1\alpha_2 - 3a_2\alpha_1$, to A/γ is α_1, and to β/γ is $\beta_1/2$.

We do not employ eqs 6−13 directly in the evaluation of $\Delta\alpha$, $\Delta\mu$, A, and B, but these equations are useful in that they identify possible reasons for failure of our numerical variational scheme. Molecular parameters such as β_3 are very difficult to evaluate, while others such as m_3, α_3, and β_2 are quite difficult. Nevertheless, m_3 contributes directly to $\Delta\alpha$, and all other terms contribute beyond the harmonic level of approximation. Typically the electroabsorption responses are insensitive to the values calculated for these high-order derivatives, with accuracy to within an order of magnitude usually all that is essential. Hence, by the explicit evaluation of these derivatives, we monitor possible problems with the calculations before they arise.

3. Computational Issues

Computationally, satisfactory results must be obtained for each of four aspects.

(1) Choice of Electronic Structure Computational Scheme. We investigate 11 ab initio computational schemes: SCF, MP2,[36] MP4,[37] CEPA,[38] QCISD,[39] QCISD(T),[40] CCSD,[41] CCSD(T),[42] CASSCF,[43,44] contracted MRCI,[45,46] and Davidson quadruples-corrected contracted MRCI,[47] MRCI+Q, all evaluated using MOLPRO,[48] as well as the B3LYP[49] density-functional scheme, evaluated using Gaussian-94,[50] and the BLYP[51,52] density functional, evaluated using both Gaussian-94[50] and MOLPRO.[48] Except where explicitly noted, core-valence correlation is not included in the ab initio calculations, as is the default for most computational packages.

(2) Choice of Basis Set. We obtain convergence of calculated properties with respect to basis set through systematic expansion using the augmented correlation-consistent basis sets[53,54] aug-cc-pVDZ, aug-cc-pvTZ, aug-cc-pVQZ, and aug-cc-pV5Z, these ranging in quality from double-ζ to penta-ζ, respectively. Note, however, that the aug-cc-pV5Z basis set was found to be, for both molecules, feasible to use only for the SCF, MP2, MP4, CEPA, QCISD, QCISD(T), CCSD, and CCSD(T) methods; for the CASSCF, MRCI, and MRCI+Q methods, aug-cc-pV5Z results were obtained for CN$^-$ but not CO due to convergence problems. A variety of technical problems were also found for density-functional calculations with large basis sets. First, B3LYP calculations were not feasible using aug-cc-pV5Z. However, BLYP results with this basis set were satisfactorily obtained for CO using MOLPRO, but similar calculations for CN$^-$ failed to converge. Even with the smaller aug-cc-pVQZ basis set, satisfactory results for CN$^-$, were difficult to obtain, with MOLPRO and GAUSSIAN-94 producing significantly different results which appear to be inconsistent with the results obtained using smaller basis sets.

(3) Convergence of the Variational Calculations for Vibration Frequency and the Transition Moment. We test this through the deletion of the two sets of r data points corresponding to the extremum values and repeating the calculations.

(4) Convergence of the Numerical Differentiation with Respect to Field Strength F. This is tested through the application of the Hellmann−Feynman theorem to evaluate the dipole moment directly from the wave function rather than numerically through eq 13. This theorem holds only for some of the computational methods employed herein: SCF, CASSCF, BLYP, and B3LYP.

4. Convergence of Results

Results for 24 calculated molecular properties evaluated from a total of 3570 single-point energy calculations are shown in Table 1 for the CCSD(T), MRCI+Q, and B3LYP methods obtained using the largest practicable basis sets (either aug-cc-pVQZ or aug-cc-pV5Z, see table caption). Convergence of these results with respect to the four aspects described in the previous section are shown in Figure 1 for the basis set, r integration, and F differentiation, and in Figure 2 for the treatment of electron correlation. Specifically, these figures tabulate the maximum “error” of each molecular property associated with all variations considered within that figure. This error is taken as the calculated deviation from the notionally most accurate method considered: for the correlation variation (these are the CCSD(T) results), for the basis set variation (these are those for the largest basis set considered), for the r integration (these are the results obtained using all data points), and for the field differentiation (these are the results obtained with use of the Hellmann−Feynman theorem). The degree of shading in each rectangle indicates the actual error for that particular variation

TABLE 1: Calculated Properties of CO and CN^{-a}

	CO						CN$^-$					
property	obs	CCSD-(T)*^{b}	CCSD-(T)^b	MRCI+Q^c	B3LYP^c	B/C	obs	CCSD-(T)*^{b}	CCSD-(T)^b	MRCI+Q^b	B3LYP^c	B/C
r_e	$2.132^{d,e}$	2.130	2.137	2.142	2.124	1.45	2.224^l	2.223	2.231	2.235	2.211	1.29
ν	2143^d	2156	2138	2124	2188	.53	2053^n	2059	2040	1971^o	2106	.25
a_1	$.6109^{d,e}$	.6181	.6073	.5999	.6351	.55	$[.551]^q$	.5312	.5211	.5162	.5542	.25
a_2	$-.7727^e$	−.7863	−.7651	−.7568	−.7887	.95	$[-.639]^q$	−.6282	−.6125	−.6109	−.6408	.26
a_3	$.606^e$	.6167	.6030	.5941	.6227	.82		.4478	.4443	.4381	.4677	.01
m_0	$.0483^f$	.0484	.0418	.0534	.0404	8.86		.2578	.2549	.2643	.2425	.69
m_1	$-.6698 \pm .0012^g$	−.674	−.675	−.673	−.749	.06	$.27 \pm .06^q$	−.301	−.301	−.297	−.379	.04
m_2	$0.032 \pm .011^g$	.013	.015	.021	−.089	.13		.063	.062	.090	.006	.31
m_3	$.159 \pm .008^h$	.143	.145	.149	.112	.47		.048	.053	.039	.037	.02
α_0	15.7^i	15.4	15.5	15.4	15.4	1.15		37.0	37.3	36.1	39.0	.35
α_1		10.8	10.9	11.2	10.2	.02		18.4	18.5	19.3	18.7	2.56
α_2		4.1	4.2	3.9	3.8	.88		6.0	6.6	6.1	7.9	1.07
α_3		−.2	.4	−.4	−.1	.17		−5.8	−2.4	−.6	−2.8	1.35
β_0		29.5	29	31	32	.39		203	202	205	135	.99
β_1		−5.4	−7.0	−4.7	−4.4	.97		−173	−168	−138	−102	.91
β_2		−1.8	2	−75	4	.59		181	189	−110	240	1.93
β_3		8	49	−85	−13	.01		−233	−272	67	−248	6.09
$\Delta\mu$	$-.01006 \pm .00014^k$	−.01025	−.01027	−.01028	−.01188	.05	$[-.0042 \pm .001^q]$	−.00422	−.00422	−.00386	−.00574	.02
$\Delta\alpha/2$		.106	.107	.110	.101	.05		.177	.180	.179	.182	.26
$2A\Delta\mu/M$		.344	.346	.355	.342	.05		.521	.528	.511	.576	.16
F_e		.451	.453	.464	.443	.05		.698	.708	.691	.758	.15
$2B/M$		49	51	51	48	1.09		633	619	532	337	.58
$(A/M)^2$		282	284	298	208	.03		3830	3910	4380	2519	.07
D_e		330	335	349	255	.02		4560	4530	4920	2857	.04

[a] All properties are in atomic units except for ν which is in cm^{-1}; B/C is the ratio of the error associated with using the aug-cc-pVDZ basis set instead of the largest one for B3LYP calculations to the difference between B3LYP and CCSD(T) results; CCSD(T)* includes core-valence correlation. [b] aug-cc-pV5Z basis. [c] aug-cc-pVQZ basis. [d] From refs 76, 77. [e] From refs 78, 79. [f] From ref 80. [g] From analysis of ref 15. [h] From ref 81. [i] From ref 82. [k] Calculated using experimental data, see text. [l] From ref 83, ±0.008. [n] From ref 84. In neon matrix in which the observed matrix shift for CN under similar conditions compared to gas phase is +1.3 cm^{-1} while other reports include 2038 cm^{-1} (in salts, extrapolated to gas phase[85]), and 2035 ± 40 cm^{-1} (gas phase[83]). [o] This aug-cc-pV5Z result appears anomalous, the aug-cc-pVQZ value being 2134 cm $^{-1}$. [q] Crystal data from ref 16, see text.

as a fraction of this maximum error. To interpret the magnitude of the maximum error, it is shown in *chemical* terms relative to the difference calculated at the most accurate level between CO and CN$^-$, as well in *absolute* terms relative to the average absolute value obtained for CO and CN$^-$.

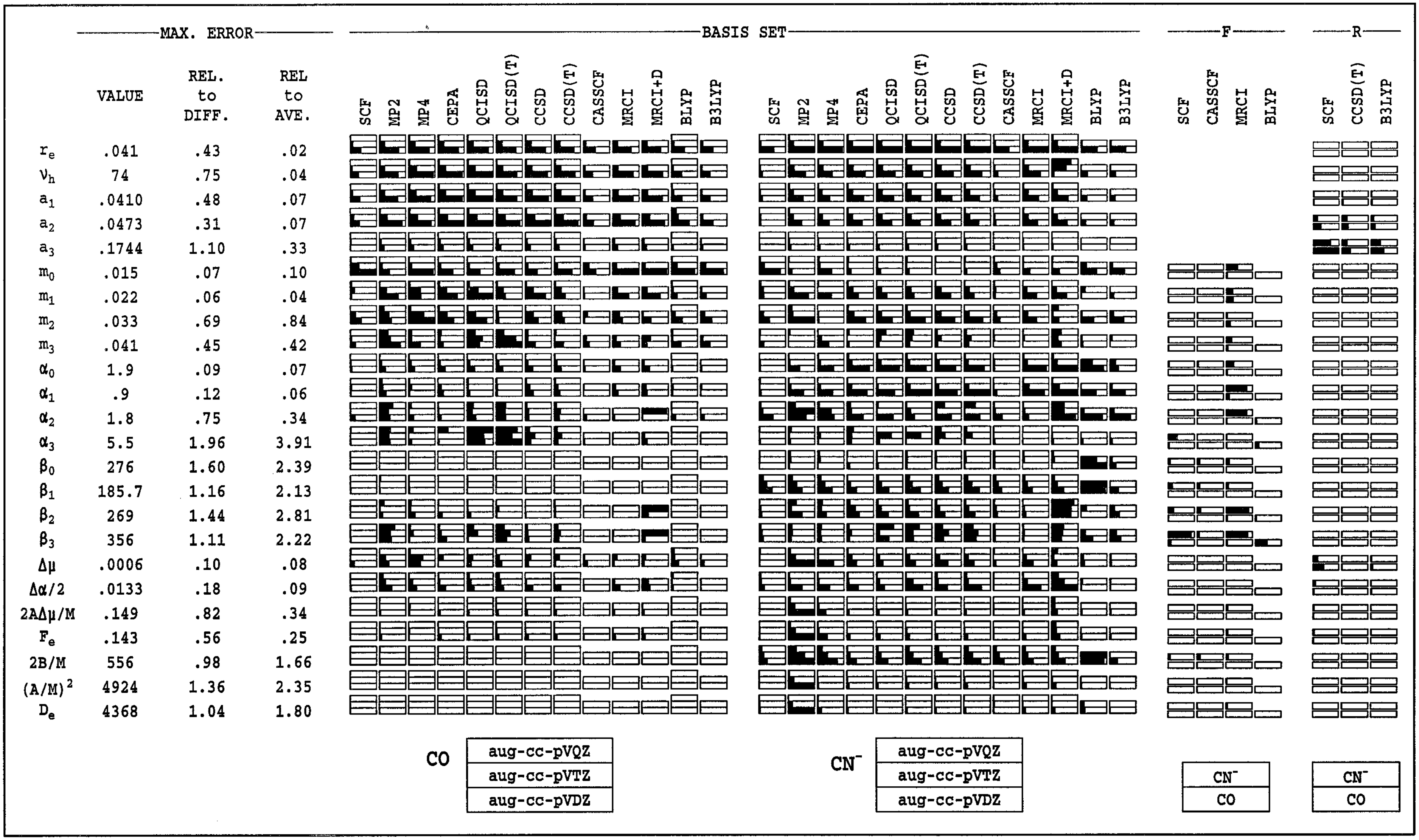
Concerning convergence with respect to basis set, Figure 1 indicates that the calculated well minimum r_e converges rapidly. The stacks of three boxes indicate the differences between the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ results from those of aug-cc-pV5Z, while the stacks of two boxes indicate deviations with respect to the aug-cc-pVQZ results. The maximum deviation found is 0.041 au (0.022 Å) which is 43% of the difference between the CN and CN$^-$ bond lengths and 2% of their average. From this figures, the largest errors occur for the smallest basis set, aug-cc-pVDZ, with a factor of 5 reduction apparent on going to the next largest, aug-cc-pVTZ. A similar reduction occurs also on going to aug-cc-pVQZ and so convergence of the calculated bond lengths to better than 0.001 Å is achieved.

In general, the variationally calculated vibrational frequency ν shows similar basis set convergence properties to those of r_e. The maximum deviation as a function of basis set is 74 cm^{-1} which is 75% of the difference between the two molecules and 4% of the average; the results converge rapidly as the basis set increases, the striking exception being the contracted MRCI+Q results for CN$^-$ which possibly reflect computational difficulties.

Calculated values for the harmonic force constant a_1 and the cubic anharmonicity a_2 closely parallel those reported for the vibration frequency, while for the quartic anharmonicity a_3 it is clear that the use of just 5 different bond lengths does not lead to accurate values. This is not surprising as the derivative evaluation is fully determined in this case; from eqs 6−13 we see that the spectroelectric properties are not particularly sensitive to this parameter, however, but instead the figure shows that the numerical evaluation of the important property a_2 produces quite adequate results.

For the calculated dipole, polarizability, and hyperpolarizability derivatives, Figure 1 indicates excellent convergence for all lower derivatives, with sporadic problems evidenced for the higher derivatives m_3, α_2, α_3, β_2, and β_3. Clearly, more than 5 points are required in order to obtain accurate field derivatives for these quantities, and some methods show basis set convergence problems that possibly arise as a consequence of this. However, while α_2 and m_3 do appear in the correction term $\Delta\alpha''_H$ from eq 7, like a_3 these terms do not contribute significantly to the key electroabsorption properties. There is one exception to this scenario, the evaluation of β_1 by BLYP for CN$^-$, and it appears that this is due to instabilities in the electronic-structure computational methods. It is clear that caution is essential in calculations of this type.

Finally we consider the calculated electroabsorption properties $\Delta\mu$, $\Delta\alpha/2$, $2A\Delta\mu/M$, F_e, $2B/M$, $(A/M)^2$, and D_e. The most noticeable features of Figure 1 are the large values for the maximum errors and the striking qualitative differences of these found between CO and CN$^-$. These are particularly obvious in the MP2 results for CN$^-$, which show large variations with respect to the basis set for most properties. For the properties involving $\Delta\mu$, the differences are due to the fact that for CN$^-$ the two contributions $2m_2a_1$ and $-3m_1a_2$ in eq 6 almost completely cancel each other, resulting in extreme sensitivity of $\Delta\mu$ to the details of the calculation. For $(A/M)^2$, the MP2 value is an order of magnitude too large (see Figure 2) and hence the basis set sensitivity shown in Figure 1 is further enhanced by this factor; the origin of this effect is the near-



	MAX. ERROR		
	VALUE	REL. to DIFF.	REL to AVE.
r_e	.041	.43	.02
ν_h	74	.75	.04
a_1	.0410	.48	.07
a_2	.0473	.31	.07
a_3	.1744	1.10	.33
m_0	.015	.07	.10
m_1	.022	.06	.04
m_2	.033	.69	.84
m_3	.041	.45	.42
α_0	1.9	.09	.07
α_1	.9	.12	.06
α_2	1.8	.75	.34
α_3	5.5	1.96	3.91
β_0	276	1.60	2.39
β_1	185.7	1.16	2.13
β_2	269	1.44	2.81
β_3	356	1.11	2.22
$\Delta\mu$	.0006	.10	.08
$\Delta\alpha/2$	.0133	.18	.09
$2A\Delta\mu/M$	.149	.82	.34
F_e	.143	.56	.25
$2B/M$	556	.98	1.66
$(A/M)^2$	4924	1.36	2.35
D_e	4368	1.04	1.80

Figure 1. The error associated with using smaller basis sets, finite field (*F*) differentiation, and integration points (*R*) for CO and CN$^-$, see text. The maximum error is the largest found for all variations of a particular property, and the degree of shading indicates the ratio of the actual error in a particular case to this maximum error. The maximum error is also shown on a chemical scale relative to the difference between CO and CN$^-$ for that property, as well as an absolute error relative to the average absolute value of the property. All values are in atomic units except for ν_h which is in cm^{-1}; key conversion factors have been given elsewhere.[13]

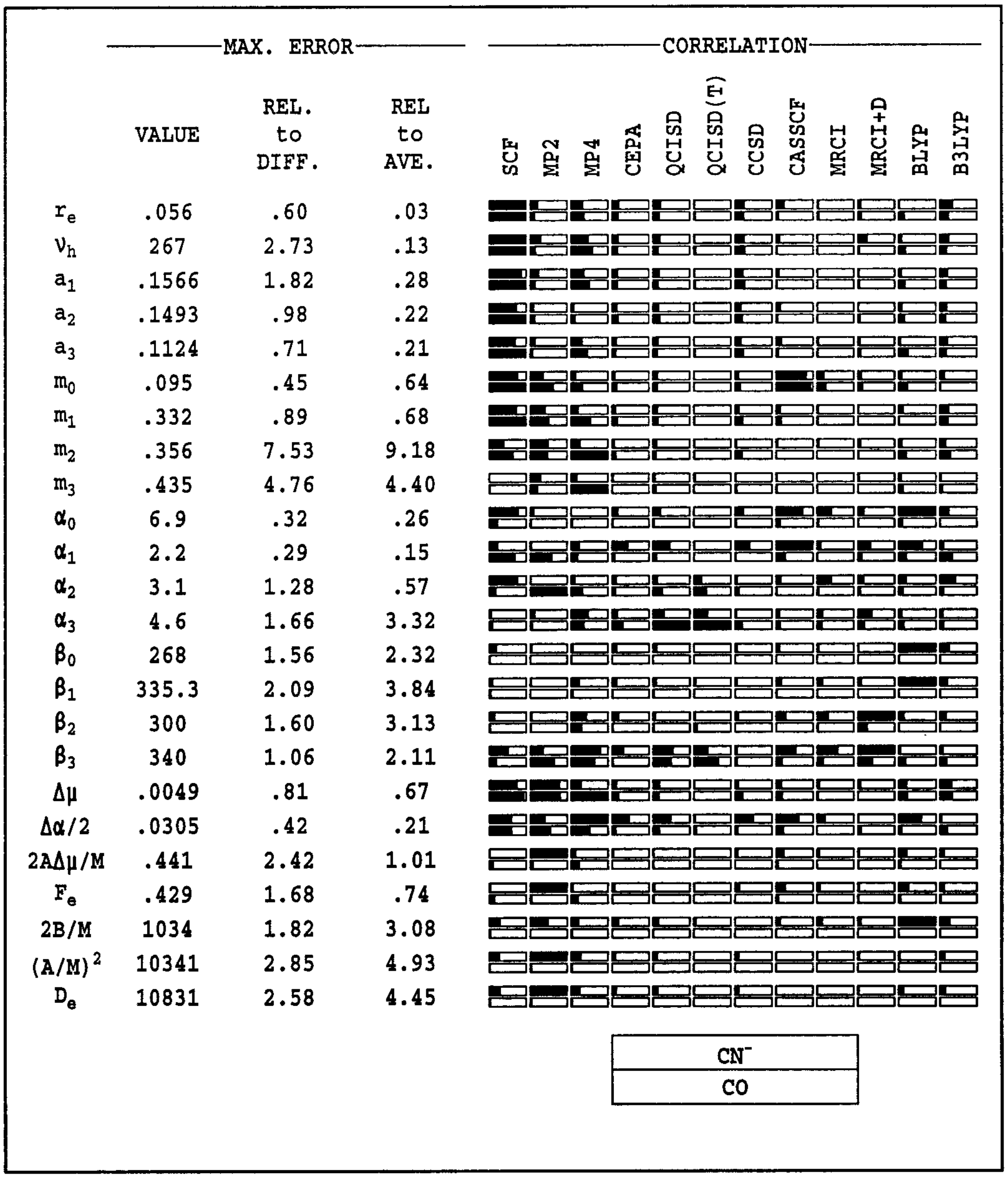


Figure 2. The error associated with using different treatments of electron for CO and CN$^-$, see text and Figure 1. The maximum error is the largest found for all variations of a particular property, and the degree of shading indicates the ratio of the actual error in a particular case to this maximum error. The maximum error is also shown on a chemical scale relative to the difference between CO and CN$^-$ for that property, as well as an absolute error relative to the average absolute value of the property. All values are in atomic units except for ν_h which is in cm^{-1}; key conversion factors have been given elsewhere.[13]

zero value of m_1 predicted by MP2. Excluding the MP2 results for CN$^-$, the errors are quite small with respect to both the difference between the two molecules and the average values except for $2B/M$ for CN$^-$. It is clear that these calculations have not produced a reliable estimate for this quantity, but in all cases $(A/M)^2$ is calculated to be much larger and so the electroabsorption constant-term D_e appears well represented. Improved calculations for CN$^-$ will require more accurate differentiation with respect to applied field and should also benefit from the use of doubly augmented basis sets.

From the plot of the deviations from CCST(T) shown in Figure 2, it is clear that the SCF, CASSCF, MP2, and MP4 methods perform quite poorly. BLYP performs poorly for CN$^-$, as previously discussed, while QCISD, QCISD(T), MRCI, and MRCI+Q perform well for all important properties. In particular, the efficient CEPA and B3LYP methods give results which are typically accurate to within 10−20% absolute accuracy which differentiate properly between CO and CN$^-$ and hence may become the methods of choice for large molecules.

5. Comparison to Experiment

A large variety of calculations have previously been performed for CO and CN$^-$, concentrating on properties such as the ionization energy, equilibrium bond length and vibration frequency,[55−63] polarizabilities and hyperpolarizabilities,[64−71] and the Stark tuning rate.[7,13,17,31,35,55,72−74] Their results, when compared to experimental data, have demonstrated the basic applicability of computational methods including CEPA, CCSD(T), and B3LYP to the calculation the properties considered.

Numerical results obtained for all calculated properties are compared to the available experimental data in Table 1 for the CCSD(T), MRCI+Q, and B3LYP methods; in addition, results for CCSD(T) using the aug-cc-pV5Z basis set are also shown including provision for core-valence correlation and named

TABLE 2: CCSD(T) Calculations of the Vibrational Frequency of CO and CN$^-$ (in cm^{-1})[a]

	CO		CN$^-$	
basis	CCSD(T)	CCSD(T)*	CCSD(T)	CCSD(T)*
aug-cc-pVDZ	2078	2082	1991	1995
aug-cc-pVTZ	2118	2147	2023	2055
aug-cc-pVQZ	2134	2175	2036	2050
aug-cc-pV5Z	2138	2156	2040	2059
observed	2143[76]		2053[84,b]	

[a] The results marked CCSD(T)* include core-valence correlation. [b] See Table 1 caption for alternate estimates.

CCSD(T)*. We investigate the effects of core-valence correlation, as it is known[62] that this relatively minor effect must be included in very accurate calculations for bond lengths and vibration frequencies. As the aug-cc-p?DZ basis sets have been optimized for calculations which neglect core-valence correlation, the use of these basis sets in such calculations is problematic though common;[62] indeed, much more extensive basis sets such as the aug-cc-pCV?DZ series are actually appropriate in this case. However, as our interest lies primarily in the electroabsorption properties, the smaller basis sets suffice for our purpose.

Compared to experiment, all methods shown in Table 1 predict equilibrium bond lengths to within an accuracy of 0.01 au (0.005 Å), with the CCSD(T)* results falling within 0.001 Å. For all observed properties, the MRCI+Q, CCSD(T), and CCSD(T)* results agree with experiment very well, the largest deviations being for the m_2 and m_3. However, many more observed properties are available for CO than for CN$^-$ and the errors in the calculated properties for the anion are expected to be larger than those for the neutral species. Core-valence correlation is also seen to be important for the calculated vibration frequency (its effects are of order 1%), and, to investigate this further, the CCSD(T) and CCST(T)* results obtained using all basis sets are shown in Table 2. Through cancellation of errors, the aug-cc-pVTZ basis set used in calculations including core-valence correlation gives the best results, but the effects of core-valence correlation on the vibration frequency appear to be overestimated by a factor of 2 using the aug-cc-pV5Z basis set. Core-valence correlation corrects the calculated equilibrium dipole moments by 10% and aligns them with the experimental results, but much smaller changes are calculated for most other properties. We conclude that at the current time it is not necessary to include core-valence correlation in calculations of electroabsorption response properties, and that results obtained using CCSD(T), MRCI+Q, and B3LYP techniques are, in general, display adequate agreement both with each other and with experiment. The most significant problems with the B3LYP results arise from the second derivative of the dipole moment, m_2; for both molecules the value of this quantity is quite small, and B3LYP differs significantly from CCSD(T) and MRCI+Q for this property.

One of the most relevant observed properties listed in Table 1 is the electroabsorption response property $\Delta\mu$. Experimental values of $\Delta\mu$ for CO or CN$^-$ have not been directly measured in either the gas phase or an inert solvent. However, values may be estimated from experimental data using eq 6. This has been done for CO by Lambert,[15] and the result is $\Delta\mu = 0.01003 \pm 0.00014$ au. Equation 6 is, however, only valid in the harmonic approximation. Our CCSD(T)/aug-cc-pV5Z and other (variational) calculations indicate that the anharmonicity correction for CO is +0.00003 au, a value which agrees both with that obtained using the full perturbation-theory expressions and all calculated parameters as well as the estimate obtained by Lambert[75]using perturbation-theory expressions and the available set of experimental data. Hence, the most reliable experimentally derived estimate for $\Delta\mu$ is 0.01006 ± 0.00014 au. This and the ab initio computed values are in excellent agreement. Spitzer, Sievers, and Silsbee[16] have determined for CN$^-$ values for a_1, a_2, and m_1 for CN$^-$ in KBr and their results are shown in Table 2, along with $\Delta\mu$ evaluated using eq 6 assuming that $m_2 = 0$. While the term involving m_2a_1 is 1−2% of the main contribution for CO, the ab initio calculations indicate that it is 12% for CN$^-$, but it is clear that their neglect of this term remains a minor source of error compared to the uncertainty in the experimental measurement of m_1. However, this scenario is not generally applicable, with, e.g., both terms being of the same magnitude but opposite sign for HCN.[24] For CN$^-$ Spitzer et al.[16] have also determined $\Delta\mu$ directly using Stark spectroscopy in KBr crystal. The value thus obtained is −0.0075 au, a value which, given the available raw experimental data and possible difficulties with its interpretation, was felt to "agree reasonably well" with their computed value, −0.0042 au.

6. Conclusions

To study vibrational frequency shifts in condensed phases or at electrode surfaces, it is necessary to know with high accuracy at least[17,72] the basic electroabsorption response properties of the molecule. In these benchmark calculations for the important molecules CO and CN$^-$, we have shown that modern high-end computational methods using finite fields can produce results which agree with each other and with the available experimental data for a wide range of properties; other high derivatives are less reliably evaluated, however, but modified computational strategies could be designed if the need required it. In particular, improved results would most readily be obtained by improving the accuracy of the finite-field differentiation, inclusion of double augmentation in the basis sets, and proper treatment of core-valence correlation. For very accurate calculations, inclusion of relativistic effects or the treatment of electron correlation beyond that included in MRCI+Q and CCSD(T) will be needed. However, we suggest that, at the present time, key properties such as $\Delta\alpha$ and $\Delta\mu$ for general molecules of this type could readily be evaluated to within 10−20% accuracy, providing an important complement to experimental electroabsorption techniques. In particular for CO and CN$^-$, our calculations indicate that the observed constant (D_e) and first-derivative (F_e) terms in vibrational electroabsorption spectra of molecules of this type should be dominated by the transition moment polarizability rather than the vibrational polarizability or other terms.

As the efficiency of density-functional calculations increases dramatically compared to ab initio calculations such as CCSD(T) and MRCI as the size of the molecule increases, it is clear that methods such as B3LYP offer the best available compromise between accuracy and computational cost. To further investigate this, Table 1 shows the ratio of the error associated with using the smaller aug-cc-pVDZ basis set as a ratio of the difference between the CCSD(T) and B3LYP results. If this ratio is large for a particular property then B3LYP calculations with large basis sets are warranted; alternatively, if this ratio is small, then use of aug-cc-pVDZ is adequate. Differing properties for differing molecules fall into different categories, but for the key electroabsorption properties the ratios are typically less than 0.1. Hence, to calculate electroabsorption properties of large molecules to within 10−20% accuracy, the optimum scheme appears to be B3LYP/aug-cc-pVDZ.

References and Notes

(1) Chattopadhyay, A.; Boxer, S. G. *J. Am. Chem. Soc.* **1995**, *117*, 1449.

(2) Bublitz, G. U.; Boxer, S. G. *Annu. Rev. Phys. Chem.* **1997**, *1997*, 213.

(3) Hush, N. S.; Williams, M. L. *J. Mol. Spectrosc.* **1974**, *50*, 349.

(4) Gready, J. E.; Bacskay, G. B.; Hush, N. S. *Chem. Phys.* **1977**, *24*, 333.

(5) Gready, J. E.; Bacskay, G. B.; Hush, N. S. *Chem. Phys.* **1977**, *23*, 9.

(6) Gready, J. E.; Bacskay, G. B.; Hush, N. S. *Chem. Phys.* **1977**, *22*, 141.

(7) Gready, J. E.; Bacskay, G. B.; Hush, N. S. *Chem. Phys.* **1978**, *31*, 467. Note that in Table 11 the field strength Ez in the second column should read −0.01.

(8) Gready, J. E.; Bacskay, G. B.; Hush, N. S. *Chem. Phys.* **1978**, *31*, 375.

(9) Hush, N. S.; Williams, M. L. *Chem. Phys. Lett.* **1970**, *5*, 507.

(10) Hush, N. S.; Williams, M. L. *Chem. Phys. Lett.* **1970**, *6*, 163.

(11) Hush, N. S.; Williams, M. L. *Theor. Chim. Acta* **1972**, *25*, 346.

(12) Hush, N. S.; Williams, M. L. *Theor. Chim. Acta* **1972**, *26*, 141.

(13) Hush, N. S.; Reimers, J. R. *J. Phys. Chem.* **1995**, *99*, 15798.

(14) Lambert, D. K. *Solid State Commun.* **1984**, *51*, 297.

(15) Lambert, D. K. *Electrochim. Acta* **1996**, *41*, 623.

(16) Spitzer, R. C.; Sievers, A. J.; Silsbee, R. H. *J. Opt. Soc. Am. B* **1992**, *9*, 978.

(17) Head-Gordon, M.; Tully, J. C. *Chem. Phys.* **1993**, *175*, 37.

(18) Hill, J. R.; Dlott, D. D.; Rella, C. W.; Peterson, K. A.; Decatur, S. M.; Boxer, S. G.; Fayer, M. D. *J. Phys. Chem.* **1996**, *100*, 12100.

(19) Zou, S.; Weaver, M. J. *J. Phys. Chem.* **1996**, *100*, 4237.

(20) Inukai, J.; Morioka, Y.; Kim, Y.-G.; Yau, S.-L.; Itaya, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1787.

(21) Villegas, I.; Weaver, M. J. *J. Phys. Chem. B* **1997**, *101*, 5842.

(22) Weaver, M. J.; Williams, C. T.; Zou, S.; Yeung, H.; Chan, H.; Takoudis, C. G. *Catal. Lett.* **1998**, *52*, 181.

(23) Cuesta, A.; Gutiérrez, C. *Langmuir* **1998**, *14*, 3397.

(24) Reimers, J. R.; Zeng, J.; Hush, N. S. *J. Phys. Chem.* **1996**, *100*, 1498.

(25) Reimers, J. R.; Hall, L. E. *J. Am. Chem. Soc.* **1999**, *121*, 3730.

(26) Oh, D. H.; Sano, M.; Boxer, S. G. *J. Am. Chem. Soc.* **1991**, *113*, 6880.

(27) Oh, D. H.; Boxer, S. G. *J. Am. Chem. Soc.* **1989**, *111*, 1130.

(28) Liptay, W. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 177.

(29) Liptay, W. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1974; p. 129.

(30) Broo, A. *Chem. Phys.* **1993**, *174*, 127.

(31) Martí, J.; Bishop, D. M. *J. Chem. Phys.* **1993**, *99*, 3860.

(32) Reimers, J. R.; Hush, N. S. *J. Phys. Chem.* **1991**, *95*, 9773.

(33) Reimers, J. R.; Hush, N. S. In *Mixed Valence Systems: Applications in Chemistry, Physics, and Biology*; Prassides, K., Ed.; Kluwer Academic Publishers: Dordrecht, 1991; p 29.

(34) Bublitz, G. U.; Boxer, S. G. *J. Am. Chem. Soc.* **1998**, *120*, 3988.

(35) Bishop, D. M. *J. Chem. Phys.* **1993**, *98*, 3179; erratum **1993**, *99*, 4875.

(36) Møller, C.; Plesset, M. S. *Phys. Rev. A* **1971**, *46*, 618.

(37) Kirshnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91.

(38) Meyer, W. *Int. J. Quantum Chem. Symp.* **1971**, *5*, 341.

(39) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(40) Gauss, J.; Cremer, C. *Chem. Phys. Lett.* **1988**, *150*, 280.

(41) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(42) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(43) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1985**, *82*, 5053.

(44) Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1985**, *115*, 259.

(45) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1988**, *89*, 5803.

(46) Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1988**, *145*, 514.

(47) Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61.

(48) Werner, H.-J.; Knowles, P. J.; Almlöf, J.; Amos, R. D.; Deegan, M. J. O.; Elbert, S. T.; Hampel, C.; Meyer, W.; Peterson, K.; Pitzer, R.; Stone, A. J.; Taylor, P. R.; Lindh, R.; Mura, M. E.; Thorsteinsson, T. MOLPRO-97 program package.

(49) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(50) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. A.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*; Gaussian Inc.: Pittsburgh, 1995.

(51) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(52) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 789.

(53) Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys* **1992**, *96*, 6796.

(54) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(55) Bauschlicher, C. W., Jr. *Chem. Phys. Lett.* **1985**, *118*, 307.

(56) Botschwina, P. *Chem. Phys. Lett.* **1985**, *114*, 58.

(57) Peterson, K. A.; Woods, R. C. *J. Chem. Phys.* **1987**, *87*, 4409.

(58) Tellinghuisen, J.; Ewig, C. S. *J. Chem. Phys.* **1989**, *91*, 5476.

(59) Scuseria, G. S.; Lee, T. J. *J. Chem. Phys.* **1990**, *93*, 5851.

(60) Wang, C.-R.; Huang, R.-B.; Liu, Z.-Y.; Zheng, L.-S. *Chem. Phys. Lett.* **1995**, *237*, 463.

(61) Pudzianowski, A. T. *J. Chem. Phys.* **1995**, *102*, 8029.

(62) Botschwina, P.; Seeger, S.; Mladenovic, M.; Schulz, B.; Horn, M.; Schmatz, S.; Flügge, J.; Oswald, R. *Int. Rev. Phys. Chem.* **1995**, *14*, 169.

(63) Zhan, G. G.; Iwata, S. *J. Chem. Phys.* **1996**, *104*, 9058.

(64) Fowler, P. W.; Diercksen, G. H. F. *Chem. Phys. Lett.* **1990**, *167*, 105.

(65) Colwell, S. M.; Murray, C. W.; Handy, N. C.; Amos, R. D. *Chem. Phys. Lett.* **1993**, *210*, 261.

(66) Lee, A. M.; Colwell, S. M. *J. Chem. Phys.* **1994**, *101*, 9704.

(67) Sauer, S. P. A.; Oddershede, J. *Int. J. Quantum Chem.* **1994**, *50*, 317.

(68) Hermansson, K.; Tepper, H. *Mol. Phys.* **1996**, *89*, 1291.

(69) Luis, J. M.; Martí, J.; Andrés, J. L. *Chem. Phys.* **1997**, *217*, 29.

(70) Simon, S.; Duran, M. *THEOCHEM* **1998**, *455*, 165.

(71) Itskowitz, P.; Berkowitz, M. L. *J. Chem. Phys.* **1998**, *109*, 10142.

(72) Bagus, P. S.; Nelin, C. J.; Müller, W.; Philpott, M. R.; Seki, H. *Phys. Rev. Lett.* **1987**, *58*, 559.

(73) Andrés, J. L.; Duran, M.; Lledós, A.; Bertrán, J. *Chem. Phys.* **1991**, *151*, 37.

(74) Luis, J. M.; Martí, J.; Duran, M.; Andrés, J. L. *Chem. Phys.* **1995**, *102*, 7573.

(75) Lambert, D. K. *J. Chem. Phys.* **1988**, *89*, 3847.

(76) Herzberg, G. *Molecular spectra and structure. I. Spectra of diatomic molecules*, 2nd ed.; D. Van Nostrand: Princeton, 1965.

(77) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand: Princeton, 1979.

(78) Mantz, A. W.; Watson, J. K. G.; Rao, K. N.; Albritton, D. L.; Schmeltekopf, A. L.; Zare, R. N. *J. Mol. Spectrosc.* **1971**, *39*, 180.

(79) Mantz, A. W.; Maillard, J.-P.; Roh, W. B.; Rao, K. N. *J. Mol. Spectrosc.* **1975**, *57*, 155.

(80) Chackerian, C., Jr.; Tipping, R. H. *J. Mol. Spectrosc.* **1983**, *99*, 431.

(81) Bouanich, J.-P.; Brodbeck, C. *J. Quant. Spectrosc. Radiat. Transfer* **1974**, *14*, 1199.

(82) Bridge, N. J.; Buckingham, A. D. *Proc. R. Soc.* **1966**, *295A*, 334.

(83) Braeforth, S. E.; Kim, E. H.; Arnold, D. W.; Newmark, D. M. *J. Chem. Phys.* **1993**, *98*, 800.

(84) Forney, D.; Thompson, W. E.; Jacox, M. E. *J. Chem. Phys.* **1992**, *97*, 1664.

(85) Sherman, W. F.; Wilkinson, G. R. In *Vibrational spectroscopy of trapped species*; Halam, H. E., Ed.; Wiley: London, 1973.