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Recommendations from the raden data base for the electronic transition moments on diatomic molecules of astrophysical interest. I: C₂, CH, and CN molecules L. A. Kuznetsova ^a; N. F. Stepanov ^a ^a Department of Chemistry, Moscow State University, Moscow, Russia

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RECOMMENDATIONS FROM THE RADEN DATA BASE FOR THE ELECTRONIC TRANSITION MOMENTS ON DIATOMIC MOLECULES OF ASTROPHYSICAL INTEREST. I: C₂, CH, AND CN MOLECULES

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Within the scope of the data base RADEN an analysis of the radiative parameters has been carried out for a number of astrophysically significant molecular systems. Result of the experimental studies and the *ab initio* calculations of transition dipole moments D(R), electronic f_e and band $f_{v'v''}$ oscillator strengths, and radiative lifetimes $\tau_{nv'}$ have been analysed. Finally, the electronic transition moments D(R) are recommended for the Swan and Phillips systems of C_2 , the $A^2\Delta$ - $X^2\Pi$ system of CH, and the red and violet systems of CN. The recommended functions provide the most reliable data at present and they should be used in preparing lists of molecular line parameters (to calculate gf-values).

KEY WORDS Recommendations, diatomic molecules, electronic transition moments, oscillator strengths, radiative lifetimes

1 INTRODUCTION

Molecules, due to the highly developed structure of their energy levels and a variety of the experimentally observed transitions, are a useful means for investigating such properties and parameters of the interstellar and circumstellar matter as the gas density, temperature, chemical and isotopic composition, ionization degree, radiation field density, etc. Success in such investigations is to a noticeable degree predetermined by the scope and reliability of the available spectral information, because the absorption coefficients should be calculated for a large number of spectral lines, including very weak ones. Such calculations are based on the tabulated data on spectral lines: the line centre positions, the energy values for the lower levels, the gf-values, and, in a number of cases, the line broadening parameters.

At present, several scientific groups are developing such tables. Most complete data for the diatomic molecules have been prepared by Kurucz (1993). His tables

contain the parameters of more than 50 millions of lines belonging to the electronic spectra of H₂, CH, OH, NH, MgH, SiH, C₂, CO, CN, and TiO molecules. Some tabulated parameters, namely, the lower level energies and frequencies of observed transitions, are from experimental measurements. But frequencies and energies of the transitions, which were not observed, and all gf-values were calculated. The electronic transition moments that were necessary for such calculations were taken from *ab initio* studies or from the corresponding experiments.

However, all the calculations were made by Kurucz more than 15 years ago. Over recent years, a large volume of both experimental and theoretical results have been accumulated for the aforementioned molecules. These results can provide a better and more precise picture of the energy-level structures and radiative properties of the molecules. In this connection, line tables prepared by Kurucz should be renewed and extended. First of all, all the available information on the spectral and radiative properties of the astrophysically important diatomic molecules should be analysed to choose the most reliable values. The present work is initial in this direction: it is devoted to the analysis of all available data on radiative parameters for the following electronic transitions: Phillips and Swan systems of C₂ molecule; $A^2\Delta X^2\Pi$ system of the CH molecule; and red and violet systems of the CN molecule. The analysis we performed was aimed at a proper choice of electronic transition moments, which in combination with reliable experimantal or theoretical potentials would enable one to obtain the most precise description of the intensity distribution for the spectra of the aforementioned systems.

The work was performed using the RADEN data base, which was created at the Department of Chemistry, Moscow State University, and is designated not only for compilation and storing information on radiative and energetic characteristics of diatomic molecules, but also for analysing the corresponding data and selecting the most reliable values (Kuznetsova *et al.*, 1993).

2 BASIC THEORETICAL RELATIONS

Within the framework of adiabatic approximation, the calculation of radiative charcteristics of molecular can be subdivided into two problems. One is to solve the electronic Schroedinger equation and, thus, determine $U_i(R)$ adiabatic potentials and $\Phi_i(r, R)$ electronic wavefunctions that describe the state of the electronic subsystem in the field of nuclei fixed at R a distance from each other. On the basis of the wavefunctions obtained, one can then calculate matrix elements of the electronic component of the transition dipole moment:

$$D_{nm}(R) = \langle \Phi_n(r,R) | \mu | \Phi_m(r,R) \rangle_r.$$
(1)

The other problem, namely, of solving the nuclear Schroedinger equation, in the case of diatomic molecules allows the separation of R radial and (θ, φ) angular variables. This equation is solved for each electronic state with the $U_i(R_i)$ potential.

When solving the radial Schroedinger equation, one finds the vibrational wavefunctions $\chi_v(R)$. Averaging $D_{nm}(R)$ with these functions provides a matrix element of the electron-vibrational transition $|D_{v'v''}^{nm}|$:

$$|D_{v'v''}^{nm}| = |\langle \chi_{v'}(R)|D^{nm}(R)|\chi_{v''}(R)\rangle|.$$
(2)

Accordingly, the squared matrix element of a rovibronic transition is as follows

$$|D_{mv''J''}^{nv'J'}|^2 = |D_{v'v''}^{nm}|^2 \frac{\mathbf{S}_{J'J''}}{2J+1}.$$
(3)

where $S_{J'J''}$ is the Hoenl-London factor. Determination and normalization of Hoenl-London factors are uniquely related to the determination of the electronic transition moment and depends on the separation of electronic and rotational wavefunctions. At present, the recommendations of Whiting *et al.* (1980) are accepted as conventional and, according to these, for the spin-allowed transitions:

$$\begin{split} D(R) &= \langle \Lambda' S' \Sigma' | \mu_z | \Lambda'' S'' \Sigma'' \rangle & \text{for transitions} \\ D(R) &= \langle \Lambda' S' \Sigma' | 1 / \sqrt{2} (\mu_x \pm i \mu_y) | \Lambda'' S'' \Sigma'' \rangle & \text{for transitions} \\ & \text{with } \Lambda' - \Lambda'' = 0. \end{split}$$

$$\mathbf{S}_{J'J''} = |T_n^{-1} \langle \Lambda' S' \Sigma' | \langle \Omega' J' | \alpha | \Omega'' J'' \rangle | \Lambda'' S'' \Sigma'' \rangle T_m |^2,$$

and

$$\Sigma \mathbf{S}_{J'J''} = (2 - \delta_{0,\Lambda'} \delta_{0,\Lambda''})(2S+1)(2J+1).$$
(4)

In the latter equation, summation of the Hoenl-London factors is performed over all the allowed transitions from $(2 - \delta_{0,\Lambda})(2S + 1)$ rotational levels with the given J-value.

Other radiative characteristics of molecules often given in the original papers are also related to the transition moments. These are the strengths of electronic transitions $(S_e(R))$, bands $(S_{v'v''})$ and rotation lines $(S_{J'J''})$; the oscillator strengths for bands $(f_{v'v''})$ and rotation lines $(f_{J'J''})$; the Einstein coefficients for bands $(A_{v'v''})$ and rotation lines $(A_{J'J''})$, and radiative lifetimes $(\tau_{nv'})$:

$$S_e(R) = (2 - \delta_{0,\Lambda'} \delta_{0,\Lambda''})(2S+1) |D(R)|^2,$$
(5)

$$S_{v'v''} = (2 - \delta_{0,\Lambda'} \delta_{0,\Lambda''})(2S+1) |D_{v'v''}^{nm}|^2, \tag{6}$$

$$S_{J'J''} = |D_{v'v''}^{nm}|^2 \mathbf{S}_{J'J''} \tag{7}$$

$$f_{v'v''} = \frac{8\pi^2 m c a_0^2}{3h} \nu_{v'v''} \frac{(2 - \delta_{0,\Lambda'} \delta_{0,\Lambda''})}{(2 - \delta_{0,\Lambda''})} |D_{v'v''}^{nm}|^2, \tag{8}$$

$$f_{J'J''} = \frac{8\pi^2 m c a_0^2}{3h} \nu_{J'J''} |D_{v'v''}^{nm}|^2 \frac{\mathbf{S}_{J'J''}}{2J''+1},\tag{9}$$

$$A_{v'v''} = \frac{64\pi^4 a_0^2 e^2}{3h} \nu_{v'v''}^3 \frac{(2 - \delta_{0,\Lambda'} \delta_{0,\Lambda''})}{(2 - \delta_{0,\Lambda''})} |D_{v'v''}^{nm}|^2, \tag{10}$$

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$$A_{J'J''} = \frac{64\pi^4 a_0^2 e^2}{3h} \nu_{J'J''}^3 |D_{v'v''}^{nm}|^2 \frac{\mathbf{S}_{J'J''}}{2J'+1},\tag{11}$$

$$\tau_{nv'}^{-1} = \frac{64\pi^4 a_0^2 e^2}{3h} \frac{(2 - \delta_{0,\Lambda'} \delta_{0,\Lambda''})}{(2 - \delta_{0,\Lambda''})} \sum_{\nu''} |D_{\nu'\nu''}^{nm}|^2 \nu_{\nu'\nu''}^3.$$
(12)

Throuhout the standard notation (Larsson, 1983; Kuznetsova, 1987) is used and the electronic transition moments are expressed in atomic units, i.e. in units of (ea_0) .

3 METHODS FOR DETERMINING THE ELECTRONIC TRANSITION MO-MENTS

3.1 Ab Initio Calculations

To solve the electronic Schroedinger equation to a high precision is a complex problem that requires substantial effort in the case of molecules with more than two electrons. In the framework of most approaches, the solution is constructed as a double expansion in basis sets. As a result of the first expansion (in the so-called single-particle basis), molecular orbitals are represented as linear combinations of functions (usually of Gaussian or contracted Gaussian type) centred on the atoms. The selfconsistent field approximation (SCF) allows one to find the molecular orbitals involved in the wavefunction as an antisymmetrized product of orbitals; however, this method does not take into account the electron correlation effects.

The correlation is usually taken into account by constructing the wavefunction in the form of a linear combination of determinants corresponding to the excitations of one or more electrons from the initial SCF occupied orbitals to the virtual ones. This expansion is usually referred to as *n*-particle expansion. The techniques involving such estimates for electron correlation are called the configuration interaction methods (CI).

Provided that all possible excitations are taken into account (up to N-fold excitations in the N-electron molecules), one deals with the particular case of the full configuration interaction method (FCI) which provides an accurate result for the chosen single-particle basis. However, its usage is complicated, for the expansion size rapidly increases (as a factorial) with increasing number of electrons.

To estimate the electronic transition dipole moments, one must describe the combining electronic states in a certain range of internuclear distances, which involves the Franck-Condon region. The CI methods based on the SCF wavefunctions may not be adequate to solve the problem in question. To estimate CI, one must sometimes use the orbitals and wavefunctions obtained in the multiconfigurational SCF approximation (MC SCF). With this technique, molecular orbitals are optimized together with the coefficients of the configurational expansion. In so far as the calculation aspects of the problem require the same set of orthonormalized molecular orbitals to be used to describe both combining states, the optimization of MC SCF functions is often performed for the energy averaged over these states.

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One of the widely used variety of MC SCF wavefunctions is represented by the so-called CASSCF wavefunctions, i.e. those of the complete active space SCF approximation. These functions correspond to the complete account of the configuration interaction within a certain comparatively small space, spanned by the configurations of active orbitals (subsystem of orbitals that dominate in the description of the correlation effects). The active space should provide an accurate description of each state in the corresponding range of internuclear distances. CI calculations that treat the CASSCF wavefunctions as the zerothorder approximation and involve, for example, configurations singly and doubly excited with respect to the CASSCF wavefunctions, are usually denoted as multi-reference CI (MRCI).

Unfortunately, the size of MRCI expansion rapidly increases with an increase in the dimension of CASSCF active space even faster than with the ordinary CI approach. There are several ways of reducing the expansion size. One of them was proposed by Buenker and Peyerimhoff (1974): on the basis of the second-order perturbation theory, one estimates the contributions from various configurational state functions (CSF) to the energy and excludes the least important configurations from the subsequent wavefunction expansion. Another method is as follows: only those configurations are involved in the set of initial configurations that are contained in the CASSCF wavefunctions with the coefficients exceeding a certain limit. Werner and Knowles (1988) proposed an efficient technique for reducing the number of varied parameters, called the method of internally-contracted MRCI or IC-MRCI. Here the relation between the coefficients of the wavefunction obtained from the original function by applying the given creation-annihilation operator is the same as in the original MRCI function.

The reliability of the quantum-chemical structural and radiative parameters of molecules substantially depends on the choice of the atomic-orbital (AO) basis set. Analysis performed by Zaitsevski *et al.* (1986) shows that those AO sets that are used for calculating the radiative characteristics should somewhat differ from the sets used for structure investigations. The former should contain at least two basis orbitals to describe each atomic valence shell with the given principal and orbital quantum numbers. Furthermore, the basis should also be augmented with at least two polarization functions, which allows the proper description of the deformation of atomic electron density in a molecule, and with diffuse functions, which slowly decay with increasing distance from the nucleus and, thus, provide the proper description of the electron density far from nuclei.

As a criterion of reliability of the non-empirical results, one usually considers the experiment. The quality of estimates of the electronic transition dipole moments is controlled by comparing both the radiative lifetimes $\tau_{nv'}$ and the oscillatory forces of lines $f_{J'J''}$ and bands $f_{v'v''}$ calculated using the D(R) functions with the experimental values. However, when performing such a comparison, one should take into account the following. The experimentally measured lifetimes can differ from the radiative lifetimes calculated according to equation (12) due to: incorrectly taking into account collisional deactivation of the level; resonant collisional transfer; trapping of radiation; cascading transitions; and perturbation and predissociation of the level studied. Other sources of systematic error in the experimental values

are also possible, namely: superposition of the structure of the studied transition and the structure of other systems or spectra of other molecules; thermodiffusion of the excited molecules from the observation zone; and Coulombic repulsion of charged particles during the measurement of $\tau_{nv'}$ of molecular ions. Reliability of the experimental data depends not only on the method, but also on the subject of investigation. The larger the measured lifetime, the more noticeable the effect of collisional processes and thermodiffusion phenomena. The most reliable data are obtained when measuring the lifetimes that lie in the range from 10 to several hundreds of nanoseconds. In this case, an accuracy of 3-5% is actually attainable.

Oscillator strengths of the rotational lines and bands cannot be measured directly by experiment, but they can be calculated from the measured intensities of the corresponding transitions. Thus, for a line

$$f_{J'J''} = \frac{mc}{\pi e^2} \frac{\int k_{\nu} \, d\nu}{N_{J''}} \tag{13}$$

and for a band

$$f_{\nu'\nu''} = \frac{mc}{\pi e^2} \frac{(2 - \delta_{0,\Lambda'+\Lambda''})}{(2 - \delta_{0,\Lambda''})} \frac{\nu_{\nu'\nu''}}{\nu_{J'J''}} \frac{(2J''+1)}{\mathbf{S}_{J'J''}} \frac{\int k_{\nu} \, d\nu}{N_{J''}}.$$
 (14)

As follows from these equations, the calculation of oscillator strengths from the integral absorption coefficients requires that the concentration of molecules in the original state $N_{J''}$ be known. In so far as most diatomic molecules can be obtained in substantial amounts only at high temperature and usually in a mixture with other atoms and molecules, the source for the molecular spectrum should meet the condition of local thermodynamic equilibrium (LTE). In fact, only under this condition, the concentrations of absorbing (radiating) molecules can be estimated. The reliability of $f_{v'v''}$ and $f_{J'J''}$ values so obtained depends, first of all, on how close the conditions for recording the spectrum are to the equilibrium conditions, as well as on the accuracy of the thermodynamic and thermochemical parameters used for the calculation of equilibrium composition. Analysis of the literature data on the oscillatory strengths of CH, CN, C₂, SiH, SiO, MgH, and other molecules measured within the framework of this technique shows that errors can be as high as 20-40%.

3.2 Empirical Methods

The dependence of the electronic transition dipole moments on the internuclear distances can be determined by measuring the intensities and radiative lifetimes. In this case, the D(R) dependence is usually expanded in a power series $D(R) = \sum a_k R^k$, the unknown coefficients of which are found by minimizing one or other functional involving experimental $I_{mv'JJ'}^{nv'J'}$ or $\tau_{nv'}$ values. The techniques usually applied are analysed in detail by Zaitsevski *et al.* (1986). Except for some specific cases, most empirical D(R) dependences are obtained using a simplified scheme referred to as *R*-centroid approximation. It is based on the relation:

$$\langle \chi_{v'} | R^k | \chi_{v''} \rangle \approx (R_{v'v''})^k \langle \chi_{v'} | \chi_{v''} \rangle \tag{15}$$

where $R_{v'v''}$ is the *R*-centroid:

$$(R_{\boldsymbol{v}'\boldsymbol{v}''}) = \langle \chi_{\boldsymbol{v}'} | R | \chi_{\boldsymbol{v}''} \rangle / \langle \chi_{\boldsymbol{v}'} | \chi_{\boldsymbol{v}''} \rangle.$$
(16)

The *R*-centroid approximation is described in Noda and Zare (1982), Kuz'menko et al. (1983) and Zaitsevski et al. (1986) where the conditions and limits of its applicability are analysed. As shown, approximation (15) works better in the case of heavier molecules, transitions with larger Franck-Condon factors, and transitions between higher vibrational levels.

Taking equation (15) into account, one has

$$|D_{v'v''}^{nm}|^{2} = |\langle \chi_{v'}|D^{nm}(R)|\chi_{v''}\rangle|^{2} = |\langle \chi_{v'}|\sum_{k}a_{k}R^{k}|\chi_{v''}\rangle|^{2}$$
$$\approx |\langle \chi_{v'}|\chi_{v''}\rangle|^{2}|\sum_{k}a_{k}R^{k}_{v'v''}|^{2} \approx q_{v'v''}|D(R_{v'v''})|^{2}, \qquad (17)$$

$$I_{mv''J''}^{nv'J'} = \frac{16\pi^3 c a_0^2 e^2}{3} \nu_{J'J''}^4 N_{v'J'} |\sum_k a_k R_{v'v''}^k |^2 q_{v'v''} \mathbf{S}_{J'J''} / (2J'+1), \qquad (18)$$

$$\tau_{nv'}^{-1} = \frac{64\pi^4 a_0^2 e^2}{3h} \frac{(2 - \delta_{0,\Lambda'} \delta_{0,\Lambda''})}{(2 - \delta_{0,\Lambda'})} \sum_{v''} q_{v'v''} \nu_{v'v''}^3 |\sum_k a_k R_{v'v''}^k|^2.$$
(19)

Thus, determining the D(R) dependence by least-squares fitting to the experimentally found lifetimes or intensities, the problem can be reduced to solving the system of linear equations like (18) or (19). However, when the number of a_k parameters exceeds two, it is almost impossible to find the exact solution due to the illconditioned plane matrices. This results in a strong dependence of the solutions obtained on the errors of the parameters present, on the rounding errors, on the solution technique, etc. In fact, these very uncertainties can result in the differences between the D(R)dependences found by different authors. The aforementioned difficulties have been analysed in detail in the work of Stolyarov *et al.* (1985) using the positive system of nitrogen as an example. It is shown that with the method of singular expansion one can substantially improve the stability of the solution.

We should also mention some additional difficulties and restrictions that occur when experimentally determining the electronic transition moments.

- (1) Since in most cases the concentrations of the molecules studied are unknown, only relative dependences $D(R_{v'v''})$ are determined from the measured intensities. Then these dependences can be normalized with respect to the results of some absolute measurements, often to the measured radiative lifetimes.
- (2) The *R*-centroid region, which corresponds to the measured intensities, is usually very restricted, and the extrapolation of $D(R_{v'v''})$ dependence beyond the limits of this region is often incorrect and even dangerous because of the instability of solution.

(3) When finding $D(R_{v'v''})$ from the measured radiative lifetimes, the domain of definition of the functions is unknown. Moreover, the definition itself is possible only when the Einstein coefficients can be calculated from the measured lifetime

$$\tau_{nv'}^{-1} = A_{nv'} = \sum_{v''} A_{v'v''}^{nm},$$

which implies the absence of other allowed transitions from the nv' levels, the absence of non-radiating transitions, the absence of perturbations and predissociations, etc.

To sum up, we may conclude that, for relatively light molecules, the most reliable information on the electronic transition moments can be obtained from quantumchemical calculations. For the molecules formed by the elements of the first and second periods, an accuracy of non-empirical calculations of the D(R) functions within 5-10% is quite attainable. Experimental D(R) dependences should be used only for those molecules, theoretical calculations on which are not sufficiently reliable at present. These are, e.g. the molecules involving transient elements.

4 RECOMMENDATIONS FOR THE ELECTRONIC TRANSITION MOMENTS OF THE C₂, CH, AND CN MOLECULES

The choice of the most reliable D(R) functions for these molecules was based on an analysis of all the accumulated data on their radiative characteristics. First, the results of *ab initio* calculations were analysed. Then with the chosen D(R) functions and RKR potentials, the $\tau_{nv'}$ and $f_{v'v''}$ values were calculated and compared with the results of experimental measurements. If $\tau_{nv'}$ or $f_{v'v''}$ values were calculated by the authors of *ab initio* calculations their results were compared with the experimental data. The results of comparison were tabulated and plotted. All D(R) functions that were chosen as the most reliable are listed in the summary Table 9 of the recommended electronic dipole transition moments.

4.1 C₂ Molecule: Swan $d^3\Pi_g - a^3\Pi_u$ System

This is one of the most thoroughly studied systems of bands of the C₂ molecule. Electronic transition dipole moments were calculated by Arnold and Langhoff (1978), Zeitz and Peyerimhoff (1978), Cooper (1981), Chabalowski *et al.* (1981). Arnold and Langhoff (1978), and Cooper (1981) used almost the same calculation technique (SCF+CI). The results obtained, namely, $S_e(R)$ values for R = 2.44 au listed in Table 1, almost coincide. Zeitz and Peyerimhoff (1978) and Chabalowski *et al.* (1981) calculated transition dipole moments D(R) with the MRCI wavefunctions. Configuration expansions involved 1000-2000 CSFs and 9000 CSFs correspondingly. According to Chabalowski *et al.* (1981), the insufficient size of configu-

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Table 1. C_2 : Theoretical and experimental estimate of the electronic transition strengthsfor the Swan system (all values are given in atomic units)

Authors	Method	$S_e(R)$ for $R = 2.44$	$^{a}S_{e}(R_{c})$ for $R_{c} = 2.44$
Zeitz and Peyerimhoff (1978)	Ab initio	5.20	
Arnold and Langhoff (1978)	Ab initio	4.12	
Cooper (1981)	Ab initio	4.10	
Chabalowski et al. (1981)	Ab initio	4.22	
Sviridov (1970)	Shock tube		3.00 ± 0.24
Cooper and Nicholls (1975)	Shock tube		3.52 ± 0.50
Arnold (1968)	Shock tube		3.56 ± 0.50
Fairbairn (1966)	Shock tube		3.42 ± 1.14
Brewer and Hagan (1979)	King furnace		3.67
Harrington et al. (1966)	Shock tube		2.8 ± 0.9

Note. ${}^{a}R_{c} = R_{v'v''}(R\text{-centroid}).$

Table 2. C_2 : radiative lifetimes of the vibrational levels of the $d^3\Pi_g$ state

Authors	Method	$\tau(v)(ns)$
Fink and Welge (1967)	PEE	200 ± 50
Smith (1969)	PEE	$170 \pm 20 \ (v = 0 - 2)$
Velghe and Leach (1973)	Laser pyrolysis	220 ± 20
Tatarczyk et al. (1976)	LIF	$120 \pm 10 \ (v = 1-5)$
Erman (1980)	HFD	$120 \pm 40 (v = 0-5)$
Nishi et al. (1982)	LIF	111 + 5 (v = 0)
Stark and Davis (1985)	LIF	$92 \pm 5 (v = 0)$
Bauer et al. (1986)	LIF	$106 \pm 15 (v = 0)$
		$106 \pm 15 (v = 1)$
Naulin et al. (1988)	LIF	$101.8 \pm 4.2 \ (v = 0)$
		$96.7 \pm 5.2 (v = 1)$
Bergstrom et al. (1989)	LIF	$100 \pm 10 \ (v = 0 - 4)$
Arnold and Langhoff (1978)	Ab initio	102.3 (v = 0);
		104.9 (v = 1)

Note. HFD, high-frequency deflection; LIF, laser-induced fluorescence; PEE, pulsed electron excitation.

ration expansion in earlier calculations of Zeitz and Peyerimhoff (1978) predetermined the fact that the corresponding results were overestimated as compared with Arnold and Langhoff (1978), Cooper (1981) and Chabalowski *et al.* (1981).

In Table 1 the non-empirically calculated $S_e(R)$ values are compared with the experimental data obtained from measured spectral intensities. The experiments were performed in shock tubes and King furnaces, which allow registration of spectra under conditions of LTE.

In Table 2 the experimentally measured lifetimes are listed along with the values that we calculated with the $S_e(R)$ function taken from Arnold and Langhoff (1978). This paper was chosen, because only in it were $S_e(R)$ functions tabulated for a wide

range of internuclear distances. Agreement between the experimental and calculated values is sufficiently good, especially for the recent lifetime measurements.

The summary Table 9 of electronic transition moments for the Swan system also contains D(R) values that we calculated from the data of Arnold and Langhoff (1978). A sharp rise of the function in the range $3.2 \le R \le 3.8$ au is assigned by the authors to the interaction of the $d^3\Pi_g$ and $e^3\Pi_g$ states.

4.2 C₂ Molecule: Phillips System

A large number of *ab initio* calculations were performed for the $A^1 \prod_u -X^1 \Sigma_g^+$ system of C₂, including estimates of radiative parameters, D(R), $f_{v'v''}$, and $\tau_{v'}$ values. The results obtained are in accord with each other, but differ from the experimental data. For example, the f_{00} values calculated in Chabalowski *et al.* (1983), Pouilly *et al.* (1983), van Dishoeck (1983), O'Neil *et al.* (1987), Theodorakopoulos *et al.* (1987), Langhoff *et al.* (1990) and Bruna and Wright (1991) lie within the range (2.17-2.70) $\times 10^{-3}$, whereas the experimental values determined in Cooper and Nicholls (1975), Roux *et al.* (1976), Brault *et al.* (1982) and Davis *et al.* (1984) from the absorption measurements are equal to $(3.9 \pm 0.8) \times 10^{-3}$, $(2.5 \pm 0.3) \times 10^{-3}$, 1.41×10^{-3} , and $(1.38 \pm 0.14) \times 10^{-3}$, respectively. The range of variations in the experimental f_{00} values is substantially larger than the range of experimental errors given by the authors. This indicates that noticeable systematic errors can probably be caused by the uncertainties in the calculation of C₂ concentrations. We do not consider this series of experimental data in further discussion.

The radiative lifetimes of the $A^1\Pi_u$ state of the C₂ molecule calculated by Chabalowski *et al.* (1983), Van Dishoeck (1983), O'Neil *et al.* (1987), Theodorakopoulos *et al.* (1987) and Langhoff *et al.* (1990) and measured by Erman *et al.* (1982), Bauer *et al.* (1985, 1986) and Erman and Iwamae (1995) are shown in Table 3. Being in accord with each other, all the theoretical values are lower than the experimental estimations.

Let us turn to the reliability of the theoretical values. The calculations in Chabalowski et al. (1983), Van Dishoeck (1983), O'Neil et al. (1987) and Theodorakopoulos et al. (1987) were performed within the framework of the MRCI approximation. Probably, the most reliable results were obtained by O'Neil et al. (1987), where a large AO basis set was used, all valence orbitals were involved in the optimization of the state-averaged CSFs obtained at the CASSCF level (SACASSCF), and CI was constructed taking into account not only the multireference state function, but also all CSFs singly and doubly excited with respect to it. In this work, the problem of accuracy and stability of solutions was also analysed with regard to the following factors.

(1) AO basis set. All calculations were performed with the Gaussian basis, the kernel of which was an (11s, 7p) Huzinaga set condensed to [7s, 5p] by contracting the innermost five s and three p primitive functions. The basis was augmented with diffuse s, p, d, and f functions on each atom. Specially performed calculations showed that adding to the [7s, 5p, 3d] basis either diffuse

	Theoretical						Ea	perimental	
v'	Ä	В	C	D	E	F	G	Н	I
0	14.1	13.0	11.1	10.7	11.64	11.1	13.4 ± 2.5^{a} 18.5 ± 3.0^{b}		
1	11.1	10.4	9.0	8.3	9.30	9.0	15.0 ± 4.0^{a}		
2	9.3	8.8	7.6	6.9	7.79	7.6	14.4 ± 2.0^{a}		
3	8.1	7.6	6.6	6.0	6.77	6.6	12.0 ± 2.0^{a} 11.4 ± 2.0^{b}	12.1 ± 2.0	6.8 ± 2.0
4	7.2	6.8	5.9	5.3	6.05	5.9	10.7 ± 2.0^{a}	11.0 ± 1.1	7.1 ± 1.1
5	6.5	6.2	5.3	4.9	5.52	5.3	7.9 ± 2.0^{a}		
6	6.0	5.7	4.9	4.5	5.12		7.0 ± 1.5^{a}	10.2 ± 1.3	6.4 ± 1.0
7	5.6	5.3	4.6	4.3	4.80		6.7 ± 1.0^{a}	12.5 ± 1.3	6.4 ± 1.1
8	5.3	5.0	4.3	4.0	4.55		6.8 ± 1.0^a		

Table 3. C₂: radiative lifetimes (μ s) of the vibrational levels of the $A^1 \Pi_u$ state

Note. A, O'Neil et al. (1987); B, Langhoff et al. (1990); C, Van Dishoeck (1983); D, Chabalowski et al. (1983); E, Theodorakopoulos et al. (1987); F, Bruna and Wright (1991); G, Bauer et al. (1985a, 1986b); H, Erman et al. (1982); I, Erman et al. (1995).

s and p functions or f functions only slightly affects the value of transition moment, i.e. further extension of the AO set could not substantially change the results.

- (2) The method of optimizing MOs and multireference state function. Three versions were considered: (a) optimization with respect to the $A^1 \Pi_u$, $X^1 \Sigma_g^+$, and $2^1 \Sigma_g^+$ states simultaneously (the curves of the two latter states have a non-crossing point close to R = 3.0 au); (b) optimization with respect to the $A^1 \Pi_u$ and $X^1 \Sigma_g^+$ states; and (c) optimization with respect to the $X^1 \Sigma_g^+$ and $2^1 \Sigma_g^+$ states. The difference between the calculated transition moments is substantial (approximately 20%) only near the non-crossing point, while at the other internuclear distances it is insignificant (approximately 2%).
- (3) The method for reducing the number of varied parameters. As was shown, use of the internally condensed CSF sets in the MRCI calculations insignificantly affects the D(R) values, resulting in differences of about 2% at R = 2.4 au (as compared with other calculations at a similar level) and somewhat larger values near the non-crossing point.
- (4) The size of configuration expansion. The calculations of radiative lifetimes were performed not only with the CI wavefunctions, but also with the MCSCF functions. The divergence was about 4% for v = 0. This allows one to hope that an increase in the size of CI expansion does not substantially change the results.

The D(R) and $\tau_{v'}$ values calculated by O'Neil *et al.* (1987) for the $A^1 \Pi_u - X^1 \Sigma_g^+$ system of the C₂ molecule are in good agreement with the corresponding results of Langhoff *et al.* (1990). In the latter work, the accuracy of the results obtained

was thoroughly analysed. The convergence in *n*-particle space was controlled by comparison with the results of FCI calculation with a DZP basis set (double-zeta plus polarization functions). The convergence of the single-particle basis was verified by systematically expanding the AO basis up to adding *g* orbitals to it. The relation between the spaces of single-particle basis sets and the configuration *n*-particle state functions was also controlled by systematically expanding the active space of the CASSCF/MRCI calculation. The relation was found to be insignificant. On the whole, Langhoff *et al.* (1990) came to the conclusion that the calculation technique they applied allows one to describe the behaviour of D(R) in the Franck-Condon region to a high level of precision. The divergence from the FCI results was about 1%. The radiative lifetimes estimated with this function differ from the true values by no more than 5% and may be considered as the lower bound on $\tau_{v'}$ values; that is, the true $\tau_{v'}$ values lie between those obtained by O'Neil *et al.* (1987) and those obtained by Langhoff *et al.* (1990).

Direct lifetime measurements of the $A^1 \Pi_u$ state were performed by Erman *et al.* (1982), Bauer *et al.* (1985, 1986) and Erman and Iwamae (1995). In Erman *et al.* (1982) the vibrationally excited $A^1 \Pi_u$ molecules were obtained by electron bombarding of C_2H_2 ; a high-frequency deflection (HFD) technique was used. The measurements were performed over a pressure range of the target gas from 10 up to 120 mTorr. The results were fitted into a Stern-Volmer plot from which the radiative lifetime was obtained in the normal way by extrapolation to zero pressure.

In Bauer *et al.* (1985) electronically excited C_2 molecules were produced by ArF laser photolysis (ELP) of C_2H_2 and C_2HBr , both diluted with Ar. In general, on multiphoton UV photolysis the molecular fragments might be produced in different excited states. Therefore, possible disturbances of lifetime determinations by cascading processes from higher electronic levels of C_2 and by reactions between other primary products of the photolysis were considered.

In all experiments Bauer *et al.* (1985) observed an increase of the Phillips band intensities for a time period of approximately 100 ns after the photolysis pulse, indicating secondary processes which also lead to $C_2(A^1\Pi_u)$ production. Since the increase period was at least 10 times shorter than the observed fluorescence decay, the authors concluded that the lifetime measurements should not have been influenced by the secondary processes producing excited C_2 molecules. By recording the emission spectrum with a delay of 4 μ s relative to the photolysis pulse, the authors excluded the influence of cascading transitions from the $C^1\Pi_g$, $C'^1\Pi_g$ and $E^1\Sigma_g$ states, because these states have lifetimes of the order of nanoseconds. The lifetimes for v' = 3 and 4 obtained by Bauer *et al.* (1985) are in a good agreement with the results of Erman *et al.* (1982), whereas the values obtained for the higher vibrational levels are significantly shorter than those of Erman *et al.* (1982).

Later (Bauer *et al.*, 1986) measurements of the lifetime for levels v' = 0 and 3 were also carried out by the laserinduced fluorescence technique (LIF). The $\tau(v = 3)$ value obtained agrees with ELP results, but $\tau(v = 0)$ is somewhat larger (18.5 \pm 3.0 μ s instead of 13.4 \pm 2.5 μ s).

One can see that all measured lifetimes of the $A^1\Pi_u$ state are larger than the corresponding *ab initio* values. Bruna and Wright (1991) proposed that this differ-

ence results from the cascades from the B'^1 state which is generated in situ along with the $A^1 \Pi_u$ state and has approximately about the same lifetime.

However, recently Erman and Iwamae (1995) gave another explanation of the difference between the measured and calculated lifetimes of the $A^1\Pi_u$ state. The authors supposed that collisional transfer from the other close-lying levels is present which tends to raise the registered lifetime as compared with the real radiative lifetime. As follows from a level scheme of the C_2 molecule several levels of the $B^1\Delta_g$ and $B'^1\Sigma_g^+$ states are close to those of the $A^1\Pi_u$ state ($\Delta E < kT$). High populations of these B and B' state levels should occur at particle excitations since the Franck-Condon factors for excitation of the $B^1\Delta_g$ and $B'^1\Sigma_g^+$ levels from the ground state are large and calculated lifetimes are also significant: 45-140 and 7-8 μ s, respectively. Consequently, transfer processes must be present. Indeed, the authors showed that catalyst gases (Ar, Kr) influence the intensities of the A-X system and the lifetime measurements for the v' = 6, J' = 18 level gave $\tau = 6.4 \pm 0.2 \ \mu$ s at 5 mTorr C_2 H₂ target pressure and $\tau = 11.4 \pm 0.2 \ \mu$ s in the presence of Ar at 85 mTorr.

Using the HFD technique Erman and Iwamae (1995) remeasured radiative lifetimes for a number of vibrational levels of the $A^1\Pi_u$ state at a lower pressure (5 mTorr) than earlier (Erman *et al.*, 1982) to reduce the autocatalytic effects of the target gas. The values obtained were shorter than the results of ealier direct measurements.

Taking into account all of the above we believe that the *ab initio* calculated lifetimes of the $A^1 \Pi_u$ state are the more reliable and that the true $\tau_{\nu'}$ values lie between those obtained by O'Neil *et al.* (1987) and those obtained by Langhoff *et al.* (1990). This conclusion should be valid for the D(R) function as well. Therefore, the summary Table 9 of the electronic transition moments for the $A^1 \Pi_u - X^1 \Sigma_g^+$ system of C₂ contains the results of both works.

4.3 CH Molecule: $A^2\Delta - X^2\Pi$ System

Ab initio calculations of the transition dipole moment for the $A^2\Delta-X^2\Pi$ system of the CH molecule were performed by Hinze *et al.* (1975), Larsson and Siegbahn (1983), Van Dishoeck (1987), Kanzler *et al.* (1991) and Hettema and Yarkony (1994). The results obtained shown in Figure 1 are in good accord with each other, except for the data of the first work. Kanzler *et al.* (1991) used the correlated, size-consistent *ab initio* effective valence-shell dipole operator method based on the quasi-degenerate many-body perturbation theory. Larsson and Siegbahn (1983) evaluated electronic wavefunctions within the framework of the CASSCF technique. The convergence of the results was studied as a function of the size and quality of the AO basis set and the size of the active space. As shown, accurate results can be obtained only when the atomic basis contains extended sets of *s* and *p* functions augmented with *d*-polarization functions and the active space involves δ orbitals. The calculations were performed with the following basis sets: C (11s, 8p, 3d)/[6s, 6p], 3d and H (9s), 3p/[4s], 3d. The active space involved 5σ , 3π , and 2δ orbitals.



Figure 1 Ab initio transition dipole moments D(R) for the $A^2\Delta - X^2\Pi$ system of the CH molecule.

The wavefunctions for the $A^2\Delta$ and $X^2\Pi$ states were constructed from 5620 and 5320 CSFs, respectively, and optimized separately for each state, though for such a large active space, the transition-moment estimate was insensitive to the way in which the orbitals were optimized.

Van Dishoeck (1987) calculated D(R) for the $A^2\Delta - X^2\Pi$ system of CH using a conventional MRCI procedure, which involved configuration selection and energy extrapolation to the zeroth-order threshold. The Hamiltonian matrix was constructed for 4000-5000 CSFs. The energies corresponding to the full configuration

Authors	Method	au(ns)	
Ortiz and Campos (1982)	DCM	565 ± 20	
Becker et al. (1980)	LIF	537 ± 5	
Brzozowsci et al. (1976)	HFD	534 ± 5	
Carozza and Anderson (1977)	DCM	508 ± 25	
Bauer et al. (1989)	LIF	526 ± 11	
Larsson and Siegbahn (1983)	Ab initio	536	
Hinze et al. (1975)	Ab initio	414	
Van Dishoeck (1987)	Ab initio	464	
Kanzler et al. (1991)	Ab initio	513	
Hettema and Yarkony (1994)	Ab initio	520	

Table 4. CH: radiative lifetimes of the v = 0 level of the $A^2 \Delta$ state

Note. DCM, delayed coincidence method; HFD, high-frequency deflection; LIF, laser-induced fluorescence.

expansion for the given AO basis set were estimated including the Davidson correction. A slight divergence of the results obtained and those of Larsson and Siegbahn (1983), the author explained as due to the difference in the sets of carbon s and pfunctions.

Hettema and Yarkony (1994) performed a series of calculations of potential energy curves, dipole moments, and transition dipole moments for a number of electronic states and transitions of the CH molecule, including the $A^2\Delta - X^2\Pi$ system. The SA-MCSCF/CI method was applied, and the wavefunctions of the $A^2\Delta$ and $X^2\Pi$ states were constructed from 378 188 and 365 628 CSFs, respectively. The results were very close to those of Larsson and Siegbahn (1983).

With the non-empirical D(R) functions obtained in Hinze *et al.* (1975), Larsson and Siegbahn (1983), Van Dishoeck (1987), Kanzler *et al.* (1991) and Hettema and Yarkony (1994), we calculated the radiative lifetimes of the vibrational levels of the CH $A^2\Delta$ state. The results for v = 0 are listed in Table 4 along with the experimental values. There were more than 10 works devoted to measuring the lifetimes of the $A^2\Delta$ state. Examining these works, we chose and included in Table 4 only those where the applied technique allowed the authors to obtain values that were not distorted by predissociation. For the $A^2\Delta$ state, predissociation is observed already for v = 1, J > 11; therefore, if these levels fell within the observation range, the measured lifetime did not correspond to the radiative lifetime. As can be seen from Table 4, the calculated and measured lifetimes for v = 0 are in good agreement with each other. On the basis of this comparison, we chose the D(R)function obtained by Larsson and Siegbahn (1983) as the most reliable.

4.4 CN Molecule: Violet System

A sufficiently large number of studies on the radiative characteristics of the CN molecule have been performed in shock tubes, which allows one to obtain molecules under conditions of LTE. These conditions provide the possibility of calculating

Table 5. CN: shock-tube measurements of the electronic oscillator strength (f_e) for the $B^2\Sigma^+ - X^2\Sigma^+$ system

Authors	Assumed D ₀ (CN) (eV)	Received fe	$f_e at D_0 = 7.89 eV$
Arnold and Nicholls (1973)	7.89	0.035 ± 0.005	0.035
Davies (1969)	8.1	0.033 ± 0.003	0.042
Levitt and Parsons (1969)	7.8	0.027	0.025
Kudryavtsev et al. (1963)	7.5	0.0276	0.019
McKenzie and Arnold (1967)	8.2	0.023 ± 0.003	0.032
Menard et al. (1967)	7.7	0.027	0.023
Colket (1984)	7.95	0.036 ± 0.003	0.044
Reis (1965)	8.2	0.019 ± 0.004	0.022
Fairbairn (1964)	8.35	0.016 ± 0.008	0.026

equilibrium concentrations of the molecules studied and, consequently, of applying a technique to measure the absolute intensities. However, as mentioned above, the reliability of the results obtained is predetermined to a noticeable degree by the reliability of the thermodynamic parameters used in calculating the equilibrium composition. Table 5 is a good illustration of this statement. It contains the oscillator strength values for the $B^2\Sigma^+ - X^2\Sigma^+$ transition of the CN molecule determined in experiments with shock tubes. The second column contains the values of dissociation energy used in the evaluetion of equilibrium composition; the third column contains the corresponding f_e values; and the fourth column contains the f_e values that could be obtained with the same experimental results provided that

Table 6. CN: radiative lifetimes of vibrational levels of the $B^2\Sigma^+$ state

Authors	Method	v'	$\tau(v)(ns)$
Cook and Levy (1972)	Hanle	0	39.4 ± 9.3
Jackson (1974)	LIF	0, N = 0 - 14	65.6 ± 1.0
Bennet and Dalby (1962)	Decay fluorescence	0-4	85 ± 10
Liszt and Hesser (1970)	Phase shift	0-2	59.3 ± 6.0
Luk and Bersohn (1973)	Photolysis	0-4	60.8 ± 2.0
Mohamed et al. (1977)	PPD	0-1	61.1 ± 7.6
Duric et al. (1978)	HFD	0, N = 0 - 16	
· · ·		0, head	63.8 ± 0.6
		1, head	66.3 ± 0.8
		2, head	64.3 ± 2.0
Davis et al. (1986)	LIF	0, N=17	62 ± 6
Cartwright and Hay (1982)	Ab initio	0	62.05
Lavendy et al. (1984)	Ab initio	0	72
Larsson et al. (1983)	Ab initio	0	66.6
Knowles et al. (1988)	Ab initio	0	60.73
Bauschlicher et al. (1988)	Ab initio	0	62.36

Note. HFD, high-frequency deflection; LIF, laser-induced fluorescence; PPD, photon-photon delayed.



Figure 2 The calculated radiative lifetimes for the vibrational levels of the $B^2\Sigma^+$ state of CN.

 $D_0 = 7.89$ eV was used. Comparing columns 3 and 4, one sees that even small changes in D_0 lead to substantial changes in the results. The question on the true dissociation energy of CN is still open (Pradhan *et al.*, 1994). That is why we did not take into account the results obtained from the intensity measurements when choosing the most reliable functions of the dipole moments of the $A^2\Pi - X^2\Sigma^+$ and $B^2\Sigma^+ - X^2\Sigma^+$ transitions.

The results of studying the lifetimes of vibrational levels of the $B^2\Sigma^+$ state are shown in Table 6. With the exception of the obviously incorrect data of Bennet and Dalby (1962) and Cook and Levy (1972), the experimental results are in sufficiently good agreement with each other. The investigations based on the LIF technique (Jackson, 1974) showed that cascade transitions from the $H^2\Pi$ level did not substantially affect the lifetime of the $B^2\Sigma^+$ state in contrast to the supposition of Mohamed *et al.* (1977). Measurements of lifetimes of separate rotational levels performed in Jackson (1974), Duric *et al.* (1978) and Davis *et al.* (1986) for v = 0 showed that the perturbations of rotational $B^2\Sigma^+$ (v = 0) levels by the $A^2\Pi$ (v = 10) levels do not substantially affect the lifetimes of the $B^2\Sigma^+$ levels. An exception was noted for the level N = 4, where higher lifetime values were obtained, i.e. $\tau = 71.3 \pm 0.3$ ns in Jackson (1974) and $\tau = 72.9 \pm 0.6$ ns in Duric *et al.* (1978). As follows from the above discussion, the measured τ values correspond to the radiative lifetime, and agreement between these data and the *ab initio* values (except for Lavendy *et al.*, 1984) indicates the reliability of the *ab initio* calculations.

The *ab initio* results are also in accord with each other (again except for Lavendy et al., 1984). We compared D(R) functions given in Knowles et al. (1988) and Bauschlicher et al. (1988) and the $\tau_{v'}$ sets taken from Cartwright and Hay (1982), Larsson et al. (1983), Lavendy et al. (1984), Knowles et al. (1988) and Bauschlicher et al. (1988) and shown in Figure 2. Especially good agreement was noted for the works of Cartwright and Hay (1982), Knowles et al. (1988) and Bauschlicher et al. (1988): within the accuracy of calculation, the results of these works practically coincide. These calculations were performed following almost the same sufficiently high levels of theory. We would like to draw special attention to the works of Bauschlicher et al. (1988) and Knowles et al. (1988) where the most complete basis sets of single-electron functions and configuration state functions were used. The latter work can even serve as a benchmark of highly accurate calculations. This is why, in the summary Table 9 of the recommended values, we included the D(R)function taken from Knowles et al. (1988).

4.5 CN Molecule: red $A^2\Pi - X^2\Sigma^+$ System

In contrast to the violet system, for which numerous theoretical and experimental studies of radiative characteristics provided compatible results, data on the red system are noticeably scattered. This is expecially evident in the case of measured lifetimes of vibrational levels of the $A^2\Pi$ state. The corresponding results are listed in Table 7 and can be schematically divided into three groups. The first group involves the results obtained by Duric *et al.* (1978) using the high-frequency deflection (HFD) technique. It was shown that for the levels with v' = 2-10 the radiative lifetime of the $A^2\Pi$ state is about 4.2 μ s and independent of vibrational level. The addition of argon leads to an increase in the $A^2\Pi$ lifetime. This is explained by the collisional transfer between the isoenergetic vibrationally excited levels of the A and X states. The collisional transfer effect distorts the measured decay curve even at pressures in the millitorr range, but can be accounted for on the basis of a simple two-state model.

Results similar to those of Duric *et al.* (1978) were also obtained by Katayama *et al.* (1979). The authors studied collisional coupling between the energetically

υ	A	В	С	D	E	F	G
0	14.2		8.50 ± 0.45				7.3ª
1	11.6	7.29 ± 0.15	8.02 ± 0.55				
2	10.2	7.05 ± 0.28	6.67 ± 0.60	6.96 ± 0.3	3.83 ± 0.5	7.1 ± 0.6	8.5 ^b
3	9.0	6.95 ± 0.31	5.50 ± 0.45	5.09 ± 0.2	4.05 ± 0.4		
4	8.0	6.58 ± 0.34	4.70 ± 0.23	3.83 ± 0.2	3.98 ± 0.4		
5	7.4	7.40 ± 0.41	4.30 ± 0.70	3.38 ± 0.2	4.20 ± 0.4		4.2°
6	6.8	6.45 ± 0.38		2.26 ± 0.2	4.35 ± 0.4		
7	6.3	6.48 ± 0.28		1.84 ± 0.3	4.35 ± 0.4		
8	5.9	6.91 ± 0.36			4.50 ± 0.4		
9	5.5	6.43 ± 0.23			4.20 ± 0.4		
10	5.2			4.10 ± 0.4			

Table 7. CN: measured lifetimes (μs) for vibrational levels of the $A^2\Pi$ state

Note. A, Sneden and Lambert (1982) analysis of the solar spectrum. B, Jeunehomme (1965) discharge in acetonitrile. C, Taherian and Slanger (1984) measurements of emission accompaning photodissociation of C_2N_2 . D, Lu et al. (1992) laser photolysis of C_2N_2 and CICN, followed by LIF measurements. E, Duic et al. (1978) high-frequency deflection measurements. F, Nishi et al. (1982) multiphoton dissociation of C_2H_3 CN in molecular beam. G, other results: ^aConley and Halpern (1980) averaged over the values mesured for $v = 0 \ {}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ states by laser excitation; ^bWentink et al. (1964) τ averaged over the data for v = 1-3 obtained with pulsed discharge; ^cKatayama et al. (1979) laser fluorescence measurements of the lifetime averaged over the v = 3-9 states.

close states of CN excited by a dye laser. The data were analysed by fitting to a complicated kinetic scheme, wherein a group of parameters included the lifetimes of several CN $A^2\Pi$ vibrational levels. The conclusion was arrived at that a lifetime of 4.2 μ s gave the best overall fit to all recorded decay curves in the range v' = 3-9.

The second group involves the results obtained by Jeunehomme (1965). He measured the CN emission following electrodeless radio-frequency discharge in acetonitrile and found that lifetimes of the levels with v' = 1-9 were about 7 μ s independent of the vibrational state. The same technique was applied by Wentink *et al.* (1964). In that work it was found that $\langle \tau \rangle = 8.5 \ \mu$ s for v' = 0-3.

The results obtained by Taherian and Slanger (1984) and Lu *et al.* (1992) form the third group. Taherian and Slanger (1984) measured the CN $A^2\Pi$ emission accompaning the laser photolysis of C_2N_2 . They found that for the series v' = 0-5the lifetime decreases from 8.5 to 4.3 μ s. Lu *et al.* (1992) measured the radiative lifetimes for the levels with v' = 2-7 using the laser photolysis-laser excitation technique. They also found that in this interval of vibrational quantum number changes the lifetime decreases from 6.96 to 1.84 μ s.

Conley and Halpern (1980) and Nishi *et al.* (1982) measured $\tau_{v'}$ for one vibrational level only. For this reason, their results may equally be assigned to either the second or the third group. Conley and Halpern measured $\tau(v'=0)$ by laser excitation following C_2N_2 photolysis. Measurements were performed for both ²II substates and gave the following results: $\tau_0({}^2\Pi_{1/2}) = 8.4 \pm 2.1 \ \mu s$ and $\tau_0({}^2\Pi_{3/2}) = 6.2 \pm 0.9 \ \mu s$. Nishi *et al.* (1982) observed the CN red emission accompaning the multiphoton dissociation of C_2H_3CN in a molecular beam. Because of

υ'	Cartwright and Hay (1982)	Larsson et al. (1983)	Lavendy et al. (1984)	Knowles et al. (1988)	Bauschlicher et al. (1988)
0	11.1	8.1	11.3	11.16	11.2
1	9.6	7.0	9.6	9.71	9.7
2	8.6	6.3	8.4	8.66	8.6
3	7.8	5.7	7.6	7.87	7.8
4	7.2	5.3	6.9	7.25	7.2
5	6.7	4.9	6.4	6.75	6.7
6	6.3	4.6	6.0	6.35	6.3
7	6.0	4.3	5.7	6.01	6.0
8	5.7	4.2	5.4	5.73	5.7
9	5.5	4.0	5.2	5.49	5.5
10	5.3	3.9		5.29	

Table 8. CN: calculated radiative lifetimes (μs) for vibrational levels of the $A^2 \Pi$ state

the collision-free nature of the beam, the corresponding result (τ for v' = 2) can be considered as a reliable one.

Sneden and Lambert (1982) measured the equivalent widths for CN lines in the solar photospheric spectrum. Then the CN A-X electronic transition moment was calculated from the equivalent widths and the radiative lifetimes of the levels v' = 0-10 were estimated with this D(R) function. However, we should note that the absolute lifetimes obtained (not the relative ones) depend on the accepted model of the solar atmosphere, accepted solar C, N, and O abundances and the assumed value of the CN dissociation energy. Therefore, the results obtained by Sneden and Lambert may indicate the character of changes in the radiative lifetimes of various vibrational levels of the $A^2\Pi$ state rather than reflect the absolute τ values.

Table 8 contains the results of non-empirical calculations performed in Cartwright and Hay (1982), Larsson *et al.* (1983), Lavendy *et al.* (1984), Knowles *et al.* (1983), and Bauschlicher *et al.* (1988). All the data, except for $\tau_{v'}$ obtained by Larsson *et al.* (1983), are in good accord with each other. To date, the most accurate calculations of the CN A-X system as regards the sizes of basis sets and an account of the electron correlation effects have been performed by Knowles *et al.* (1988), and Bauschlicher *et al.* (1988). This was confirmed by Pradhan *et al.* (1994) who recalculated the radiative lifetimes of the red system using the SACASSCF/IC-MRCI (internally contracted MRCI) approach with the augmented correlationconsistent polarized-valence basis sets of Dunning. The resulting lifetime turned out to exceed the results of Knowles *et al.* (1988), and Bauschlicher *et al.* (1988) by only 1%.

Comparing the values given in Tables 7 and 8, one can see that all the directly measured lifetimes are smaller than the corresponding theoretical estimates. The reason for this is still unclear. On the one hand, the main cause typical of most of these experiments, i.e. the collisional energy transfer, would increase rather than lower the lifetimes. On the other hand, because of the high quality of the theoretical works and the excellent agreement between them, there do not seem to be any

Molecule System	C_2 $d^3\Pi_g - a^3\Pi_u$	$A^1\Pi_u$	C_2 - $X^1\Sigma_g^+$	CH $A^2\Delta - X^2\Pi$	CN $A^2\Pi - X^2\Sigma^+$	$CN B^2 \Sigma^+ - X^2 \Sigma^+$
R	Å	В	Ċ	D	E	${oldsymbol E}$
1.40		<u> </u>		0.3940		
1.60				0.3640	0.2819	0.3666
1.70				0.3480	0.2957 ^a	0.4797 ^a
1.80		0.3766	0.3687	0.3310	0.3043	0.5676
1.90		0.3823ª	0.3744ª	0.3130	0.3084^{a}	0.6316 ^a
2.00		0.3826	0.3746	0.2940	0.3085	0.6731
2.10		0.3780	0.3698 ^a	0.2750	0.3053ª	0.6937ª
2.17	0.9850	0.3722ª	0.3638ª	0.2580 ^a	0.3014ª	0.6970 ^a
2.20	0.9690	0.3690	0.3606	0.2510 ^a	0.2994	0.6960
2.30	0.9133ª	0.3558	0.3475 ^a	0.2390	0.2912 ^a	0.6826 ^a
2.34	0.8900	0.3495ª	0.3412 ^a	0.2413ª	0.2873 ^a	0.6731 ^a
2.40	0.8537 ^a	0.3390	0.3306	0.2200	0.2811	0.6543
2.479	0.8030	, 0.3228°	0.3143ª	0.2110 ^a	0.2721 ^a	0.6217 ^a
2.50	0.7889ª	0.3181	0.3095ª	0.2020	0.2696 ^a	0.6116^{a}
2.60	0.7220	0.2921	0.2831	0.1742 ^a	0.2570	0.5569
2.75	0.6294 ^a	0.2347 ^a	0.2301 ^a	0.1560	0.2368	0.4600 ^a
2.80	0.5929ª	0.2144	0.2074	0.1491 ^a	0.2298 ^a	0.4264^{a}
2.90	0.4960	0.1685 ^a	0.1522	0.1317^{a}	0.2157ª	0.3618 ^a
3.00	0.3578ª	0.0725	0.0856	0.1130	0.2015	0.3055
3.20	0.0290	-0.2420	-0.0305	0.0822ª	0.1735 ^a	0.2304 ^a
3.40		-0.2103	-0.0965 ^a	0.0603ª	0.1466	0.1950
3.50		-0.1623 ^a	-0.1037ª	0.0520	0.1337 ^a	0.1870^{a}
3.60		-0.1307ª	-0.0901	0.0451 ^a	0.1212ª	0.1826 ^a
3.80	0.3110	-0.1068ª		0.0344 ^a	0.0977 ^a	0.1764^{a}
4.00		-0.1189		0.0259 ^a	0.0767	0.1598
4.50		-0.1777^{a}		0.0000		
5.00		-0.0314				

Table 9. Recommended transition dipole moments for some molecular systems (all values are in atomic units)

^aThe values were calculated using spline interpolation.

grounds (like errors or inaccuracy of the calculations) for the observed disagreement between theory and experiment. Because of substantial scattering of the experimental data, we assume the theoretical results to be more reliable. In Table 9 containing the recommended electronic transition dipole moments, we have included the D(R)function obtained by Knowles *et al.* (1988).

5 SUMMARY

Experimental and theoretical methods for determining the electronic transition moments of diatomic molecules have been briefly considered. All published results on experimental studies and *ab initio* calculations of radiative characteristics for a

Note. A, Arnold and Langhoff (1978); B, Langhoff et al. (1990); C, O'Neil et al. (1987); D, Larsson and Siegbahn (1983); E, Knowles et al. (1988).

number of astrophysically significant molecular systems have been analysed. As a result the most reliable electronic transition moments D(R) are recommended for the Swan and Phillips system of C₂, the $A^2\Delta - X^2\Sigma^+$ system of CH and the red and violet systems of CN. The recommended functions are listen in the summary Table 9.

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