

Computational Approaches to Determining Accurate Band Strengths

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1 Introduction

With the advent of high-speed computing and improved algorithms, computational chemistry techniques have become competitive with the best experimental techniques for determining line strengths for rovibrational and electronic transitions in molecular systems (Bauschlicher & Langhoff 1991). This is particularly the case at high temperatures where the molecules are highly rotationally excited. While it is difficult to measure line strengths at stellar temperatures, the theoretical values can be very reliable if a globally accurate transition moment function (TMF) is used in conjunction with high-quality experimental or theoretical potentials.

In this review we demonstrate the current state-of-the-art in theoretically determining accurate transition probabilities for a variety of astrophysically interesting molecules. The quality of the results is shown to be strongly dependent on the system studied. For example, transition probabilities for first-row diatomic systems rival the best experiments in accuracy, whereas calculations for transition metal systems are much more difficult.

To illustrate a molecular transition where very accurate benchmark studies have been performed (Bauschlicher & Langhoff 1987), we first consider the ultraviolet ($A^2\Sigma^+ - X^2\Pi$) band system of the hydroxyl radical (OH). Besides being of interest in a variety of astrophysical sources, this band system has been used extensively for combustion diagnostics. To deduce the temperature in a flame or to determine the opacity in the stellar environment, accurate line strengths are required. The lifetimes in OH vary markedly with rotation owing to the rapid decrease in the transition moment with internuclear distance (r), the high degree of centrifugal distortion, and predissociation of higher rotational levels of $v=0-2$ from a crossing on the outer limb of the $A^2\Sigma^+$ state by the repulsive $4\Sigma^-$ state. The experimental lifetimes for the lowest ro-vibrational level vary significantly. To determine which of these experimental values is best, very extensive and carefully benchmarked calculations are required. We demonstrate that 5% accuracy can be achieved in the calculated line strengths by carrying out full configuration-interaction (FCI) calculations to benchmark the electron correla-

tion methods in conjunction with a systematic saturation of the one-particle basis.

We next consider the calculation of the line strengths for the ro-vibrational bands in the $X^1\Sigma^+$ ground state of SiO (Langhoff & Bauschlicher 1993). The $\Delta v=1$ and 2 sequences have been observed in absorption in the infrared spectra of cool stars (Cohen et al. 1992; Rinsland & Wing 1982; Ridgway et al. 1984). The line strengths that are in current use are based on the electric dipole moment function (EDMF) of Tipping & Chackerian (1981), which is in the form of a Padé approximant, chosen to reproduce the accurate experimental dipole moments for $v=0-3$, to have the proper united and separated atom limits, and to have the correct long-range dependence on internuclear separation. We study the convergence of the EDMF with improvements in the calculations. Line strengths based on our most accurate *ab initio* EDMF are larger than Tipping & Chackerian by a factor of about 1.2 and 2.0 for the fundamentals and first overtone transitions, respectively.

We illustrate calculations on transition metal systems by discussing the spectroscopy of ZrO. Since the absorption bands of ZrO have been used to classify S stars (Johnson 1982; Littleton & Davis 1985), it is important to have accurate electronic transition probabilities for the important band systems of this molecule. Theoretical calculations (Langhoff & Bauschlicher 1990a) have characterized both the singlet and triplet band systems of this molecule up to an energy of about $30\,000\text{ cm}^{-1}$. The theoretical radiative lifetimes are in reasonable accord with the experimental lifetimes that are available for three states. In addition, recent absorption experiments give line strengths that are also in good accord with theory. Thus, overall the band systems of this molecule are relatively well known, although some uncertainties remain. For example, theory predicts a strong $E^1\Phi - A^1\Delta$ transition in the $16\,000\text{--}17\,000\text{ cm}^{-1}$ region, but this transition has not been observed in the laboratory or in stellar spectra. Possibly this transition is obscured by the γ bands of ZrO or the upper state lies too high to be significantly populated. Analogous calculations for TiO have proven to be very challenging. We conclude this review by discussing the complexity of studying first transition row metal systems such as FeH and TiO.

2 Methods

The ultimate goal of quantum chemistry is to solve the electronic Schrödinger equation, which would give the exact nonrelativistic electronic wave function within the Born-Oppenheimer approximation. However, the exact solution of this integral differential equation is not achievable for more than two electrons. Thus most theoretical approaches (excluding methods such as Monte Carlo (Diedrich & Anderson 1992) and density functional (Parr & Yang 1989)) formulate the solution as a double basis set expansion. The first expansion (or so-called one-particle basis) determines the molecular orbitals as a linear combination of atom centered functions usually taken to be Gaussian functions. The best single Slater determinant (antisymmetrized product of molecular orbitals) gives the so-called

self-consistent-field (SCF) approximation. This ignores the instantaneous correlation of the electrons. The second expansion accounts for the electron correlation by formulating the wave function as a linear combination of determinants with one or more electrons promoted from occupied orbitals into virtual orbitals (single, double, triple excitations etc.). This expansion is generally referred to as the n -particle expansion and these various approaches of including electron correlation are often referred to as configuration-interaction (CI) methods (see, for example, Shavitt 1977; Saunders & van Lenthe 1983). An alternative approach is to start from an exponential ansatz, which leads to the singles and doubles coupled cluster (CCSD) approach (see for example Bartlett 1981).

If all excitations (up to n -tuple excitations for n electrons) are included in the wave function, we have the special case of a full configuration-interaction (FCI) calculation. This gives the exact result for the one-particle basis set employed and is an unambiguous standard with which to compare approximate electron correlation approaches that truncate the configuration expansion. Since the size of the expansion increases factorially with the number of electrons correlated, it is computationally intensive to carry out FCI calculations in a high-quality one-particle basis set if more than about six electrons are correlated. However, improvements in algorithms (Siegbahn 1984; Knowles & Handy 1984) and high-speed computers have allowed a rather complete set of benchmark calculations (Bauschlicher et al. 1990a) to be performed. The goal is to find a truncated electron correlation procedure that reproduces the FCI result in a realistic one-particle basis set (one that obtains a significant fraction of the correlation energy) and then carry out a systematic study of the property as a function of improvements in the one-particle basis set at the truncated correlation level. The property should approach the exact non-relativistic result as the one-particle basis approaches completeness if there is not an unexpected strong coupling between the one- and n -particle expansions. We demonstrate this approach for the electronic transition moment of the ultraviolet system of OH in the next section.

To compute accurate spectroscopic constants and transition probabilities it is necessary to describe the ground and excited states for a range of internuclear distances that encompass the Franck-Condon region. Configuration-interaction methods based on a single reference (SCF wave function) are not adequate for this purpose. To describe the multireference character and near degeneracy effects in the wave functions it is necessary to begin with a multiconfigurational SCF or MCSCF description, where the molecular orbitals are optimized simultaneously with the CI coefficients in the MCSCF wave function. One particular choice of an MCSCF wave function that is widely used is the so-called complete-active-space SCF (CASSCF) wave function (Roos 1987), where an FCI calculation is performed within some specified active space (subset of orbitals that describe the important correlation effects). The active space is designated by the number of orbitals in each of the symmetries. For example, an active space of (3221) denotes the number of orbitals in the a_1 , b_1 , b_2 , and a_2 C_{2v} symmetries in which the calculations for a heteronuclear diatomic molecule are carried out. Since it is computationally much easier to use one set of orthonormal molec-

ular orbitals, the energy optimization is generally carried out for the average energy of all states treated in the subsequent CI calculations. The active space must be large enough to provide an accurate description of each of the states over the relevant range of internuclear distances. A CASSCF calculation where the average energy of several states is optimized is generally referred to as a state-averaged or SA-CASSCF treatment. A CI calculation based on a CASSCF zeroth-order wave function (i.e. single and double excitations from all configurations in the CASSCF wave function) is generally referred to as a multireference configuration-interaction (MRCI) treatment to distinguish it from one based on the SCF wave function (generally referred to as a singles and doubles CI or SDCI calculation).

Unfortunately the length of the MRCI expansion grows very rapidly with the size of the active space in the CASSCF calculation. Several procedures have been used to reduce the size of this expansion. One procedure is to not include all excitations in the wave function, but to discard the less important configurations based on their contribution to the energy using second-order perturbation theory (Shavitt 1977; Buenker & Peyerimhoff 1974). A second approach is to generate single and double excitations not from the full CASSCF wave function, but from a subset of important configurations (based on their coefficients in the CASSCF wave function). For example, the notation SA-CASSCF/MRCI(0.05) denotes that a state-averaged CASSCF calculation is performed followed by an MRCI calculation where the zeroth-order reference contains configurations that have a coefficient larger than 0.05 (for any state at any relevant internuclear distance) in the CASSCF wave function. Finally, a relatively new procedure called the internally-contracted MRCI (Werner & Knowles 1988) or IC-MRCI has been introduced as an efficient means of greatly reducing the number of variational parameters. Here the ratio of the coefficients in the final CI wave function are constrained to be those in the zeroth-order wave function. This method closely reproduces the fully variational MRCI calculation when the zeroth-order wave function is adequate. This approach can greatly extend the size of configuration spaces (and thus CASSCF active spaces) that can be employed.

There are electron correlation methods that attempt to incorporate the effects of higher than double excitations into the wave function. A simple empirical approach is to use the so-called Davidson correction (Langhoff & Davidson 1974; Blomberg & Siegbahn 1983) (denoted +Q). However, there are other single-reference based methods, such as the coupled-electron pair approximation (CEPA) (Ahlrichs 1979) and coupled-pair functional (CPF) (Ahlrichs et al. 1985) methods, that incorporate the effect of higher excitations in a more rigorous manner. The accuracy of the CCSD method can also be greatly enhanced by incorporating a perturbational estimate of connected triple excitations (Raghavachari et al. 1989), denoted CCSD(T). A multireference variation of CPF is the averaged coupled-pair functional (ACPF) (Gdanitz & Ahlrichs 1988) method. Our experience (Bauschlicher et al. 1990b) is that this method provides superior properties such as dipole moments compared with the analogous MRCI method. A further discussion of these methods is outside the scope of this review.

We close the discussion of methods by describing the one-particle basis sets currently employed. The FCI benchmark studies (Bauschlicher et al. 1990a) showed that CASSCF/MRCI calculations accounted for most of the electron correlation. Thus the principal limitation of theoretical calculations could often be ascribed to incompleteness in the one-particle basis set. Recently, considerable progress has been made in improving the quality of these bases. For example, the atomic natural orbital (ANO) basis sets developed by Almlöf & Taylor (1987) and the correlation-consistent basis sets developed by Dunning and co-workers (Woon & Dunning 1993 and references therein) have contraction coefficients determined at the correlated level. We discuss basis sets here only to the extent to define the notation and to indicate what is required for high accuracy. For example, an oxygen atom basis set containing four *s* and two *p* functions, $[4s\ 2p]$, would be considered to be of double-zeta quality, since it contains two functions for each of the oxygen $1s$, $2s$, and $2p$ orbitals. Basis sets of triple-zeta or larger are required for quantitative accuracy. In addition, polarization functions (in this case *d*, *f* and higher angular momentum functions) are required to reach basis set convergence. In general, basis sets saturated up through *g* functions are necessary for very accurate calculations on first-row atoms. For second-row and transition metal atoms the basis set requirements become even more severe. More details of the actual basis sets employed are given in the following sections.

3 The Ultraviolet System of OH

In this section we describe our work (Bauschlicher & Langhoff 1987) on the $A^2\Sigma^+ - X^2\Pi$ electronic transition moment function (TMF) of OH that included FCI benchmark calculations. While it is not feasible to place meaningful rigorous error bounds on calculated properties, an estimate of the accuracy can be obtained by studying the convergence of the property with respect to a systematic expansion of the one- and *n*-particle spaces. The utility of this procedure is enhanced if FCI calculations can be performed in a meaningful one-particle basis. Thus our approach is to find a truncated correlation method that reproduces the FCI in a relatively small (but realistic) one-particle basis, and then carry out this truncated CI in a nearly complete one-particle basis.

For OH the FCI benchmark calculations were carried out in a $[4s3p2d]$ contracted set for oxygen and a $[2s1p]$ contracted set for hydrogen described in more detail in the original reference. The subsequent MRCI calculations used to generate the TMF utilized a $[6s\ 5p\ 4d\ 2f\ 1g]$ basis for oxygen and a $[4s\ 3p\ 2d]$ basis for hydrogen. The oxygen basis set provides an accurate description of both O and O⁻ character in the wave function. These basis sets were contracted using the ANO approach and should give results close to the basis set limit. Calculations were carried out with several extensions to this basis set to ensure that the TMF was converged with respect to adding additional functions.

In Table I we compare the FCI $A^2\Sigma^+ - X^2\Pi$ transition moment with those obtained from a variety of both single-reference and multireference-based corre-

Table 1. Study of the $A - X$ transition moment of OH with level of correlation treatment at $r=1.80 a_0$ in the $[4s3p2d/2s1p]$ Gaussian basis set

Calculation	moment
FCI 5-electron	0.100959
FCI 7-electron	0.119530
SCF	0.173121
SDCI	0.125307
MCPF	0.121417
(222) CASSCF	0.161812
(222) CASSCF ^a	0.169252
(222) MRCI(0.0)	0.122965
(222) MRCI(0.05)	0.123246
(322) MRCI(0.0)	0.122522
(3221) CASSCF	0.123482
(3221) MRCI(0.0)	0.119841
(3221) MRCI(0.01)	0.120024
(3221) MRCI(0.02)	0.122090

^a Separate CASSCF calculations are performed for the two states and a non-orthogonal transition moment is evaluated.

lation methods that truncate the n -particle space. All values were obtained at $r=1.80 a_0$ using the $[4s3p2d/2s1p]$ Gaussian basis. Since oxygen $2s$ correlation increases the transition moment by 20% at the FCI level, all calculations were carried out correlating all but the oxygen $1s$ electrons.

We first consider the methods based on a single reference treatment given in the upper portion of Table I. The SCF moment is significantly too large, but the magnitude decreases substantially with the addition of electron correlation. The discrepancy with the FCI result is nearly an order of magnitude less at the SDCI level than at the SCF level. Furthermore, the error at the modified CPF (MCPF) (Chong & Langhoff 1986) level is a factor of three less than at the SDCI level, giving a lifetime only 3% shorter than at the FCI level. It is expected, however, that this approach will become less satisfactory as the molecule is displaced further from its equilibrium value.

The $A - X$ transition moment is also significantly too large at the (222) CASSCF level. Note that the moment is only slightly different if instead of the SA-CASSCF procedure, which employs a common set of orthogonal orbitals, we carry out separate (222) CASSCF calculations for each state and compute the moment using a non-orthogonal transition moment method. Hence, the differences with the FCI are *not* principally due to using a common set of averaged orbitals. Significant improvements are also observed as the level of correlation

is increased for the multireference-based approaches. The (222) MRCI moment is about 3% larger than the FCI, whether reference configurations are selected using a threshold of 0.05 or all CASSCF configurations are included. The addition of the 5σ orbital to the CASSCF and MRCI active space has virtually no effect on the computed transition moment, as was the case for the $X^2\Pi$ dipole moment of OH (Langhoff et al. 1987). However, the addition of the 1δ orbital to the active space results in a CASSCF transition moment that is superior to the SDCl, and virtually identical to the (222) MRCI results. The addition of more extensive correlation to the (3221) CASSCF wave function yields a transition moment in excellent agreement with the FCI value. This (3221) MRCI calculation is sensitive to the reference selection threshold, with 0.01 reproducing the unselected results, but a threshold of 0.02 giving a TM more similar to the (222) MRCI result, because most of the references involving the 1δ orbital have coefficients less than 0.02. Since the (3221) MRCI(0.01) transition moment is in excellent agreement with the FCI result, a very accurate transition moment is expected at this level of correlation treatment in the limit of a complete one-particle Gaussian basis. The moment should be globally accurate, because the (3221) CASSCF calculation is sufficiently flexible to provide a uniform treatment at all r values.

In our theoretical study of the $A - X$ transition moment we carried out the (3221) CASSCF/MRCI(0.01) calculation using the very complete basis sets for oxygen and hydrogen described above. Basis set saturation studies indicated that this basis was near the basis set limit. Using either the theoretical or RKR potentials in the vibrational analysis produced ratios of Einstein coefficients that were in reasonable accord with the limited experimental data. Experimental lifetime measurements for the $v=0$, $N=1$ level vary from about 625 ± 25 ns for experiments based on the Hanle effect (German et al. 1970) to 760 ± 20 ns measured by Brzozowski et al. (1978) using the high-frequency deflection technique. The lifetimes measured by laser excitation fluorescence range from 721 ± 5 ns measured by McDermid & Laudenslager (1982) to 686 ± 14 ns and 693 ± 10 ns determined by Dimpfl & Kinsey (1979) and German (1976), respectively. Our best estimate for the lifetime of the $v'=0$ $N'=1$ level of the $A^2\Sigma^+$ state of OH is 685 ± 20 ns. This value is in excellent agreement with the LEF experiments of German (1976) and of Dimpfl & Kinsey (1979). This would imply that lifetimes deduced by McDermid & Laudenslager (1982) using LEF techniques are somewhat too long and those based on the Hanle effect too short. In addition, the lifetimes based on the high-frequency deflection technique appear to be too long at least for $N' < 5$. Since the r -centroid of the transition increases with N' and the transition moment decreases with r , the vibrationally averaged moment decreases (lifetime increases) monotonically with increasing r (and increasing N'). Thus we have suggested that there is systematic error in the high-frequency deflection lifetimes for small N' , such as collisional quenching, which would preferentially increase the population of the lower N' levels giving an apparent increase in the lifetimes.

In our opinion the best transition probabilities for an opacity calculation

would be obtained using the *ab initio* transition moment function in Bauschlicher & Langhoff (1987). The transition probabilities could be computed using RKR potentials, which are now known with sufficient accuracy to eliminate any substantial error from this source. Naturally, some estimate of the effect of predissociation is required for those levels affected by the crossing of the $^4\Sigma^-$ and other states on the outer limb of the $A^2\Sigma^+$ state. It is our understanding that these calculations have been carried out to high rotational quantum numbers (Crosley 1993). These data should be accurate to 5% or better for states that have only a radiative component to the lifetime.

4 The electric dipole moment function of SiO

We next consider the calculation of the line strengths for the ro-vibrational bands in the $X^1\Sigma^+$ ground state of SiO. Here it is not possible to carry out FCI calculations, so we estimate the accuracy of the resulting EDMF by studying how it converges with improvements in the theoretical calculation. We employ large contracted Gaussian basis sets: $[8s\ 7p\ 4d\ 2f\ 1g]$ and $[7s\ 6p\ 4d\ 2f\ 1g]$ for silicon and oxygen, respectively, to study valence correlation. The silicon basis was contracted very flexibly in both the valence and inner-shell regions. Further details of the basis sets are given in the original reference (Langhoff & Bauschlicher 1993).

While it is possible to obtain near convergence of the EDMF with respect to improvements in the one-particle basis, it is much more difficult to demonstrate convergence with respect to the n -particle treatment. Calculations showed that a (433) CASSCF active space is required for an adequate zeroth-order description of the wave function when the oxygen $2s$ electrons are not correlated in the CASSCF. To obtain an equivalent description when the oxygen $2s$ electrons are correlated requires a (633) active space. Larger active spaces did not give significantly different results and the IC-MRCI calculations based on (633) and larger active spaces are exceedingly computationally intensive. The dipole moments are evaluated as expectation values, but the results are not significantly different when formulated as an energy derivative using the finite-field method. The effects of inner-shell (Si $2s$ and $2p$) correlation are not included in the final calculations, but have a relatively small (0.01 Debye) contribution to the permanent moment. Finally, relativistic effects are found to have only a very small effect on the dipole moment (Kellö & Sadlej 1993). Thus IC-MRCI and IC-ACPF calculations based on the (433) and (633) active spaces should provide globally accurate EDMFs for SiO.

In Table 2 we show the variation in the calculated dipole moments for $v=0-3$ and Einstein coefficients for the fundamental and first two overtones with the level of correlation treatment. At the CASSCF level the effect of including the oxygen $2s$ electrons in the active space is to increase the dipole moment by about 0.21–0.22 Debye. At the IC-MRCI level the difference decreases to about 0.07–0.08 Debye and at the IC-ACPF level the difference is only about 0.03–0.04 Debye. The convergence with level of theory is more rapid for the

Table 2. Theoretical dipole moments (Debye), Einstein coefficients (sec^{-1}), and dipole derivatives (a.u./ a_0) as a function of the level of correlation treatment.

	(433) CAS	(633) CAS	(433) MRCI	(633) MRCI	(433) ACPF ^a	Exp ^t ^b
$v=0$	2.9998	3.2165	3.0541	3.1293	3.0436(3.0983)	3.0982
$v=1$	3.0210	3.2379	3.0746	3.1500	3.0639(3.1184)	3.1178
$v=2$	3.0420	3.2590	3.0951	3.1706	3.0836(3.1380)	3.1372
$v=3$	3.0628	3.2798	3.1153	3.1911	3.1028(3.1572)	3.1574
A_{10}	7.25	7.77	6.92	6.97	6.73(6.68)	
A_{20}	0.281	0.329	0.273	0.270	0.264(0.266)	
A_{30}	0.004	0.004	0.004	0.004	0.005(0.004)	
$(d\mu/dr)_{r_e}$	0.635	0.657	0.621	0.623	0.613(0.610)	

^a The values in parentheses correspond to a dipole moment that has been shifted in r by $-0.010 a_0$ and increased in magnitude by 0.0391 Debye.

^b Raymonda et al. 1970.

(433)-based treatment and the (433) IC-ACPF results are expected to be superior, especially since the calculation can be carried out without reference selection. By shifting the (433) IC-ACPF EDMF globally by $-0.010 a_0$ in r and 0.0391 Debye in magnitude, we are able to reproduce the experimental dipole moments (Raymonda et al. 1970) for $v=0-3$ to within 0.0008 Debye. The shift in r , which is equal to the error in our r_e at this level of theory, can be partially rationalized in terms of the neglect of Si inner-shell correlation. The shift in magnitude is due primarily to neglect of oxygen $2s$ correlation. It is clear that an extensive treatment of electron correlation is required to compute the dipole moment to an accuracy of better than a few hundredths of a Debye.

The (433) IC-ACPF and (633) selected reference IC-MRCI EDMFs are compared with the Padé approximant EDMF of Tipping and Chackerian (TC) in Fig. 1, upon which the currently accepted line strengths are based. The true EDMF is expected to lie between the two theoretical ones, but closer to the (433) IC-ACPF EDMF. The present line strengths are about a factor of 1.2 larger than TC for the fundamentals and about a factor of two larger than TC for the overtones. The present line strengths should be accurate to at least 10%.

To aid in spectroscopic and astronomical studies we have generated line strengths in the form of gf values. These are the oscillator strengths (f) multiplied by the Hönl-London factors ($J/(2J+1)$ for the P branch and $(J+1)/(2J+1)$ for the R branch where J is the lower state rotational quantum number). The values are based on our “shifted” (433) IC-ACPF EDMF, which reproduces the experimental dipole moments for $v=0-3$. The gf values were generated for all P and R branch lines for which $J \leq 250$, $v \leq 15$ and $\Delta v \leq 4$. These data are on a file that is available upon request. We recommend using these values in conjunction with an SiO dissociation energy of about $D_0=8.26$ eV (Hildenbrand

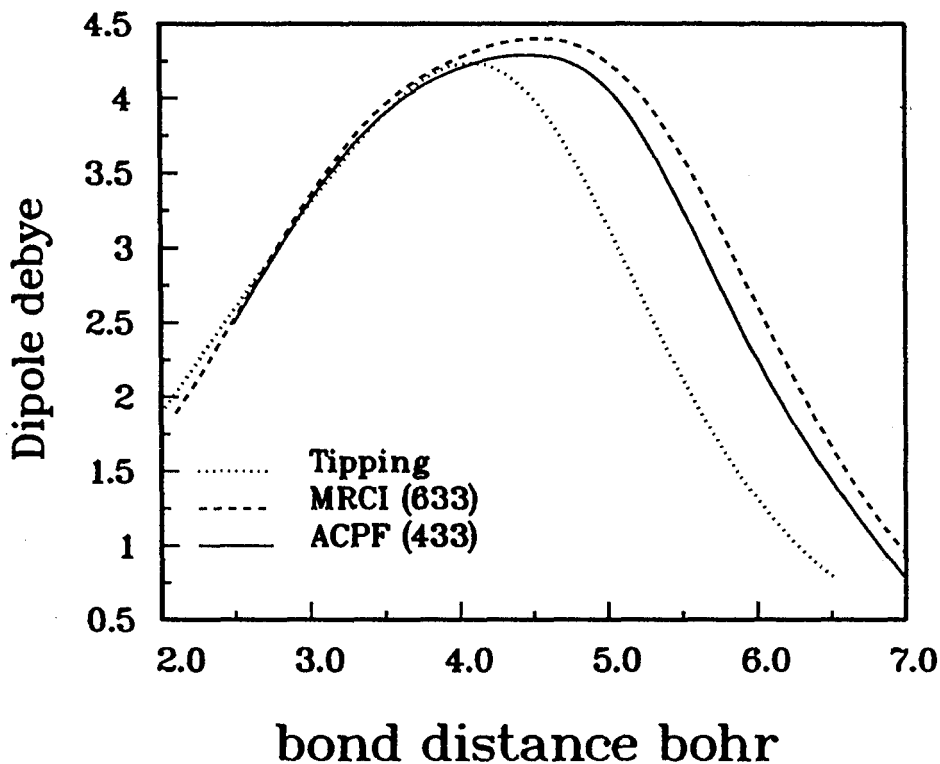


Fig. 1. Three electric dipole moment functions (EDMFs) for the $X^1\Sigma^+$ state of SiO. The solid and dashed lines denote the (433) IC-ACPF and (633) IC-MRCI EDMFs of the present work. The EDMF denoted by the dotted line is from the work of Tipping and Chackerian (1981).

& Murad 1974) to assess the abundance of this molecule in stellar atmospheres.

5 Spectroscopy of ZrO

Since the absorption bands of ZrO have been used to classify S stars (Johnson 1982; Littleton & Davis 1985), it is important to have accurate electronic transition probabilities for the band systems. Although the ground state is $X^1\Sigma^+$, the $a^3\Delta$ state is low-lying (Hammer & Davis 1980), so that transitions in both the singlet and triplet manifolds must be considered. Thus we have carried out calculations (Langhoff & Bauschlicher 1990a) to determine the singlet and triplet potentials in the Franck-Condon region up to an energy of about $30\,000\text{ cm}^{-1}$. Since calculations for transition metal systems are more difficult than for first- and second-row molecules, some compromises were necessary to be able to treat a

large number of states over a large range of internuclear distances. Nevertheless, the theoretical results are generally in very good agreement with the available experimental data.

For brevity, the calculations are described only briefly here (see Langhoff & Bauschlicher 1990a for details). The inner shell of Zr atom is described using the relativistic effective core potential (RECP) of Hay & Wadt (1985), which incorporates the mass-velocity and Darwin relativistic effects. The outermost core orbitals (corresponding to $4s^2 4p^6$) are included in the valence shell together with the $4d$ and $5s$ electrons. This RECP is used in conjunction with a flexible valence basis for Zr consisting of $[5s\ 4p\ 4d\ 3f]$ contracted Gaussian functions. For oxygen atom we used a $[5s\ 5p\ 2d\ 1f]$ ANO basis that accurately describes both O and O^- character in the wave function. The molecular orbitals were determined using the SA-CASSCF approach, averaging separately for the lowest six singlet and triplet states. The six electrons in the Zr $4d$ and $5s$ and oxygen $2p\pi$ orbitals were included in the CASSCF treatment, which was carried out using a (3331) active space. More extensive electron correlation was included using an MRCI approach. The effect of higher excitations was estimated using a multireference analog of the Davidson correction (denoted +Q). This correction significantly improves the $X^1\Sigma^+ - a^3\Delta$ energy separation.

The Einstein coefficients and radiative lifetimes ($\tau_{v'}$) were determined numerically (using finite difference techniques) based on spline representations of the theoretical potentials and TMFs. The experimental T_e values were used to position the states when available (otherwise the theoretical values were used). In all cases the MRCI potentials encompass a sufficiently large range of r values to ensure that this formalism gives a reliable estimate of the lifetime for the lowest few vibrational levels.

The MRCI potentials for the $X^1\Sigma^+$, $A^1\Delta$, $B^1\Pi$, $C^1\Sigma^+$, $D^1\Gamma$, and $E^1\Phi$ states and for the $a^3\Delta$, $b^3\Pi$, $c^3\Sigma^-$, $d^3\Phi$, $e^3\Pi$, and $f^3\Delta$ states are shown in Figs. 2 and 3, respectively. We have adopted the spectroscopic designations based on the ordering of the states shown in these two figures.

The spectroscopic constants (r_e , ω_e , T_e) at the MRCI and MRCI+Q levels are in good agreement with experiment. For example, the MRCI+Q T_e values are within 900 cm^{-1} of experiment for all of the singlet and triplet states that have been characterized experimentally (Huber & Herzberg 1979; Hammer et al. 1981; Simard et al. 1988; Hammer & Davis 1980; Phillips et al. 1979). The MRCI+Q r_e values are uniformly about $0.03\ a_0$ too long, probably as a result of neglecting Zr inner-shell ($4s\ 4p$) correlation. The calculated moments plotted in Langhoff & Bauschlicher (1990a) for the strong transitions such as $B^1\Pi - X^1\Sigma^+$, $e^3\Pi - a^3\Delta$, and $d^3\Phi - a^3\Delta$ are probably accurate to about 10%. Our calculations indicate that the as yet unobserved $E^1\Phi - A^1\Delta$ transition is quite strong, which could provide a means of characterizing the $E^1\Phi$ state.

In Table 3 we have tabulated the theoretical Franck-Condon factor (q_{00}), the transition moment squared (r_e^2), and the Einstein coefficient (A_{00}) for the $0 - 0$ band of the strong singlet and triplet band systems. Included for comparison are the transition moment squared values deduced from a laboratory absorption

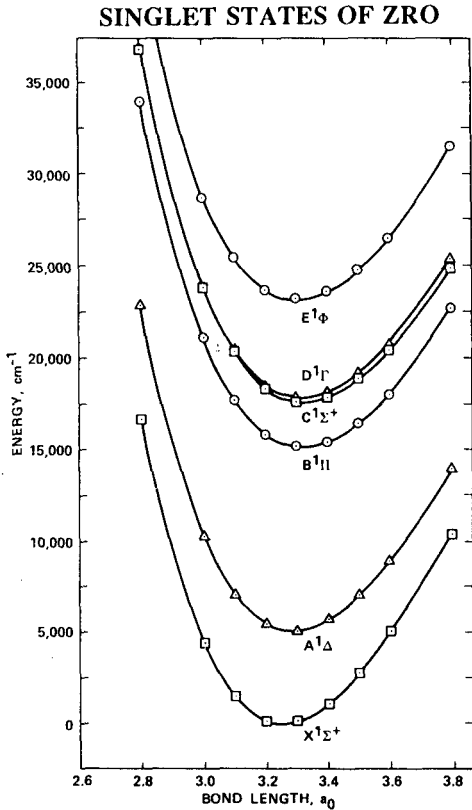


Fig. 2. The MRCI potential curves for the singlet states of ZrO

spectrum by Littleton et al. (1993). These values are determined as ratios to the β system, and given absolute magnitude by requiring them to be consistent with the lifetime measurement (Hammer & Davis 1979) for the $v=0, J=77$ level of the $e^3\Pi$ state. These “experimental” values agree with the theoretical values to within the combined uncertainty of the calculations and measurements. This lends considerable credence to the accuracy of the theoretical values for the other band systems. The $E^1\Phi - A^1\Delta$ transition has not been characterized experimentally. This band system should probably be included in opacity models, because it should be prominent in emission at transition energies of $\approx 16\,000 - 17\,000\text{ cm}^{-1}$, if the $E^1\Phi$ state, which lies $\approx 22\,000\text{ cm}^{-1}$ above the ground state, is populated at stellar temperatures.

Radiative lifetimes based on the MRCI transition probabilities are given in Table 4. Although these lifetimes include all radiative channels, there is generally a dominant channel, which is noted in the last column of the table. Experimental values for the $e^3\Pi$, $B^1\Pi$, and $C^1\Sigma^+$ states are included in Table 4 for comparison. The theoretical values are based on rotationless potentials, but

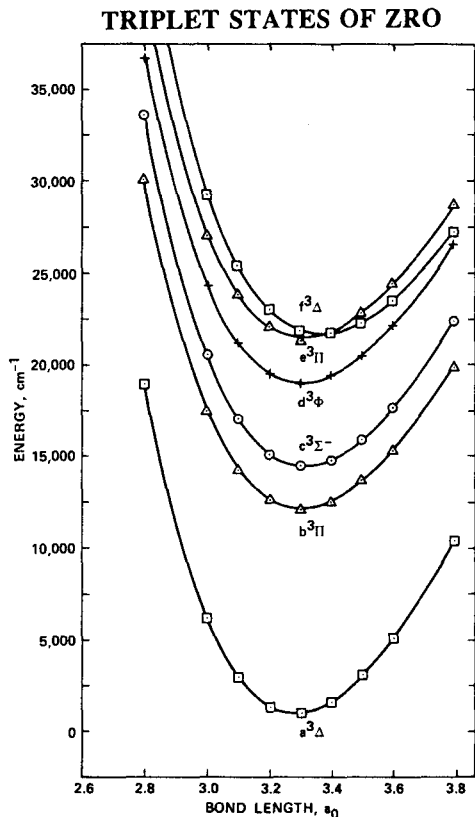


Fig. 3. The MRCI potential curves for the triplet states of ZrO

have a very weak dependence on J . For example, increasing J from 0 to 77 for the $e^3\Pi$ state increases the lifetime from 24.4 to 25.1 ns. The calculated value is about 25% less than the experimental value obtained by Hammer and Davis (1979) using the technique of resonant fluorescence decay. This difference is about the expected accuracy of the theoretical calculations. The discrepancy for the $B^1\Pi$ state lifetime is a little larger. However, our value is very stable to refinements in the theoretical treatment. The agreement is excellent between theory and experiment for the $C^1\Sigma^+$ state lifetime. Thus overall the agreement between the theoretical and experimental lifetimes is excellent. The $d^3\Phi$ and $E^1\Phi$ states are also predicted to have relatively short lifetimes. We recommend using the theoretical values in Table 4 until more reliable experimental values become available.

The isovalent TiO molecule is a very important opacity source in many stars. Thus analogous calculations for this system would be worthwhile. Preliminary calculations (Langhoff unpublished) indicate, however, that the characterization of the states is more difficult due to the large number of low-lying excited states

Table 3. Transition probabilities for selected ZrO band systems

Band system	q_{00}	$r_e^2(e^2 a_0^2)^a$		$A_{00}(s^{-1})$
		MRCI	Expt.	MRCI
$b^3\Pi - a^3\Delta$	0.981	0.370	...	9.27(+5)
$d^3\Phi - a^3\Delta(\gamma)$	0.973	2.702	3.5 ± 0.6^b	2.15(+7)
$e^3\Pi - a^3\Delta(\beta)$	0.949	3.552	3.8 ± 0.2^c	3.98(+7)
$f^3\Delta - a^3\Delta(\alpha)$	0.672	1.443	...	2.51(+7)
$B^1\Pi - X^1\Sigma^+$	0.796	1.724	2.1 ± 0.4^b	1.28(+7)
$B^1\Pi - A^1\Delta$	0.946	1.519	...	2.65(+6)
$C^1\Sigma^+ - X^1\Sigma^+$	0.763	0.567	...	5.70(+6)
$E^1\Phi - A^1\Delta$	0.986	2.635	...	3.16(+7)
$E^1\Phi - C^1\Gamma$	0.989	2.250	...	6.76(+5)

^a The value of the transition moment squared for the (0 – 0) band.

^b Values from a laboratory absorption spectrum, Littleton et al. (1993).

^c Littleton and Davis (1985).

and numerous avoided crossings. This makes it difficult to obtain both an accurate and precise description of the electronic states over a wide range of internuclear distances using the SA-CASSCF approach. Previous calculations (Langhoff & Bauschlicher 1990b) on the FeH molecule also underscored the limitations of the SA-CASSCF method to provide an adequate zeroth-order description, primarily due to the large difference in correlation energy between atomic states with different numbers of *d* electrons. These problems are much more severe in the first transition row, because of the larger correlation energies and smaller radial extents of the orbitals. Nevertheless, it would be very interesting to perform high-level theoretical calculations for TiO to compare with the available experimental data and to ensure that all important band systems have been included in the opacity models.

6 Conclusions

We have discussed three applications of computational chemistry to the determination of accurate transition probabilities in diatomic molecules. For first-row molecules such as OH, the theoretical values rival the best experimental values in accuracy. An advantage of theory is that globally correct transition moment functions can be obtained using MRCI techniques. Thus if theory agrees with observed line strengths at relatively low temperatures, it is capable of providing results of nearly equal accuracy for lines where there is a high degree of vibrational and/or rotational excitation. For transition-metal systems such as ZrO, it

Table 4. Radiative lifetimes for the low-lying states of ZrO

State	Lifetime($v'=0$)		Dominant transition
	Theory	Expt.	
$b^3 \Pi$	1.07 μ s		$b^3 \Pi - a^3 \Delta$
$d^3 \Phi$	45.9 ns		$d^3 \Phi - a^3 \Delta$
$e^3 \Pi$	24.4 ns	32.5 ± 2 ns ^a	$e^3 \Pi - a^3 \Delta$
$f^3 \Delta$	28.3 ns		$f^3 \Delta - a^3 \Delta$
$B^1 \Pi$	56.4 ns	83 ns ^b	$B^1 \Pi - X^1 \Sigma^+$
$C^1 \Sigma^+$	136 ns	126 ± 9 ns ^b	$C^1 \Sigma^+ - X^1 \Sigma^+$
$E^1 \Phi$	30.8 ns		$E^1 \Phi - A^1 \Delta$

^a The experimental value for $v'=0$, $J'=77$ from Hammer & Davis (1979). The theoretical value for $J'=77$ is 25.1 ns.

^b The experimental values for $v'=0$, from Simard *et al.* (1988).

is more difficult to obtain reliable line strengths, but in many cases the corresponding experiments are difficult or impossible. Thus theory may still provide the best method of obtaining opacity data. Clearly these *ab initio* methods can be applied to triatomic and larger systems (see, for example, Jørgensen & Jensen (1993) or Jørgensen this volume on the opacity of water vapor). Although it is much more difficult to solve the nuclear problem for triatomic molecules and the number of accessible levels increases rapidly with energy, it is clear that theoretical methods will play an important role in determining the opacity of these molecules as well.

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