NCC2-371
IN-72-CR
158956
P.28

Theoretical study of the dissociation energy and the red and violet band systems of CN

Charles W. Bauschlicher, Jr. and Stephen R. Langhoff
NASA Ames Research Center
Moffett Field, CA 94035

and

Peter R. Taylor
ELORET Institute†
Sunnyvale, CA 94087

Abstract

The dissociation energy (D_0) of CN is determined to be 7.65±0.06 eV. This corresponds to $\Delta H_f(\mathrm{CN})=105.3\pm1.5$ kcal/mole, in excellent agreement with Engleman and Rouse (1975), but considerably larger than the recent value deduced from shock-tube studies by Colket (1984). The above result is obtained not only from extensive *ab initio* MRCI calculations using a very large Gaussian basis set, but also from extrapolation of the directly computed value by comparison of computed and experimental results for NO, C_2 and N_2. As an additional calibration of our methods, we compute the D_0 value for CN from the corresponding value for CN^- using the experimental electron affinity data. The lifetime of the $v' = 0$ level of the violet ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) system has been computed to be 62.4 ns, in good agreement with both experiment and previous calculations. Lifetimes for the red ($A^2\Pi \rightarrow X^2\Sigma^+$) system decrease with increasing v', which is consistent both with recent experiment and calculations. While our computed lifetimes are significantly longer than those obtained from experiment, they are shorter than those deduced from an analysis of the solar spectrum. However, our D_0 and f_{00} are consistent with Lambert's model for the solar spectrum

---

† Mailing address: NASA Ames Research Center, Moffett Field, CA 94035

(NASA-TM-101190) THEORETICAL STUDY OF THE DISSOCIATION ENERGY AND THE RED AND VIOLET BAND SYSTEMS OF CN (NASA) 28 p CSCL 20H
N89-10610
Unclas
G3/72 0158956

I. Introduction

The CN radical is present in flames, comets, stellar atmospheres and interstellar space. It can be observed by either the red ($A^2\Pi \rightarrow X^2\Sigma^+$) or violet ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) emission systems. In principle, these two CN band systems should be an excellent probe of the chemistry under these conditions, where direct measurements are difficult or impossible. If the dissociation energy (D_0) and the oscillator strength (f_{00}) of CN (and the temperature) were known, the observed emission intensity in a stellar atmosphere could be converted into elemental abundances. Considering the importance of CN as a probe species, it is unfortunate that, while the oscillator strength of the violet system is well known, disparate results exist for both the oscillator strength of the red system and the ground state dissociation energy. Since the red system is especially important as a nitrogen abundance indicator for red giants, and contributes to the total opacity of a red giant's atmosphere (Sneden and Lambert 1982), it would be of enormous value for the understanding and modeling of stellar atmospheres to have accurate values for both the ground state dissociation energy and the oscillator strength of the red system. Such a goal is difficult to accomplish by experimental means — the absence of suitable predissociations complicates the determination of D_0, while lifetime measurements for the red system are substantially affected by (non-radiative) $A \leftrightarrow X$ intersystem crossing. This latter effect is quite large, leading to the observed increase in emission with increase in pressure up to 0.02 torr (Duric, Erman, and Larsson 1978). Indirect methods for determining the $A^2\Pi$ state lifetime depend on a knowledge of D_0, so the uncertainty in D_0 further hampers an understanding of the red system.

From the standpoint of *ab initio* quantum chemistry, CN is no more difficult than other first-row diatomic molecules with a similar number of electrons. We have recently presented (Langhoff, Bauschlicher, and Taylor 1987; Bauschlicher and Langhoff 1987a) very accurate spectroscopic constants for a number of such molecules: advances in the methodology of electronic structure calculations have made it possible to compute, for example, the D_0 values for C_2, N_2, O_2 and F_2 with an error of less than 0.18 eV in the worst case. By using such results to provide a calibration of techniques for extrapolating the best computed value to experiment, the calculated CN D_0 values can be corrected for the remaining errors arising from truncation of both the one− and n−particle basis set expansions.

In addition to using the C_2 and N_2 molecules for calibration, we also compute D_0 values for NO and CN^-. The NO value is used to verify that the extrapolation procedure works well for a heteronuclear diatomic, while an independent calibration is obtained by using the computed D_0 of CN^- in conjunction with the experimental electron affinities (EAs) of CN and C (Hotop and Lineberger 1975; Berkowitz, Chupka and Walter 1968), via the relation

$$D_0(\mathrm{CN})+\mathrm{EA}(\mathrm{CN})=D_0(\mathrm{CN}^-)+\mathrm{EA}(\mathrm{C}). \tag{1}$$

Ideally, the use of equation (1) with the computed D_0 for CN^- will yield the same D_0 for CN as that computed (or extrapolated) directly. An advantage of equation (1), however, is that CN^- dissociates to C^- (^4S) and N (^4S), which avoids the need to describe $2s^2 \rightarrow 2p^2$ near-degeneracy effects in the C(^3P) state.

Recent calculations of spectroscopic intensities also show excellent agreement with experiment (see, for example, Bauschlicher and Langhoff 1987b), and such calculations can readily be performed for CN. The availability of good experimental data for the violet system (Duric, Erman and Larsson 1978; Jackson 1974) provides an additional calibration of the theoretical results for the red system where there is a wide variation in the experimental data. It is pertinent to note that computed lifetimes for several states of N_2^+ (Langhoff, Bauschlicher and Partridge 1987; Langhoff and Bauschlicher 1987), which is isoelectronic with CN and has similar $A - X$ and $B - X$ separations, are in excellent agreement with experimental results (Holland and Maier 1972; Peterson and Moseley 1973).

In view of the problems that the absence of reliable CN data generates for astronomical modeling, and given the accuracy of present large-scale *ab initio* calculations, we have determined the D_0 for the CN ground state and radiative lifetimes for the $A^2\Pi$ and $B^2\Sigma^+$ states. These results are compared with current experimental estimates and with previous theoretical calculations.

II. Methods

The one-particle basis sets employed in this study are constructed using general contractions based on atomic natural orbitals (ANOs) as described in previous work

(Almlöf and Taylor 1987). We use two different contractions, [4*s* 3*p* 2*d* 1*f*] and [5*s* 4*p* 3*d* 2*f* 1*g*], of the (13*s* 8*p* 6*d* 4*f* 2*g*) primitive Gaussian set. The *s* and *p* exponents are taken from van Duijneveldt (19"1) and the polarization functions are given in Bauschlicher, Langhoff and Taylor (1987) and Langhoff, Bauschlicher, and Taylor (1987) for C and N, respectively. The difference in the computed D_0 values obtained with these two contracted basis sets provides a measure of basis set incompleteness. For CN^-, the basis sets are supplemented with a diffuse *p* set on C and N ($\alpha_p(C)=0.026$ and $\alpha_p(N)=0.038$) to describe the more diffuse charge density of the negative ion. Finally, an extended [5*s* 5*p* 4*d* 3*f* 1*g*] ANO set is used as an additional test of basis set saturation. Pure spherical harmonic functions are used in all calculations. For the calculation of the lifetimes of the red and violet band systems, potential energy curves and transition moments are computed using the smaller [4*s* 3*p* 2*d* 1*f*] ANO basis set, as calibration calculations show that the lifetimes computed using this basis are essentially the same as those using the larger [5*s* 4*p* 3*d* 2*f* 1*g*] set.

In this study we use multireference configuration-interaction (MRCI) wave functions that are based on a complete-active-space self-consistent field (CASSCF) zeroth-order reference function. We also use the modified coupled-pair functional (MCPF) method (Chong and Langhoff 1986; Ahlrichs, Scharf, and Erhardt 1985), based on SCF orbitals, in investigating the one-particle basis effects on D_0. For CN^-, NO and N_2, the 2*p* electrons and orbitals are treated as active in the CASSCF calculations. For CN and C_2 the 2*s* and 2*p* orbitals and electrons are active: this is necessary to account for the 2*s*–2*p* hybridization in the molecules and $2s^2 \rightarrow 2p^2$ excitation in the ^3P state of C atom. In the study of the $A^2\Pi$ and $B^2\Sigma^+$ state lifetimes, a single set of CASSCF orbitals is used, obtained from a calculation in which the average energy of the *X*, *A* and *B* states is optimized with equal weighting for the three states. In all MRCI (and MCPF) calculations, the 2*s* and 2*p* electrons are correlated and the two 1*s*-like core orbitals are constrained to be doubly occupied. Since the configuration expansions including all single and double excitations from all configurations in the CASSCF are very lengthy, in many calculations only selected references are included. For CN, the MRCI treatment with all CASSCF configurations used as references corresponds to a second-order CI (SOCI) calculation. The selection of references is calibrated against SOCI calculations in the [4s 3p 2d 1f] basis set. In the selection of references, an occupation is included in the reference list if the absolute value of the coefficient of any one of its component spin couplings is above a designated threshold. We construct reference lists either by using only geometries close to r_e and at long range, or by merging the lists obtained at various points over the full potential curve. The former approach is used in the calculation of D_0, while the latter is used for the determination of the radiative lifetimes. In order to estimate the importance of higher excitations, we use the multireference analog of the Davidson correction (Langhoff and Davidson 1974; Blomberg and Siegbahn 1983) denoted +Q and defined as $\Delta E(1 - \sum_R C_R^2)$, where ΔE is the MRCI correlation energy and C_R is the coefficient of reference configuration R in the MRCI expansion.

The computation of radiative transition probabilities involves the expectation value of the electronic transition dipole operator between the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states. For the perpendicular ($A \rightarrow X$) transition, the transition moment operator, $D(r)$, is defined as

$$D(r) \; = \; < X^2\Sigma^+ | \frac{(x+iy)}{\sqrt{2}} | A^2\Pi > \tag{2}$$

Note that this definition of the matrix element is equivalent to the cartesian form $< X^2\Sigma^+ | x | A^2\Pi_x >$ (Whiting *et al.*, 1980). For the parallel ($B \rightarrow X$) transition, the moment is the usual

$$D(r) \; = \; < X^2\Sigma^+ | z | B^2\Sigma^+ > . \tag{3}$$

To compare with experimental observables such as lifetimes, the transition moment operator is integrated numerically over the nuclear coordinate r,

$$D_{v',v''} = \int_0^\infty \psi_{v'}(r) D(r) \psi_{v''}(r) dr, \tag{4}$$

where $\psi_{v'}$ and $\psi_{v''}$ are the upper and lower state vibrational wave functions. Note that rotationless potentials are used throughout, but the influence of vibration-rotation interactions on the Einstein coefficients and lifetimes is rather small. The vibrational eigenfunctions are determined using Klein-Dunham potentials and the theoretical transition moments. The Klein-Dunham potentials for the $X^2\Sigma^+$ and $A^2\Pi$ states were based on the Dunham coefficients given by Kotlar *et al.* (1980), while the $B^2\Sigma^+$ potential was based on the constants given by Huber and Herzberg (1979). Since the theoretical potentials are in excellent agreement with these Klein-Dunham potentials, the Einstein coefficients and radiative lifetimes would not be substantially different if the vibrational analysis was done using entirely theoretical input. The MRCI T_e values (based on a 0.2 a_0 grid of points) for the $A^2\Pi$ and $B^2\Sigma^+$ states (with experimental values in parentheses) are 9560(9245) cm^{-1} and 26336(25752) cm^{-1}. This indicates that the CASSCF/MRCI procedure provides a balanced treatment of the three states. As noted above, the transition moments were computed using the smaller $[4s\ 3p\ 2d\ 1f]$ basis and a 0.05 selection threshold on reference CSFs. The vibrational eigenfunctions in equation (3) were obtained from solutions of the radial Schrödinger equation using the numerical integration method of Cooley (1961).

Once the dipole matrix element is known, the Einstein A coefficient (s^{-1}) given as

$$A_{v'v''} = 2.026 \times 10^{-6}\ g\ \nu^3_{v'v''} |D_{v'v''}|^2 \qquad (5)$$

can be computed, where $\nu_{v'v''}$ is the transition energy in cm^{-1} between levels v' and v'', and g is a statistical weighting factor, equal to unity for $\Pi \rightarrow \Sigma$ and $\Sigma \rightarrow \Sigma$ and transitions, but two for $\Sigma \rightarrow \Pi$ transitions. The radiative lifetime ($\tau_{v'}$) of a vibrational level depends on the sum of the transition probabilities to all lower vibrational levels in all lower electronic states. If rotational effects are neglected, the lifetime can be written as

$$\tau_{v'} = \left(\sum_{v''} A_{v'v''}\right)^{-1} \qquad (6)$$

All calculations were performed using the MOLECULE-SWEDEN codes (Almlöf; Siegbahn *et al.*) on the NASA Ames CRAY X-MP/48 and the NAS Facility CRAY 2.

III. Results and Discussion

A. Calculation of D_0

One question raised in a previous study of the dissociation energy of CN by

Larsson, Siegbahn, and Ågren (1983) is whether the N 2*s* correlation must be included. As can be seen in Table 1, excluding the N 2*s* orbital from the CASSCF active space decreases the D_0 by 0.34 eV, most of which (0.21 eV) carries over to the MRCI level. Thus a nine-electron treatment is necessary for quantitative results. While it may seem contradictory that including N 2*s* correlation increases D_0 for CN, but decreases D_0 for N_2 (Langhoff, Bauschlicher and Taylor 1987), the two cases are not, in fact, parallel. In CN the third σ orbital is the N 2*s* orbital only at large r: at r_e it is significantly delocalized. Thus as the bond length varies in CN, different fractions of N 2*s* and C 2*s* correlation are recovered, and it is not possible to relate this to N_2, where eliminating 2*s* correlation has a much more consistent effect across the potential curve.

Since the SOCI expansions for CN in the [5*s* 4*p* 3*d* 2*f* 1*g*] basis set with nine electrons correlated are over 7 million CSFs, we have considered the effect of reference selection on the the spectroscopic constants (D_0, r_e and ω_e). We have found that, although the effect on r_e and ω_e of reference selection is small, the variation in D_0 is considerably larger. The MRCI and MRCI+Q results at 0.01 reference selection threshold in the [4*s* 3*p* 2*d* 1*f*] basis are compared with the corresponding SOCI and SOCI+Q results in Table 1. Since these differences are within acceptable limits, and selection reduces the CI expansion by about a factor of two, we have employed the MRCI(0.01) procedure for calculations involving the [5*s* 4*p* 3*d* 2*f* 1*g*] basis. However, at 0.025 and 0.05 selection thresholds the CI truncation errors are too large to reliably state error bars to within 0.1 eV.

Our calculated D_0 values are reported in Table 2; the C_2 $(X^1\Sigma^+)$ values are from Bauschlicher and Langhoff (1987a). For CN^-, N_2 and NO, all of the configurations in the CASSCF are references in the MRCI calculations (no reference selection). For many of the systems, we also report D_0 values at the MCPF level. As MCPF is a single-reference method, it allows us to consider the effect of further basis set saturation at a relatively modest cost. There are two sources of error in our calculations, incompleteness of the one-particle space (basis set error) and of the $n-$particle space (error in the correlation treatment). Previous work (Bauschlicher and Langhoff 1987c) involving full CI comparisons (that is, elimination of the $n-$particle space incompleteness) indicates that the largest error in D_0

comes from basis set incompleteness. It is difficult to conceive of a source of error in the n−particle space treatment which is present for CN and CN^- and absent for the systems studied previously. At the MRCI level, it is therefore vital to reduce the one-particle error as far as possible: the residual one-particle and n−particle incompleteness can then be accounted for with little uncertainty by extrapolation approaches based on the well-known D_0 value of N_2. We consider first the effect of expanding the basis set from [4*s* 3*p* 2*d* 1*f*] to [5*s* 4*p* 3*d* 2*f* 1*g*]. (As noted above the C and N basis sets include an extra *p* set for CN^-). The effect of this basis set improvement is very similar for CN, CN^- and NO; it is only slightly smaller for C_2, and is somewhat larger for N_2. For CN and NO, the MCPF calculations show the same increase in D_0 with basis set improvement as do the MRCI calculations. For N_2 the effect of basis set improvement is larger at the MRCI level than at the MCPF level, suggesting a coupling of one-particle and n−particle errors in N_2 that is either not present in the other systems or is better reproduced at the MCPF level. These results indicate that the remaining errors in CN (or CN^-) should be smaller than those in N_2. Further, for CN the expansion of the basis set to [5*s* 5*p* 4*d* 3*f* 1*g*] results in only a small increase in D_0 at the MCPF level, supporting the hypothesis that any remaining basis set incompleteness in CN is small. From these observations we expect the error in the computed D_0 for CN will be slightly larger than that for C_2, but smaller than for N_2. The effect of the +Q correction is small for all molecules except NO. This in turn suggests that the n−particle error in CN will be smaller than in NO. The overall similarity of these systems suggests that NO, C_2 and N_2 are reasonable choices for the calibration of calculations on CN and CN^-. This is in accordance with chemical intuition: CN, N_2 and CN^- have a bond order of 3, NO has bond order of 2.5 and the bond order in C_2 is probably best described as between 2 and 3. The energy required for the *sp* hybridization of C, however, results in smaller D_0 values for CN and C_2 than is indicated by their bond orders. This is an important reason for including the C_2 molecule in the calibration study.

A particular advantage of ANO basis sets is the systematic way in which the computed results improve as further ANOs are added. We may expect that the increase in D_0 observed on expanding the basis from [4*s* 3*p* 2*d* 1*f*] to [5*s* 4*p* 3*d* 2*f* 1*g*] reflects inclusion of the same effects that would be accounted for if the latter were extended to completeness: no new effects are expected to arise. Consequently, if we assume that the remaining one- and n−particle errors scale in the same way, we can extrapolate to the "experimental" D_0 for CN using the well-known experimental D_0 value for N_2

$$\frac{D_0([5s\ 4p\ 3d\ 2f\ 1g]) - D_0([4s\ 3p\ 2d\ 1f])(\mathrm{CN})}{D_0([5s\ 4p\ 3d\ 2f\ 1g]) - D_0([4s\ 3p\ 2d\ 1f])(\mathrm{N_2})} = \frac{D_0(\mathrm{expt}) - D_0([5s\ 4p\ 3d\ 2f\ 1g])(\mathrm{CN})}{D_0(\mathrm{expt}) - D_0([5s\ 4p\ 3d\ 2f\ 1g])(\mathrm{N_2})}. \qquad (7)$$

If instead, the remaining error is assumed to be proportional to D_0 as suggested by Larsson, Siegbahn and Ågren (1983), we obtain the relation

$$\frac{D_0([5s\ 4p\ 3d\ 2f\ 1g])}{D_0(\mathrm{expt})}(\mathrm{CN}) = \frac{D_0([5s\ 4p\ 3d\ 2f\ 1g])}{D_0(\mathrm{expt})}(\mathrm{N_2}). \qquad (8)$$

We refer to the extrapolation formulae (7) and (8) as methods I and II, respectively.

One test of the accuracy of these extrapolation methods is to apply them to the C_2 and NO molecules. The comparison for C_2 is complicated somewhat by the remaining uncertainty in the D_0 value of this molecule. Huber and Herzberg (1979) report a value of 6.21 eV, which is the average of two thermochemical values. The value that we adopt for comparison here is the most recent thermochemical determination of 6.17±0.11 eV by Kordis and Gingerich (1973). Lower values of D_0 based on spectroscopic methods have also been reported (see Lambert (1984) for a good review of experimental work). The most accurate of these is the value of 6.11±0.04 eV determined by Messerle and Krauss (1967) on the basis of studies of the rotational predissociation in the $c^1\Pi_g$ state. However, since our best directly computed value is 6.11 eV and remaining basis set saturation is expected to increase this value, we believe that the spectroscopic values are slightly too low. Using the value of 6.17 eV as our comparison standard, the errors in the C_2 predictions are MRCI(MRCI+Q) +0.03(-0.02) for method I and +0.05(0.00) eV for method II. Hence, the +Q values are in perfect agreement with the value of 6.17 eV, while those without the +Q correction favor a slightly larger value of D_0 for C_2.

For the NO molecule an accurate D_0 value is available for comparison— see discussion in Huber and Herzberg (1979). For NO the errors are -0.12(-0.01) eV and -0.11(-0.01) eV for Methods I and II, respectively. The largest errors are therefore for NO at the MRCI level. However, the Davidson correction effect on D_0 is quite large for NO, which is different from the situation in N_2. There is thus some difference in correlation effects between NO and the calibration standard (N_2), and it is not surprising that the extrapolation procedures fail to account for an effect that is unique to NO. The application of the extrapolation methods to CN yields D_0 values of 7.64(7.61) eV and 7.67(7.65) eV. Applying the same extrapolations to CN^- and computing the D_0 of CN using the experimental EAs and equation (1) yields 7.61(7.62) eV and 7.68(7.68) eV. The average of these extrapolated values is 7.65 eV, leading to a recommended value of 7.65±0.06 eV for CN. The error bars correspond to estimated confidence limits of 80%, or approximately 1.5 times the average of the above uncertainties.

By increasing the error bars further, we can increase the confidence limits to 99% . First, in order to obtain an upper bound to D_0, we assume that the maximum error in the computed D_0 for CN is 1.25 times that for N_2: this should be a conservative upper bound, because there is a smaller change in D_0 with basis set improvement and a smaller coupling of basis set and higher excitations for CN than for N_2. In estimating a lower bound, it should be noted that since the MRCI treatment used has virtually no CI superposition error: D_0 could then be too large only if the +Q correction substantially underestimated the effect of higher excitations (note that the +Q correction reduces D_0 for CN). This is highly unlikely as experience has shown that the correct answer for treatments of this type lies between the MRCI and MRCI+Q levels (Bauschlicher and Langhoff 1987c), and hence the largest reduction from such a source would be the 0.05 eV observed at the [$4s\,3p\,2d\,1f$] SOCI level. It is inconceivable that the remaining basis set errors are as small as 0.05 eV, given that remaining basis set error in D_0 for CH, a simpler system, is 0.03 eV (Bauschlicher and Langhoff 1987d), and thus basis set incompleteness would at the least cancel any reduction in D_0 from higher excitations. Furthermore, the directly computed value based on D_0 for CN^- is 7.50 eV, and in this case the +Q correction *increases* D_0. Accounting for a minimum remaining basis set incompleteness error of 0.05 eV in this value suggests that 7.55 eV would be an absolute lower limit to D_0 for CN. This leads us to a very conservative estimate (99% confidence limits) of D_0 as 7.65±0.10 eV.

A summary of the D_0 determinations prior to 1973 is given by Arnold and Nicholls (1973); the range of values is 7.50–8.40 eV. These authors noted that a range of 7.8–8.0 eV was consistent with their value (7.89±0.13 eV) and most of the other data available at that time. This range is outside our conservative estimate. However, the determination of D_0 by Engleman and Rouse (1975) (7.65±0.05 eV) is significantly smaller than that of Arnold and Nicholls (1973), and in excellent agreement with our value. While the Engleman and Rouse (1975) determination is an indirect result based on the Arnold and Nicholls oscillator strength of the violet system and some assumptions about the kinetics of the system, we conclude that it is the most reliable experimental determination in light of our calculated values. Lambert *et al.* (1986, see also Lambert *et al.* 1984) obtained an estimate of D_0=7.55±0.05 eV from solar red system lines with the C and N abundances obtained from either the CH $A-X$ and NH $A-X$ or CH $A-X$ and the permitted N I lines. Their estimate is based on the f_{00} for the red system calculated by Larsson, Siegbahn, and Ågren (1983). If the smaller f-value obtained in this work is adopted, Lambert *et al.*'s (1986) D_0 value is increased to D_0=7.69±0.05 eV (Lambert 1987). Our estimates for D_0 and the red system lifetimes are thus consistent with the solar data and the model used by Lambert.

As noted at the beginning of this section, Larsson, Siegbahn and Ågren (1983) have reported a D_0 value for CN using a CASSCF/externally contracted CI approach. Their best basis set is somewhat inferior to the smaller $[4s\ 3p\ 2d\ 1f]$ set used in the present work, and they select reference occupations using a 0.05 threshold. Their D_0 of 7.19 eV is slightly smaller than our SOCI value of 7.32 eV in the $[4s\ 3p\ 2d\ 1f]$ set. Using method II for extrapolation and a comparable calculation for N_2 led to an extrapolated value of 7.52 eV, which is smaller than even our directly computed result. It is very likely that their basis set is too small and their reference selection threshold not sufficiently strict to allow an accurate extrapolation of D_0, at least not to the accuracy of the present work.

B. The Red and Violet Band Systems

It is appropriate to address first the question of what level of treatment is required to accurately compute the separations (T_e) and transition dipole moments.

In Table 3 we summarize the variation in these quantities with MRCI reference selection threshold and basis set. The T_e values and transition moments are rather insensitive to both the basis set improvement and the threshold used in the selection of reference occupations. As basis set extension and the reduction of the reference selection threshold have opposite effects on the transition moment, both improvements would have to be incorporated together to improve our computed results. However, the small changes that occur as the level of treatment is improved do not warrant the expense of an MRCI(0.01) calculation in a [5*s* 4*p* 3*d* 2*f* 1*g*] basis set. We therefore use an MRCI(0.05) treatment in the [4*s* 3*p* 2*d* 1*f*] basis for the determination of transition moments over the full range of r, and these results are given in Table 4. The computed moments are used together with the Klein-Dunham potentials to compute the Einstein coefficients and lifetimes. The experimental T_e values were used in determining the transition energies. The variation in our MRCI $A-X$ transition moment with r is in good agreement with the CASSCF results reported by Larsson, Siegbahn and Ågren (1983). In addition, the r variation in the $B-X$ transition moment is in good agreement with that inferred from experiment (Danylewych and Nicholls 1978; Arnold and Nicholls 1973).

There is general agreement between previous experimental and theoretical determinations of the radiative lifetime of the $B^2\Sigma^+$ state. In Table 5, we give the Einstein coefficients for all transitions in the violet system ($B-X$) for $v' \leq 9$, where the intensity is at least 0.1% of the intensity of the 0–0 band. In Table 6, we compare our calculated lifetimes for $v' \leq 5$ with previous determinations. The lifetime of the B state is determined principally by the $B \rightarrow X$ decay: inclusion of the $B \rightarrow A$ channel reduces the lifetime by about 1%. Our results show an increase in the lifetime with v', in agreement with the results of Cartwright and Hay (1982). The results of Larsson, Siegbahn and Ågren (1983) show a decrease from $v' = 0$ to $v' = 1$, but then an increase in lifetime with increasing v'. The high frequency deflection experiments of Duric, Erman and Larsson (1978) are in general agreement with our calculation, showing an overall increase in lifetime with increasing v' (within the reported error bars). Note that the value ascribed to $v'=0$ is the average of measurements of 16 rotational levels and a measurement at the band head. The lifetimes of the individual rotational levels vary somewhat depending on the degree of perturbation by the $A^2\Pi$ state. Considering the increased uncertainty in the experimental lifetimes with vibrational excitation, the theoretical results should portray more accurately the variation in radiative lifetime with v'. The theoretical lifetimes are in overall good agreement with experiment (Duric, Erman and Larsson 1978; Jackson 1974; Luk and Bersohn 1973) Based on the calibration studies in Table 1, we believe that our lifetimes would be as much as 5% longer if the 0.01 threshold selection were used. This would bring our lifetime for v'=0 into better agreement with experiment and with Larsson, Siegbahn and Ågren (1983). However, there appears to be very little remaining uncertainty in the description of the violet system.

Einstein coefficients for $v' \leq 9$ of the red system ($A - X$) are given in Table 7; again, only those bands with intensities of at least 0.1% of the 0–0 band are reported. These Einstein coefficients are used to compute the lifetimes of the $A^2\Pi$ state which are summarized in Table 8, together with previous calculations and some experimental results. There is excellent agreement between our results and those computed by Cartwright and Hay (1982), while the lifetime results of Larsson, Siegbahn and Ågren (1983) are shorter. Note that at the CASSCF level our $A - X$ transition moment at 2.2 a_0 is considerably larger than at the MRCI level—see Table 3. External correlation, therefore, increases the lifetimes. In fact, it is likely that our lifetimes in Table 8 are lower bounds, and that further refinements in the theoretical treatment, such as expansion of the CASSCF active space and reference list to include δ orbitals, would slightly (about 5%) increase the lifetimes.

All of the theoretical treatments show a decrease in lifetime with increasing v', and all predict the lifetime to decrease by about a factor of two between v'=0 and v'=9. The only experimental results consistent with these predictions are those of Taherian and Slanger (1984), although their values show a somewhat more rapid variation of lifetime with v'. This may be contrasted with earlier experiments (Jeunehomme 1965; Katayama, Miller, and Hondybey 1979; Duric, Erman, and Larsson 1978), which show almost no variation in lifetime with v'. Since it is unlikely that the theoretical values would display the wrong variation with v', there would appear to be some systematic error in the earlier lifetime measurements. In fact, our study suggests that even the experimental lifetimes of Taherian and

Slanger (1984), which have the correct variation with v', contain some systematic error or that there are other decay mechanisms, perhaps arising from intersystem crossing between the X and A states, that shorten the lifetime.

It is disconcerting that all of the recent experiments that measure the lifetime directly (Conley *et al.* 1980; Nishi, Shinohara and Hanazaki 1982; Jackson, Payne, Halpern and Tang 1982; Taherian and Slanger 1984) obtain values in the range of 6–9 μs for $v'=0$, if indeed our theoretical value of 11.2 μs is a lower bound. However, Davis *et al.* (1986) and Arnold and Nicholls (1972) have determined oscillator strengths (f numbers) for several of the transitions in the red system that support a longer lifetime. Their results are compared with our work, that of Sneden and Lambert (1982), and that of Taherian and Slanger (1984) in Table 9. The relative magnitudes of the experimentally derived f numbers agree well with theory. We have estimated the lifetime for $v'=0$ level of the $A^2\Pi$ state from the f numbers of Davis et al. (1986) and Arnold and Nicholls (1972) by scaling our computed lifetime based on the ratio of the f_{00} values from experiment and theory. This results in lifetimes of 13.6 μs and 12.1 μs, which lie between our theoretical values and those derived from the solar data (Sneden and Lambert 1982). Although the lifetimes derived from solar data appear to be slightly too long, the variation in the lifetimes with vibrational quantum number are in excellent agreement with theory. This is consistent with the fact that the absolute lifetimes and f numbers derived from solar data are potentially less accurate than the relative values, as they depend somewhat on assumptions about the opacity of the sun. However, we feel that there is sufficient data supporting longer radiative lifetimes for the CN red system to warrant further laser-induced fluorescence studies of the $A^2\Pi$ state.

IV. Conclusions

The D_0 of CN is computed from $CN \rightarrow C(^3P)+N(^4S)$ and also from $CN^- \rightarrow C^-(^4S)+N(^4S)$ corrected using the experimental electron affinities of C and CN. The D_0 values computed using these two different approaches agree to within 0.05 eV. These results are corrected for one-particle and n–particle space incompleteness by an extrapolation using equivalent calculations and experimental results for NO, C_2 and N_2: our best estimate for D_0 is then 7.65±0.06 eV. Our determination of the lifetime of the violet system is in agreement with previous results, from both theory and experiment. Our lifetime for the red system is more consistent with the interpretation of the solar data than most of the laboratory-based experiments. Further experiments are probably required to fully understand this difference. Overall, our theoretical results for D_0 and the lifetimes of the red and violet systems almost certainly represent the best, in the sense of both accuracy and internal consistency, available set of data for CN.

Acknowledgements

Part of this work was performed under a grant of computer time provided by the NAS Facility. P. R. Taylor was supported by NASA grant NCC 2-371. The authors are grateful for enlightening correspondence with David Lambert and Mats Larsson.

Table 1. Spectroscopic constants for CN versus the level of correlation treatment using the [4*s* 3*p* 2*d* 1*f*] basis set.[a]

	r_e(Å)	D_C(eV)	ω_e(cm^{-1})
CASSCF(7)	1.176	6.758	2073
CASSCF(9)	1.182	7.101	2020
SOCI(7)	1.176	7.160	2034
SOCI(7)+Q	1.177	7.154	2028
SOCI(9)	1.182	7.316	2016
SOCI(9)+Q	1.183	7.269	2011
MRCI(0.01)(9)[b]	1.181	7.321	2020
MRCI(0.01)(9)+Q	1.183	7.306	2006
Expt.	1.1718		2068.6

[a] The number of electrons correlated is given in parentheses. The constants are based on a quadratic fit in $1/r$ to the theoretical energies on a 0.1 a_0 grid.

[b] The MRCI is based on 52 reference occupations at the 0.01 threshold.

Table 2. A comparison of the D_0 values of CN, CN^-, N_2, C_2 and NO.

Basis	MRCI	MRCI+Q	MCPF
CN (0.01 reference selection)			
[4*s* 3*p* 2*d* 1*f*]	7.32	7.31	6.96
[5*s* 4*p* 3*d* 2*f* 1*g*]	7.53[a,b]	7.52	7.18
Δ	0.22	0.22	
[5*s* 5*p* 4*d* 3*f* 1*g*]			7.19[a,c]
best Estimate[d]	7.65±0.06		
CN^- (no reference selection)			
[4*s* 4*p* 2*d* 1*f*]	9.83	9.82	
[5*s* 5*p* 3*d* 2*f* 1*g*]	10.05[b]	10.06	
Δ	0.22	0.21	0.24
N_2 (no reference selection)			
[4*s* 3*p* 2*d* 1*f*]	9.23	9.24	8.85
[5*s* 4*p* 3*d* 2*f* 1*g*]	9.58[b]	9.60	9.11
Δ	0.35	0.36	0.26
Expt.	9.76		
error in [5*s* 4*p* 3*d* 2*f* 1*g*]	0.18	0.16	
C_2 (0.01 reference selection)			
[4*s* 3*p* 2*d* 1*f*]	5.94	5.90	
[5*s* 4*p* 3*d* 2*f* 1*g*]	6.11	6.07	
Δ	0.17	0.17	
Expt.	6.17[e]		
error in [5*s* 4*p* 3*d* 2*f* 1*g*]	0.06	0.10	
NO (no reference selection)[f]			
[4*s* 3*p* 2*d* 1*f*]	6.16	6.26	5.85
[5*s* 4*p* 3*d* 2*f* 1*g*]	6.39	6.50	6.08
Δ	0.22	0.24	0.23
Expt.	6.61		

error in [5*s* 4*p* 3*d* 2*f* 1*g*]	0.23	0.12

[a] Bond length not optimized (r=2.2 a_0 used), MCPF calculations in the [5*s* 4*p* 3*d* 2*f* 1*g*] basis set suggest this introduces a 0.002 eV error in D_0.

[b] One σ orbital was deleted in the calculation near r_e; for N_2 at the MCPF level this reduced D_0 by 0.008 eV.

[c] Three σ orbitals were deleted in the calculation near r_e. Based on corresponding results for N_2, this should decrease D_0 by less than 0.03 eV.

[d] See text.

[e] Thermochemical value of 6.17±0.11 eV from Kordis and Gingerich (1973).

[f] Computed at experimental bond length: the experimental ω_e is used in the calculation of D_0.

Table 3. A comparison the separations and moments with level of treatment.[a]

Separations(cm^{-1})

Method	$\Delta(A-X)$	$\Delta(B-X)$
[4*s* 3*p* 2*d* 1*f*] basis		
CASSCF	12473	26302
MRCI(0.05)	11064	26317
MRCI(0.05)+Q	10960	25594
MRCI(0.025)	11283	26069
MRCI(0.025)+Q	11148	25716
MRCI(0.01)	11222	26026
MRCI(0.01)+Q	11155	25891
[5*s* 4*p* 3*d* 2*f* 1*g*] basis		
MRCI(0.05)	11029	26336
MRCI(0.05)+Q	10918	25589

Transition Moment(a.u.)

Method	Moment$(A-X)$	Moment$(B-A)$	Moment$(B-X)$
[4*s* 3*p* 2*d* 1*f*] basis			
CASSCF	0.33528	0.09175	0.74638
MRCI(0.05)	0.30076	0.08087	0.69961
MRCI(0.025)	0.29866	0.08173	0.68642
MRCI(0.01)	0.29688	0.08165	0.68353
[5*s* 4*p* 3*d* 2*f* 1*g*] basis			
MRCI(0.05)	0.30086	0.07928	0.70314

---

[a] All calculations were performed at r=2.2 a_0, using reference lists determined for this r value. Hence the 0.05 threshold values differ very slightly from the values in Table 4, which were determined using a combined reference list.

Table 4. Electronic transition moments(a.u.) between the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states of CN.

R(a_0)	A–X[a]	B–A[a]	B–X[b]
1.6	0.28650		
1.8	0.30608	0.12678	0.56554
2.0	0.30913	0.09975	0.66644
2.2	0.29974	0.08323	0.68640
2.4	0.28179	0.08206	0.64249
2.6	0.25820	0.09772	0.54118
3.0	0.20217	0.12138	0.28700
3.4	0.14570	0.09429	0.18454
4.0	0.07628	0.02798	0.15445

[a] The matrix element reported is $<^2\Pi|\frac{(x+iy)}{\sqrt{2}}|^2\Sigma^+>$

[b] The matrix element reported is $<^2\Sigma^+|z|^2\Sigma^+>$.

Table 5. Einstein coefficients for the $B^2\Sigma^+ - X^2\Sigma^+$ violet system of CN.

Band[a]	Strength[b]	Band[a]	Strength[b]	Band[a]	Strength[b]	Band[a]	Strength[b]
0–0	1000.0	3–3	585.0	5–8	3.8	8–5	3.8
0–1	72.6	3–4	168.3	6–3	1.3	8–7	312.0
0–2	3.9	3–5	23.1	6–4	1.4	8–8	341.0
1–0	112.1	3–6	1.9	6–5	319.4	8–9	158.9
1–1	824.1	4–2	3.0	6–6	400.0	8–10	44.0
1–2	120.7	4–3	286.5	6–7	174.5	8–11	6.9
1–3	9.9	4–4	505.7	6–8	38.5	9–6	5.3
2–0	1.4	4–5	176.4	6–9	4.9	9–7	1.5
2–1	192.8	4–6	29.1	7–4	2.4	9–8	296.8
2–2	688.8	4–7	2.8	7–6	319.9	9–9	322.9
2–3	150.9	5–3	2.5	7–7	366.0	9–10	148.3
2–4	16.5	5–4	309.0	7–8	167.8	9–11	45.5
2–5	1.1	5–5	445.5	7–9	41.8	9–12	7.8
3–1	2.6	5–6	177.8	7–10	5.9		
3–2	249.1	5–7	34.3				

[a] Upper state vibrational level given first.

[b] Einstein coefficients are given with respect to the 0-0 band. To convert to absolute values in seconds^{-1} multiply by 1.482×10^4.

Table 6. Radiative Lifetimes τ(ns) of the CN $B^2\Sigma^+$ state.

v	This work[a]	LSÅ[a,b]	CH[a,c]	Duric[d]	Jackson[e]	Luk[f]
0	62.69(62.36)	66.80(66.6)	62.29(62.05)	66.2±0.8	65.6±1.0	60.8±2.0
1	63.25(62.83)	66.63(66.4)	62.88(62.58)	66.3±0.8		
2	64.19(63.68)	67.10(66.7)	63.67(63.31)	64.3±2.0		
3	65.52(64.89)	68.22(67.8)	64.84(64.37)	65.6±3.0		
4	67.23(66.44)	69.72(69.2)	66.42(65.79)	68.2±4.0		
5	69.32(68.33)	71.43(70.7)	68.42(67.63)	67.3±5.0		

[a] Values in parentheses include also the contribution from the $B - A$ channel.

[b] CASSCF calculations of Larsson, Siegbahn and Ågren (1983).

[c] CI results of Cartwright and Hay (1982).

[d] HFD experiments of Duric, Erman and Larsson (1978). The value for v=0 is the average of measurements for 16 rotational levels and a measurement at the band head, whereas for v >0 the measurements are only at the band head.

[e] Laser induced fluorescence results of Jackson (1974); average of 14 rotational levels.

[f] Luk and Bersohn (1973).

Table 7. Einstein coefficients for the $A^2\Pi - X^2\Sigma^+$ red system of CN.

Band[a]	Strength[b]	Band[a]	Strength[b]	Band[a]	Strength[b]	Band[a]	Strength[b]
0–0	1000.0	4–0	142.0	6–5	78.4	8–7	191.8
0–1	331.9	4–1	777.0	6–6	138.8	8–8	27.7
0–2	34.1	4–2	898.5	6–7	13.0	8–9	36.2
0–3	1.1	4–3	38.2	6–8	15.7	8–10	2.1
1–0	1158.0	4–4	209.4	6–9	4.3	8–11	2.3
1–1	78.5	4–5	6.7	7–0	5.4	9–1	10.6
1–2	277.7	4–6	44.1	7–1	78.8	9–2	89.9
1–3	59.3	4–7	5.6	7–2	420.5	9–3	390.5
1–4	2.8	5–0	50.9	7–3	959.9	9–4	887.5
2–0	742.3	5–1	424.9	7–4	774.8	9–5	919.1
2–1	787.9	5–2	1012.3	7–5	50.0	9–6	234.4
2–2	23.2	5–3	551.7	7–6	155.5	9–7	37.1
2–3	147.1	5–4	7.0	7–7	74.8	9–8	181.3
2–4	66.2	5–5	196.6	7–8	27.4	9–9	4.2
2–5	4.4	5–6	1.0	7–9	7.0	9–10	37.6
3–0	354.3	5–7	28.6	7–10	3.3	9–12	1.5
3–1	1051.1	5–8	5.2	8–0	1.7		
3–2	290.7	6–0	17.0	8–1	29.7		
3–3	142.2	6–1	194.0	8–2	204.8		
3–4	50.5	6–2	738.3	8–3	675.9		
3–5	58.7	6–3	989.1	8–4	1020.0		
3–6	5.4	6–4	234.7	8–5	488.8		

[a] Upper state vibrational level given first.

[b] Einstein coefficients are given with respect to the 0-0 band. To convert to absolute values in seconds^{-1} multiply by 65.47.

Table 8. Radiative Lifetimes $\tau(\mu s)$ of the CN $A^2\Pi$ state.

v	Theoretical			SL[a]	Expt			
	This work	CH[b]	LSÅ[c]		Conley[d]	TS[e]	Duric[f]	Jackson[g]
0	11.2	11.1	8.1	14.2	7.3±1.5	8.50±0.45		7.2±1.0
1	9.7	9.6	7.0	11.6		8.02±0.55		
2	8.6	8.6	6.3	10.2		6.67±0.60	3.8±0.5	
3	7.8	7.8	5.7	9.0		5.50±0.45	4.0±0.5	
4	7.2	7.2	5.3	8.0		4.70±0.23	4.0±0.5	
5	6.7	6.7	4.9	7.4		$4.30^{+0.85}_{-0.60}$	4.2±0.5	
6	6.3	6.3	4.6	6.8			4.4±0.5	
7	6.0	6.0	4.3	6.3			4.4±0.5	
8	5.7	5.7	4.2	5.9			4.5±0.5	
9	5.5	5.5	4.0	5.5			4.3±0.5	

[a] From analysis of solar spectrum by Sneden and Lambert (1982).

[b] CI results of Cartwright and Hay (1982).

[c] CASSCF results of Larsson, Siegbahn and Ågren (1983), using molecular orbitals optimized separately for both states.

[d] Conley *et al.* (1980)—average of results for $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ measured by laser excitation.

[e] Taherian and Slanger (1984)—extrapolation of time decays to zero pressure following photodissociation of C_2N_2.

[f] Duric, Erman and Larsson (1978)— high frequency deflection measurements.

[g] Jackson, Payne, Halpern, and Tang (1982)—laser induced fluorescence.

Table 9. Oscillator strengths of the CN red system.

Band	This work	Davis[a]	AN[b]	SL[c]	TS[d]
0−0	2.361	1.94±0.06	2.19	1.9±0.2	3.10±0.16
1−0	1.911	1.50±0.03	1.66	1.5±0.2	2.30±0.16
2−0	0.908	0.76±0.02	0.77	0.84±0.08	1.17±0.10
3−0	0.335	0.28±0.02	0.28	0.33±0.05	0.48±0.04
3−1	1.350	1.12±0.07	1.15	1.2±0.2	1.92±0.16
4−1	0.770	0.74±0.05	0.64	0.66±0.1	1.18±0.06

[a] Davis *et al.* (1986) from comparison of absorption measurements made in a high-temperature furnace between red and violet systems.

[b] Arnold and Nicholls (1972) from shock tube studies. These data are based on a CN D_0 value of 7.89 eV.

[c] Sneden and Lambert (1983) based upon analysis of solar spectrum.

[d] Taherian and Slanger (1984)

REFERENCES

Ahlrichs, R., Scharf, P., and Ehrhardt, C. 1985, *J. Chem. Phys.*, **82**, 890.

Almlöf, J., and Taylor, P. R. 1987, *J. Chem. Phys.*, **86**, 4070.

Almlöf, J., MOLECULE, a vectorized Gaussian integral program.

Arnold, J. O., and Nicholls, R. W. 1972, *J. Quant. Spectrosc. Rad. Transf.*, **12**, 1435.

Arnold, J. O., and Nicholls, R. W. 1973, *J. Quant. Spectrosc. Rad. Transf.*, **13**, 115.

Bauschlicher, C. W., Jr., and Langhoff, S. R. 1987a, *J. Chem. Phys.*, **87**, 2919.

Bauschlicher, C. W., Jr., and Langhoff, S. R. 1987b, *J. Chem. Phys.*, **87**, 4665.

Bauschlicher, C. W., Jr., and Langhoff, S. R. 1987c, *J. Chem. Phys.*, **86**, 5595.

Bauschlicher, C. W., Jr., and Langhoff, S. R. 1987d, *Chem. Phys. Letters* **135**, 67.

Bauschlicher, C. W., Jr., Langhoff, S. R., and Taylor, P. R. 1987, *J. Chem. Phys.*, **87**, 387.

Berkowitz, J., Chupka, W. A., and Walter, T. A. 1968, *J. Chem. Phys.*, **50**, 1497.

Blomberg, M. R. A., and Siegbahn, P. E. M. 1983, *J. Chem. Phys.*, **78**, 5682.

Cartwright, D. C., and Hay, P. J. 1982, *Ap. J.*, **257**, 383.

Chong, D. P., and Langhoff, S. R. 1986, *J. Chem. Phys.*, **84**, 5606.

Colket III, M. B. 1984, *J. Quant. Spectrosc. Rad. Transf.*, **31**, 7.

Conley, C., Halpern, J. B., Wood, J., Vaughn, C. and Jackson, W. M. 1980, *Chem. Phys. Letters*, **73**, 224.

Cooley, J. W. 1961, *Math of Comput.*, **XV**, 363.

Davis, S. P., Shortenhaus, D., Stark, G., Engleman, R., Jr., Phillips, J. G., and Hubbard R. P. 1986, *Ap. J.*, **303**, 892.

Danylewych, L. L., and Nicholls, R. W. 1978, *Proc. Roy. Soc. London A*, **360**, 557.

van Duijneveldt, F. B. 1971, *IBM Research Report RJ 945*.

Duric, N., Erman, P., and Larsson, M. 1978, *Phys. Scripta*, **18**, 39.

Engleman, R., Jr., and Rouse, P. E. 1975, *J. Quant. Spectrosc. Rad. Transf.*, **15**, 831.

Holland, R. F., and Maier II, W. B. 1972, *J. Chem. Phys.*, **56**, 5229.

Hotop, H., and Lineberger, W. C. 1975, *J. Phys. and Chem. Ref. Data*, **4**, 530.

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

Jackson, W. M. 1974, *J. Chem. Phys.*, **61**, 4177.

Jackson, W. M., Payne, W., Halpern, J. B., and Tang, X. 1982, *Proceedings of the International Conference on Lasers*, 72.

Jeunehomme, M. 1965, *J. Chem. Phys.*, **42**, 4086.

Katayama, D. R., Miller, T. A., and Bondybey, V. E. 1979, *J. Chem. Phys.*, **71**, 1662.

Kordis, J. and Gingerich, K. A. 1973, *J. Chem. Phys.*, **58**, 5058.

Kotlar, A. J., Field, R. W., Steinfeld, J. I., and Coxon, J. A. 1980, *J. Mol. Spectrosc.*, **80**, 86.

Lambert, D. L., Brown J. A., Hinkle K. H., and Johnson H. R. 1984, *Ap. J.*, **284**, 223.

Lambert, D. L., Gustafsson B., Eriksson K. and Hinkle K. H. 1986, *Ap. J. Suppl.* **62**, 373.

Lambert, D. L. 1987, private communication.

Langhoff, S. R., and Bauschlicher, C. W. 1987, *J. Chem. Phys.*, in press.

Langhoff, S. R., and Davidson, E. R. 1974, *Int. J. Quantum Chem.*, **8**, 61.

Langhoff, S. R., Bauschlicher, C. W., Jr., and Taylor, P. R. 1987 *Chem. Phys. Letters*, **135**, 543.

Langhoff, S. R., Bauschlicher, C. W., Jr., and Partridge, H. 1987 *J. Chem. Phys.*, **87**, 4716.

Larsson, M., Siegbahn, P. E. M., and Ågren, H. 1983, *Ap. J.*, **272**, 369.

Luk, C. K., and Bersohn, R. 1973, *J. Chem. Phys.*, **58**, 2153.

Messerle, G., and Krauss, L. 1967, *Z. Naturforschg.* **22a**, 2023.

Nishi, N., Shinohara, H., and Hanazaki, I. 1982 *J. Chem. Phys.*, **77**, 246.

Peterson, J. R., and Moseley, J. T. 1973, *J. Chem. Phys.*, **58**, 172.

Siegbahn, P. E. M., Bauschlicher, C. W., Roos, B., Taylor, P. R., Heiberg, A., Almlöf J., Langhoff, S. R., and Chong, D. P., SWEDEN is a vectorized SCF-MCSCF-direct CI- conventional CI-CPF-MCPF program.

Sneden, C. and Lambert, D. L. 1982, *Ap. J.*, **259**, 381.

Taherian, M. R., and Slanger, T. G. 1984, *J. Chem. Phys.*, **81**, 3814.

Whiting, E. E., Schadee, A., Tatum, J. B., Hougen, J. T., and Nicholls, R. W. 1980, *J. Mol. Spectrosc.*, 80, 249.