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Radiative transitions in TiO: Ab initio oscillator strengths and lifetimes for low-lying electronic states

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Abstract. The dipole transition moments, oscillator strengths and radiative lifetimes for seven low-lying triplet and ten singlet electronic states of the TiO molecule have been calculated using the multireference singles and doubles configuration interaction method (MRCI) and compared with the available literature data. Our MRCI results support the previous theoretical transition moments reported by Langhoff (1997) for the most of the computed bands except for the δ and ϕ ones. For the δ band our computed electronic oscillator strength f_{e} is 0.0581 which is considerably smaller than that of Langhoff (0.096). Our f_{e} supports the proposal of Plez (1998) that the value of Langhoff should be divided by ∼2 to match observations. Our MRCI calculations give f_{e} of 0.0668 for the ϕ band. This is larger than the value of 0.036 obtained by Langhoff. We adduce strong arguments that our f_{e} for the ϕ band is reasonable. We predict two new $^1\Pi$ and one $^1\Phi$ states which exhibit avoided crossings with the known $b^1\Pi$ and $c^1\Phi$ states, respectively. These avoided crossings can appreciably perturb the rovibrational levels and, consequently, further complicate the identification of the lines in the experimental spectra. Our calculated transition moments for all the computed electronic states are available at URL `http://www.ita.uni-heidelberg.de/research/mld/`.

Key words. TiO – radiative transitions – radiative lifetimes – oscillator strengths

1. Introduction

The TiO molecule is the main opacity source in the atmospheres of cool M-type stars in the visible and near-infrared. Because of its importance in model atmosphere investigations and in quantum chemistry, this molecule is one of the best studied transition metal compounds. There are six known singlet states ($a^1\Delta$, $d^1\Sigma^+$, $b^1\Pi$, $c^1\Phi$, $f^1\Delta$ and $e^1\Sigma^+$) and ten triplet states ($X^3\Delta$, $E^3\Pi$, $A^3\Phi$, $B^3\Pi$, $C^3\Delta$, $D^3\Sigma^-$, $G^3\Phi$, $H^3\Phi$, $I^3\Pi$ and $J^3\Pi$) (see Huber & Herzberg 1979; Merer 1989; Barnes et al. 1997 and references therein). The $D^3\Sigma^-$, $G^3\Phi$, $H^3\Phi$, $I^3\Pi$ and $J^3\Pi$ states have been observed recently (Barnes et al. 1997). Using the molecular constants and electronic oscillator strengths available in the literature, Jørgensen (1994) extended the line list of Collins (Collins 1975a) to include weaker bands, satellite branches, Ti isotopes other than ^{48}Ti and improved T_{e} value for the $a^1\Delta$ state. Since then there have been several new spectroscopic studies of this molecule. These new experimental data on line positions (Amiot et al. 1995, 1996; Kaledin et al. 1995; Ram et al. 1996; Barnes et al. 1997) and theoretical transition moments (Langhoff 1997) allowed an improvement of the TiO line list. Using these new data, Plez (1998) has produced a new TiO line list based on his unpublished list used in Plez et al. (1992) and has successfully used it for simulations of M-type stars. Recently, Schwenke (1998) has revised the molecular constants for the $a^1\Delta$, $d^1\Sigma^+$, $b^1\Pi$, $c^1\Phi$ and $f^1\Delta$ singlet and $X^3\Delta$, $E^3\Pi$, $A^3\Phi$, $B^3\Pi$ and $C^3\Delta$ triplet states taking into account couplings between them. Schwenke has also predicted two new low-lying electronic states ($g^1\Gamma$ and $h^1\Sigma^+$) and has taken them into account as perturbers in his study. The new molecular constants obtained in this work for the $X^3\Delta$, $a^1\Delta$ and $f^1\Delta$ states differ considerably frome those recommended by Jørgensen (1994).

Most controversial issues in the spectroscopy of TiO are the absolute values of the oscillator strengths. Numerous and frequently very different estimates for the radiative lifetimes and consequently, for the oscillator strengths have been reported in the literature (Collins 1975b; Davis et al. 1986; Steele & Linton 1978; Brett 1990; Simard & Hackett 1991; Price et al. 1974; Doverstall & Weijnitz 1992; Carrette & Schamps 1992; Feinberg & Davis 1977, 1978; Hedgecock et al. 1995; Jørgensen 1994). It is clear that these discrepancies are due to uncontrolled experimental errors and artefacts (see for example Schamps 1994; Hedgecock et al. 1995). Because of these uncertainties in the radiative lifetimes (oscillator strengths), the oscillator strengths are often scaled to

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match particular observations in works on stellar atmospheres (see for example Plez 1998; Schiavon & Burbuy 1999).

There are only a few theoretical investigations on low-lying electronic states of TiO (Bauschlicher et al. 1983; Sennesal & Schamps 1987; Schamps et al. 1992; Langhoff 1997; Schwenke 1998). Bauschlicher et al. (1983) and Sennesal & Schamps (1987) mainly focused on the energies and chemical bonding of the ground and some low-lying excited electronic states. Schwenke used ab initio calculations to obtain an initial guess for the rotation-orbit and spin-orbit coupling parameters in TiO. Schwenke also calculated the dipole moments for the $X^3\Delta$, $a^1\Delta$, $E^3\Pi$ and $D^3\Sigma^-$ states. The are only two theoretical investigations devoted to the transition moments, oscillator strengths and radiative lifetimes (Schamps et al. 1992; Langhoff 1997). Schamps et al. used the single-reference singles and doubles configuration interaction (SDCI) method to calculate the oscillator strengths and radiative lifetimes which were computed using the dipole transition moments at a Ti-O distance of 3.1 a.u. Their radiative lifetimes for the $B^3\Pi$, $C^3\Delta$ and $f^1\Delta$ agree well with the recent measurements of Hedgecock et al. (1995). Theoretical transition moments, oscillator strengths and radiative lifetimes, obtained at a higher level of electron correlation treatment, were recently reported by Langhoff (1997). The state-averaged complete active space (SA-CASSCF) procedure followed by the internally contracted multireference configuration interaction (IC-MRCI) method was used in these calculations. The radiative lifetimes obtained by Langhoff are in a good agreement with the recent experimental values of Hedgecock et al. (1995). Langhoff's oscillator strengths are smaller than those recommended by Jørgensen (1994) which have been obtained from the earlier lifetime measurements and astrophysical calibrations. Exceptions are the $\delta(b^1\Pi-a^1\Delta)$ and $\phi(b^1\Pi-d^1\Sigma^+)$ transitions. The electronic oscillator strength f_e of 0.096 for the δ system reported by Langhoff is two times larger than the value of 0.048 recommended by Jørgensen (1994). For the ϕ system Langhoff's result (0.036) is about two times smaller than the f_e value of Jørgensen (0.052).

Here we should note that Langhoff in his original work reported for the ϕ band the f_e and f_{00} values of 0.018 and 0.0106, respectively. One obtains, however the values of 0.036 and 0.0212, respectively for f_e and f_{00} when using Langhoff's transition moments for the $b^1\Pi-d^1\Sigma^+$ transition. Thus, Langhoff missed a factor of 2 when calculated the oscillator strengths for $\Sigma-\Pi$ transitions. We, therefore, from here on will use Langhoff's oscillator strengths for the ϕ-band multiplied by a factor of 2 when referring to Langhoff's original work (Langhoff 1997). Based on his model atmosphere study, Plez (1998) has concluded that the intensity of the δ-band is overestimated by about a factor of 2 if the transition moment function of Langhoff (1997) is used. Recently, Schiavon & Barbuy (1999) have reported the electronic oscillator strengths for the $\gamma\prime$, ϵ and ϕ systems which differ from the experimental and ab initio values found in the literature. The latter authors by fitting the TiO band heads in their synthetic spectra of well-known M giants derived the oscillator strengths.

Thus, one can see that there is still considerable disagreement between the oscillator strengths reported for some transitions. At present the theoretical transition moments obtained by Langhoff (1997) must be considered as the best available data. The following procedure was used by Langhoff in his calculations. First, the molecular orbitals were determined using the SA-CASSCF approach in C_{2v} symmetry. Then, these orbitals were used as the basis for a multireference singles and doubles CI treatment with all the CASSCF configurations chosen as the reference space. This procedure allows one to account for a great fraction of electron correlation, which is especially important for the transition metal compounds. The basis of the molecular orbitals obtained at the CASSCF level already accounts for some fraction of electron correlation and the subsequent CI calculations further improve the correlation treatment. The SA procedure, however, can seriously affect electronic states in some cases. Schwenke (1998), for example, reported that the SA procedure strongly affects the relative contributions of the $\pi^1\delta^1$ and $\sigma^1\pi^1$ configurations to $^1\Pi$ states of TiO. The $b^1\Pi$ state in TiO is involved in the $\delta(b^1\Pi-a^1\Delta)$ and $\phi(b^1\Pi-d^1\Sigma^+)$ transitions. Thus, the largely overestimated theoretical intensity of the δ band may be due to an artefact of the state averaging. In this case also the intensity of the ϕ band may significantly be affected.

Ab initio calculations of the electronic states of TiO are additionally complicated by the presence of level crossings (Schwenke 1998). At relatively large Ti-O distances repulsive states cross the bound states (Langhoff 1997). This makes the SA-CASSCF calculations extremely difficult and explains why the calculations of Langhoff (1997) were restricted to Ti-O distances below 3.6 a.u. To overcome these problems is indispensable for producing reliable line lists, which could be used for model atmosphere investigations. Besides the high accuracy requirements for the oscillator strengths, the spectral line positions should be given to an accuracy of about 0.3 cm^{-1} in order to deal with contemporary high-resolution observations. The most complete TiO line list has been produced by Schwenke (1998). However, the line positions for high rovibrational excitations are not accurate in this data set. There are many factors which can be responsible for this: lack of experimental data for fitting the potentials, couplings to electronic states not accounted for, etc.

Because of the lack of convergence of both the experimental and the theoretical determinations of the radiative lifetimes and oscillator strengths it is imperative to have estimates for these quantities obtained by different methods. We thus decided to perform calculations on the low-lying electronic states of TiO without the use of the SA procedure. We also computed a few additional electronic states in order to investigate possible avoided crossings. Although we have also calculated the potential energy curves for the electronic states, we mainly focused on the transition moments. These quantities are difficult to obtain from experimental data.

2. Theoretical methods

2.1. The electronic structure calculations

We used the multireference internally contracted singles and doubles CI method as implemented in the MOLPRO98 codes (Werner et al. 1998). The [8s, 7p, 5d, 3f, 2g] (Pou-Amerigo et al. 1995) and [5s, 4p, 3d, 2f] (Widmark et al. 1990) basis sets were used for the Ti and O atoms, respectively. The electronic states were calculated in C_{2v} symmetry. We used the molecular orbitals of the closed-shell $^1\Sigma^+$ state as the basis for our subsequent CI calculations. The electronic configuration of this self consistent field (SCF) closed-shell state is $8\sigma^2 9\sigma^2 3\pi^4 1\delta^0$ (here we denote only the valence electrons). The configuration space for the CI calculations was generated as follows: the reference configurations were obtained allowing all symmetry-allowed single and double excitations of eight electrons from the 8σ, 9σ and 3π orbitals into six σ, two π and two δ orbitals unoccupied in the reference SCF state. Final configuration space included these reference configurations and all their single and double excitations into all external unoccupied orbitals of the closed-shell $d^1\Sigma^+$ SCF state. Evidently our CI calculations are biased in favor of the $d^1\Sigma^+$ state which has the leading $8\sigma^2 9\sigma^2 3\pi^4 1\delta^0$ configuration. In this case one should expect the best description of the $d^1\Sigma^+$ state, whereas the accuracy for other states should be lower. From this point of view it is worthwhile to perform CI calculations using a specific choice of the molecular orbital basis set according to the leading configuration for a particular electronic state. However, only the use of a common set of molecular orbitals for all electronic states allows for calculations of the transition moments as implemented in the computer codes MOLPRO98 (Werner et al. 1998) we used. Another way of the calculations which allows computing the transition moments is the following. First one performs a state-averaged CASSCF calculation for all desired electronic states. The output of such a calculation is a single set of molecular orbitals averaged over all calculated states. Normally, such molecular basis provides a good starting point for subsequent CI calculations. In some cases, however, the state averaging can result in some artificial disbalance of contributions of different configurations to the final many-body states (Schwenke 1998). Due to the restricted character of practical CI calculations such an artificial disbalance can remain in the electronic states obtained in CI calculations. This can considerably affect the respective transition moments. Our approach is free of state averaging effects and we will show that it gives reasonable transition moments.

The transition moments were computed in the length gauge over real orbitals. The connection with complex orbitals which are used sometimes for definition of the transition moments and oscillator strengths can be found, for example, in the work of Langhoff (1997).

Despite the progress made in the last two decades in the field of the electronic many-body calculations, the spectroscopic accuracy can hardly be achieved at the present level of theory. Because of this one usually combines the experimental data on the excitation energies with the theoretical electronic transition moments to calculate the oscillator strengths and radiative lifetimes. In the present work we replaced our theoretical potentials with the experimental Rydberg-Klein-Rees (RKR) potentials. Two sets of molecular constants to construct the RKR potentials were used. The first set is by Jørgensen (1994) and the second is by Schwenke (1998). Here we should note that the RKR potentials obtained for some states from these two sets are quite different, resulting also in very different Franck-Condon factors.

2.2. The oscillator strengths and radiative lifetimes

The oscillator strength for the absorption transition between the vibrational levels v' and v'' of the lower and upper electronic states γ' and γ'' with the spatial degeneracies $G_{\gamma'}$ and $G_{\gamma''}$, respectively, is defined as follows:

$$\begin{aligned} f_{v'v''} &= 4.557\ 10^{-6}\ \frac{2}{3}\frac{\nu_{v'v''}}{G_{\gamma'}} \\ &\quad \times \sum_{M'M''} \mid \langle v''\gamma''M'' \mid \hat{d} \mid v'\gamma'M' \rangle \mid^2, \end{aligned} \tag{1}$$

where $\nu_{v'v''}$ is the transition energy between the v' and v'' levels (cm^{-1}), the transition moments for the dipole operator $\hat{d}$ are in atomic units and the summation is over all spatial projections M' and M'' of the lower and upper electronic states, respectively. The spatial degeneracy G is equal to 1 for Σ states and 2 for all states with larger orbital momenta (Π, Δ, Φ...).

The Einstein $A_{v''v'}$ coefficients (s^{-1}) are defined by

$$A_{v''v'} = 0.6669\frac{G_{\gamma'}}{G_{\gamma''}}\nu^2_{v'v''}f_{v'v''}. \tag{2}$$

The radiative lifetime is

$$\tau_{v''} = \left(\sum_{v'} A_{v''v'}\right)^{-1} \tag{3}$$

where the summation is over all vibrational levels of lower dipole-allowed states.

The electronic oscillator strength $f_{\rm e}$ widely used in the literature is related to the oscillator strength $f_{v'v''}$ by the following expression

$$f_{\rm e} = f_{00}/q_{00}, \tag{4}$$

where the quantities $q_{v'v''}$ are the squared overlaps $\langle v' \mid v''\rangle^2$ between the vibrational levels v' and v'' of the lower and upper electronic states (Franck-Condon factors).

2.3. The diabatization procedure

It is well known that in diatomic molecules energies of electronic states as functions of the internuclear distance do not cross each other if the states has the same symmetry (Landau & Lifshitz 1977). In the vicinity of points where these (adiabatic) states closely approach each other they undergo fast changes. Such points are referred to as avoided crossings. Transition moments as functions of the internuclear distance exhibit very non monotonic behavior around avoided crossings. The adiabatic approach (Born-Oppenheimer approximation) is not valid in the vicinity of the avoided crossings and one should go beyond it. One of the most successful approaches to nonadiabatic problems is based on the concept of diabatic states (see for example the review of Köppel et al. 1984). The diabatic states are slowly varying functions of the nuclear coordinates and they cross each other at the avoided crossings. The use of the diabatic states transfers the nonadiabatic couplings from the kinetic energy part of the Hamiltonian to the potential energy. Thus, the nonadiabatic vibrational-rotational problem becomes the problem of coupled vibrating rotators which can be solved by conventional methods.

In our case we diabatized $^1\Pi$ and $^1\Phi$ states because our calculations revealed several avoided crossings in these symmetries. Our purpose was to obtain monotonic transition moment functions which can be used further for generating line lists for TiO. To calculate the intensities of the vibrational-rotational lines one has to take the nonadiabatic couplings between the diabatic states into account. Strictly speaking the couplings are uniquely defined by the diabatization scheme and the theoretical couplings must be used if one uses the respective theoretical diabatic transition moments. We surmise, however, that a better approach is to use experimentally derived couplings in calculations of line lists. The diabatization procedure used in our work is described in the Appendix.

3. The results

The MRCI energies (T_e) and equilibrium interatomic distances (R_e) for the triplet and singlet states are collected in Table 1 in comparison with the theoretical SA-CASSCF/MRCI results of Langhoff (1997) and experimental values of Jørgensen (1994) and Schwenke (1998). To avoid misunderstanding we should note that T_e specifies the energy relative to that of the $X^3\Delta$ ground state.

3.1. Triplet band systems

Our theoretical energies for the $E^3\Pi$, $A^3\Phi$, $B^3\Pi$ and $C^3\Delta$ states are systematically too high by ~2000–3000 cm^{-1} compared to the experimental values. The energies for the $E^3\Pi$, $A^3\Phi$ and $B^3\Pi$ states calculated by Langhoff (1997) at the SA-CASSCF/IC-MRCI level are closer to the respective experimental values than our IC-MRCI data. The accuracy of our results for the equilibrium distances is comparable to that of Langhoff (1997).

For the triplet manifold we have obtained $^3\Sigma^-$ and $^3\Sigma^+$ states situated 18 044 and 18 690 cm^{-1}, respectively, above the $X^3\Delta$ ground state. Barnes et al. (1997) have detected a $^3\Sigma^-$ state ($D^3\Sigma^-$) in the fluorescence spectra from $v = 0$ levels of the $I^3\Pi$ and $J^3\Pi$ states (the latter states were observed for the first time in this study). The energy reported for the $D^3\Sigma^-$ state is, however, 12 284 cm^{-1}. The corresponding energy obtained in our work is 18 044 cm^{-1}. If assigned to the experimental $D^3\Sigma^-$ state, our computed $^3\Sigma^-$ state has an energy ~6000 cm^{-1} too high. This deviation is rather large. Here we should note that for all states with a $1\delta^2$ electronic configuration our calculations give energies which are too high by ~5000–7000 cm^{-1} compared to the results obtained at the CASSCF (Bauschlicher et al. 1983) and SA-CASSCF/IC-MRCI (Schwenke 1998) levels. Bauschlicher et al. (1983) in their CASSCF study of the low-lying electronic states of TiO have predicted the $D^3\Sigma^-$ state at 12 800 cm^{-1} in excellent agreement with the experimental value of 12 284 cm^{-1} reported later by Barnes et al. (1997).

The theoretical MRCI and experimental RKR potentials for the ground $X^3\Delta$ and excited $C^3\Delta$ states are presented in Fig. 1. Here our theoretical potentials have been shifted to match the experimental T_e values. It is interesting, that the RKR potentials for the $X^3\Delta$ state obtained using molecular constants of Jørgensen (1994) and Schwenke (1998) are quite different. Our theoretical potential for this state is closer to Jørgensen's one. Our MRCI potentials for the $E^3\Pi$, $A^3\Phi$ and $B^3\Pi$ states are plotted in Fig. 2. Apart from the shift the agreement between the MRCI potentials and the experimental curves is rather good.

3.1.1. The $\alpha(C^3\Delta - X^3\Delta)$ system

The principal configuration of the ground $X^3\Delta$ state is $8\sigma^2 9\sigma^1 3\pi^4 1\delta^1$. The $C^3\Delta$ state is dominated by the $8\sigma^2 10\sigma^1 3\pi^4 1\delta^1$ configuration. The MRCI oscillator strength f_{00} for the transition between the $X^3\Delta$ and $C^3\Delta$ states is 0.0528 (Table 2) where the RKR potential of Jørgensen (1994) is used.

As we mentioned above, Jørgensen's potential for the ground $X^3\Delta$ state differs from that of Schwenke (1998). This difference results in different Franck-Condon factors (q_{00}) which are 0.410 and 0.355 for the potentials of Jørgensen and Schwenke, respectively. Due to this the oscillator strengths f_{00} are also different: 0.0528 and 0.0459, respectively. Thus, the uncertainty in these experimental potentials gives rise to the uncertainty in the oscillator strengths of ~13%. Here we should note that the theoretical value of 0.0431 reported by Langhoff (1997) has been obtained at the SA-CASSCF level. Langhoff, however, performed also the SA-CASSCF/IC-MRCI calculations at two interatomic distances of 3.0 and 3.2 a.u. Taking

Table 1. MRCI spectroscopic constants for the electronic states of TiO in comparison with the literature data

	This work		L97[a]		J94[b]		S98[c]	
State	R_e(a.u.)	T_e(cm^{-1})	R_e(a.u.)	T_e(cm^{-1})	R_e(a.u.)	T_e(cm^{-1})	R_e(a.u.)	T_e(cm^{-1})
$X^3\Delta$	3.0738	0.0	3.0934	0.0	3.0617	0.0	3.0618	3.806
$E^3\Pi$	3.0730	13713	3.1651	12580	3.1150	11936	3.1146	11868.349
$A^3\Phi$	3.1166	17249	3.1459	14754	3.1452	14166.4	3.1454	14169.057
$D^3\Sigma^-$	3.1885	18044					3.2021	12202.658
$^3\Sigma^+$	3.1726	18690						
$B^3\Pi$	3.1210	19576	3.1346	17250	3.1439	16218.7	3.1488	16219.387
$C^3\Delta$	3.2219	21650	3.2745		3.2001	19424.9	3.2028	19430.264
$a^1\Delta$	3.0672	3565	3.0830	3400.7	3.0555	3448.3	3.0550	3346.726
$d^1\Sigma^+$	3.0246	3435	3.0419	8305.9	3.0235	5663.9	3.0226	5559.070
$b^1\Pi$	3.0979	17545	3.1242	17686.5	3.1269	14770.3	3.1260	14663.772
$c^1\Phi$	3.0725	23956	3.1091	22061.7	3.0978	21338.5	3.0928	21226.587
$f^1\Delta$	3.1526	25936	3.1289		3.1613	22580.3	3.1567	22482.170
$h^1\Sigma^+$	3.1633	21795					3.2066	17564.880
$g^1\Gamma$	3.1699	22789					3.1275	15810.089
$k^1\Phi^*$	3.5465	28648						
$i^1\Pi^*$	3.1349	27052						
$j^1\Pi^*$	3.5920	29188						

[a] Langhoff (1997). [b] Jørgensen (1994). [c] Schwenke (1998). *The constants obtained for the diabatic states.

Table 2. MRCI oscillator strengths f_{00} for the transitions in TiO in comparison with the literature data. The values in parentheses have been obtained using Schwenke's potential (1998)

			f_{00}			
System	ν_{00}(cm^{-1})	q_{00}	This work	L97[a]	H95[b]	D86[c]
$\gamma(A^3\Phi - X^3\Delta)$	14092.9(14099.9)	0.720(0.666)	0.0860(0.0800)	0.0658	0.057	0.12
$\gamma\prime(B^3\Pi - X^3\Delta)$	16147.0(16148.0)	0.726(0.648)	0.1099(0.0984)	0.0781	0.065	0.10
$\epsilon(E^3\Pi - X^3\Delta)$	11893.9(11822.0)	0.872(0.814)	0.0022(0.0019)	0.0020	<0.0047	
$\alpha(C^3\Delta - X^3\Delta)$	19339.0(19341.4)	0.410(0.355)	0.0528(0.0459)	0.0431*	0.043	0.031
$\beta(c^1\Phi - a^1\Delta)$	17840.6(17836.2)	0.915(0.898)	0.1483(0.1462)	0.1609	0.11	0.26
$\delta(b^1\Pi - a^1\Delta)$	11273.3(11270.0)	0.781(0.736)	0.0455(0.0431)	0.0753		0.039
$\phi(b^1\Pi - d^1\Sigma^+)$	9054.0(9053.3)	0.599(0.600)	0.0402(0.0402)	0.0212		0.03
$f^1\Delta - a^1\Delta$	19073.1(19064.7)	0.614(0.562)	0.0787(0.0724)	0.0756	0.062	

[a] Langhoff (1997). [b] Hedgecock et al. (1995). [c] Davis et al. (1986). *This value has been calculated at the SA-CASSCF level.

the ratio of the SA-CASSCF and SA-CASSCF/IC-MRCI transition moments at $R_{\mathrm{Ti-O}} = 3.2$ a.u. (1.2820 and 1.3817, respectively) (Langhoff 1997), one can estimate f_{00} which could be obtained at the SA-CASSCF/IC-MRCI level. This gives the f_{00} value of 0.05 which is very close to our value of 0.0529 computed also using Jørgensen's potentials. The transition moments for five triplet transitions at 13 internuclear distances are listed in Table 3. Figure 3 shows the transition moment functions (TMF) together with the curves obtained by Langhoff (1997) in the bond length range of 2.4 to 3.7 a.u.

As one can see for the $\alpha(C^3\Delta - X^3\Delta)$ system our TMF and that of Langhoff are very similar within the interval 2.4–3.0 a.u. For distances larger than 3.0 a.u. the slope of Langhoff's TMF is considerably larger than ours. Here we should note that Langhoff's TMF for the α system was calculated at the SA-CASSCF level. As it was shown by Langhoff (1997) the slope decreases if a subsequent MRCI is performed.

Table 3. Electronic transition moments for the triplet band systems of TiO

r(a.u.)	$\epsilon(E^3\Pi - X^3\Delta)$	$\gamma(A^3\Phi - X^3\Delta)$	$\gamma\prime(B^3\Pi - X^3\Delta)$	$\alpha(C^3\Delta - X^3\Delta)$	$E^3\Pi - B^3\Pi$
2.5	0.1259	1.5214	1.6488	1.7818	−0.1983
2.6	0.1315	1.4732	1.5908	1.7446	−0.1589
2.7	0.1411	1.4204	1.5278	1.7041	−0.1092
2.8	0.1550	1.3624	1.4628	1.6591	−0.0519
2.9	0.1709	1.2998	1.3987	1.6090	−0.0023
3.0	0.1846	1.2391	1.3283	1.5551	0.0493
3.1	0.1824	1.1874	1.2456	1.4997	0.1096
3.2	0.1851	1.1289	1.1737	1.4447	0.1539
3.3	0.1878	1.0761	1.1088	1.3925	0.1925
3.4	0.2006	1.0315	1.0538	1.3452	0.2266
3.5	0.2445	0.9936	1.0024	1.3028	0.2600
3.6	0.3271	0.9566	0.8567	1.2596	0.2784
3.7	0.3447			1.1993	

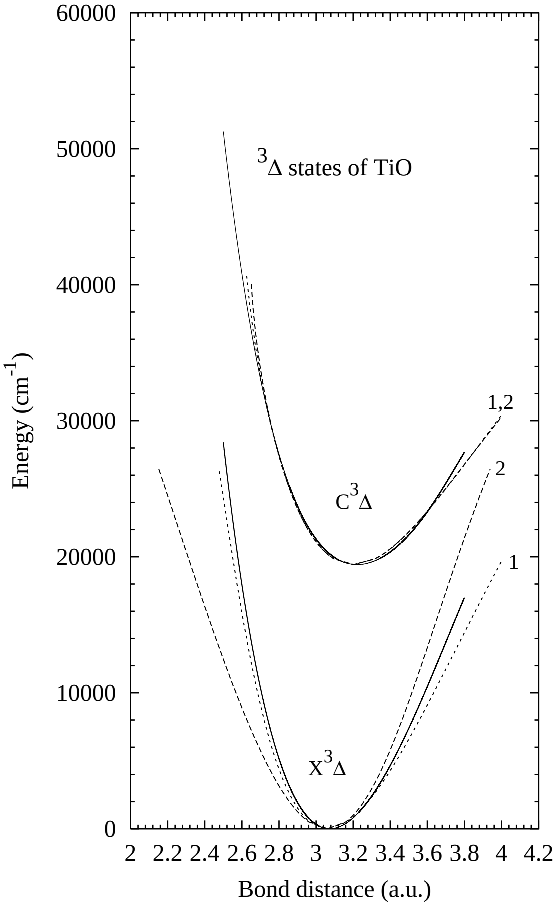

Fig. 1. The theoretical MRCI potentials (solid lines) for the $^3\Delta$ states of TiO in comparison with the RKR potentials obtained using the molecular spectroscopic constants of Jørgensen (1994) (1) and Schwenke (1998) (2)

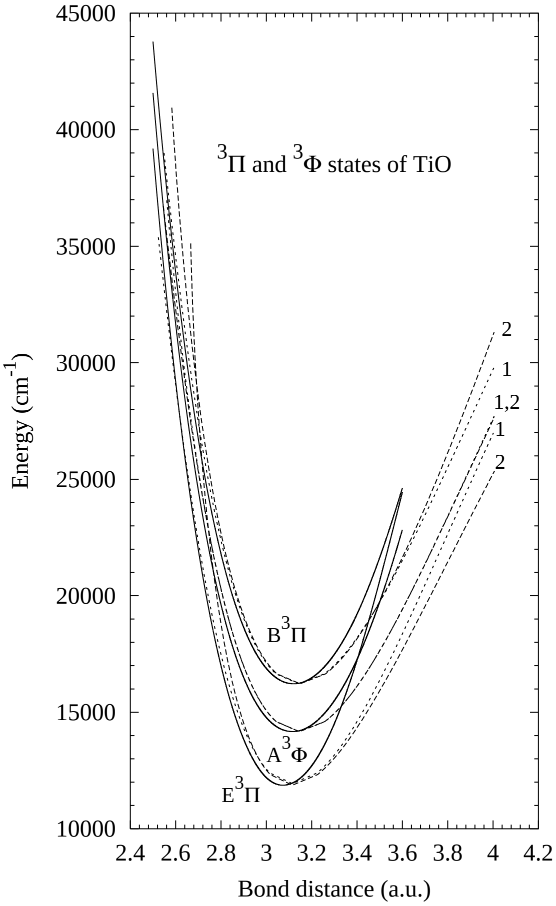

Fig. 2. The theoretical MRCI potentials (solid lines) for the $^3\Pi$ and $^3\Phi$ states of TiO in comparison with the RKR potentials obtained using the molecular spectroscopic constants of Jørgensen (1994) (1) and Schwenke (1998) (2)

The radiative lifetimes calculated for the $C^3\Delta$ state in the present work (Table 4) agree rather well with the respective experimental data of Hedgecock et al. (1995), Steele & Linton (1978) and Price et al. (1974). The agreement with the previous theoretical results of Schamps et al. (1992) and Langhoff (1997) is good as well. The decreasing lifetimes for higher vibrational levels measured in the experiments are not reproduced in our calculations. Our computed lifetimes slightly increase when going from $v = 0$ to $v = 2$ vibrational levels (Table 4).

The $C^3\Delta - X^3\Delta$ transition is not the only channel for radiative decay of the $C^3\Delta$ state. The transitions to the lower $B^3\Pi$, $A^3\Phi$ and $E^3\Pi$ states are also dipole-allowed. The oscillator strengths for the respective transitions are, however, very small. According to our MRCI calculations the oscillator strengths f_{00} are 0.0009, 0.0003, and 0.0007 for the $C^3\Delta - A^3\Phi$, $C^3\Delta - B^3\Pi$ and $C^3\Delta - E^3\Pi$ transitions, respectively. Because of this these radiative decay channels contribute negligibly to the radiative lifetime of the $C^3\Delta$ state. Similar results have been obtained by Langhoff (1997).

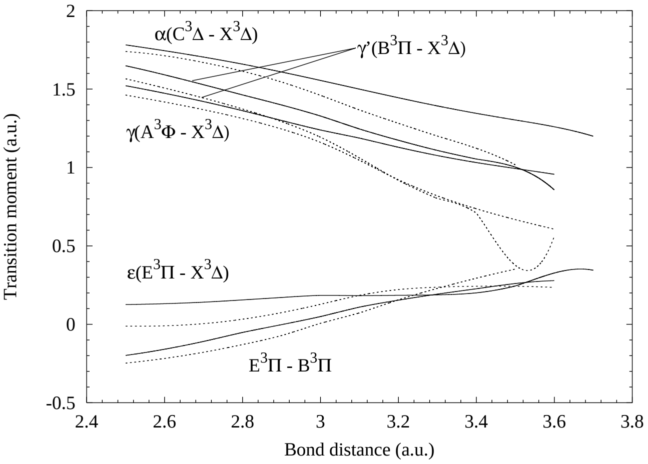

Fig. 3. MRCI transition moment functions (solid lines) for the triplet bands in TiO in comparison with those obtained by Langhoff (1997) (dashed lines)

Table 4. Radiative lifetimes (ns) for the triplet electronic states of TiO. The values in parentheses have been obtained using Schwenke's potential (1998)

		Theory			Experiment
State	v	This work	L97[j]	S92[k]	
$A^3\Phi$	0	69.6(71.1)	95.0	55.2	101.9[a], 24[b]
	1	70.6(73.8)	94.3		109.2[a], 51[c], 15[b]
$B^3\Pi_1$	0	41.9(43.1)	61.6	56.2	64.6[a], 54.4[d], 43[c]
	1	42.2(44.1)	61.0		67.6[a], 44[e]
$C^3\Delta$	0	37.1(38.6)	47.0*	38.7	43.3[a], 37[f], 31[b]
	1	37.3(39.6)	46.8*		43.0[a], 29[f], 21[b]
	2	37.5(40.7)	46.7*		28[f], 29[g], 18.5[c]
$E^3\Pi$	0	4486.6(4656.5)	4259	2300	>2000[a], 770[h],4900[i]
	1	4522.7(4866.5)	4567		

[a] Hedgecock et al. (1995). [b] Price et al. (1974). [c] Davis et al. (1986). [d] Doverstall & Weijnitz (1992). [e] Carrette & Schamps (1992). [f] Steele & Linton (1978). [g] Feinberg & Davis (1977, 1978). [h] Simard & Hackett (1991). [i] Lundevall (1998). [j] Langhoff (1997). [k] Schamps et al. (1992). *The results obtained at the SA-CASSCF level.

3.1.2. The $\epsilon(E^3\Pi - X^3\Delta)$ system

The $E^3\Pi - X^3\Delta$ transition is rather weak. Our MRCI calculations using Jørgensen's potential give f_{00} of 0.0022 This result is in excellent agreement with the SA-CASSCF/MRCI theoretical value reported by Langhoff (1997) (0.0020). The TMFs for the transitions involving the $E^3\Pi$ state ($E^3\Pi - X^3\Delta$ and $E^3\Pi - B^3\Pi$) (Table 3) are very similar to those obtained by Langhoff (1997) (Fig. 3). Our radiative lifetime of 4486 ns agrees well with that of 4259 ns reported by Langhoff (Table 4). The theoretical radiative lifetime of 2300 ns reported by Schamps et al. (1992) is close to the value of 2341 ns calculated by Langhoff (1997) at the SA-CASSCF level. Recently, Lundevall (1998) has measured the radiative lifetime for the $E^3\Pi$ state to be 4900 ± 200 ns. This value is very close to our computed one. Thus, the experimental lifetime of 770 ns reported by Simard & Hackett (1991) seems to be too short.

3.1.3. The $\gamma(A^3\Phi - X^3\Delta)$ system

The TMF for the $A^3\Phi - X^3\Delta$ transition calculated in the present work (Table 3) is similar to that reported by Langhoff (1997) for the Ti-O distances <3.0 a.u. At larger distances the slopes of these two theoretical curves differ considerably (Fig. 3). Our f_{00} oscillator strength for this transition (0.086) is larger than the value of Langhoff (1997) (0.0658) and the experimental value (0.057) of Hedgecock et al. (1995), but smaller than the value of 0.12 reported by Davis et al. (1986). Our radiative lifetime of 69.6 ns for the $A^3\Phi$ state is considerably shorter than both the theoretical value of Langhoff (95 ns) and the experimental value of Hedgecock et al. (1995) (101.9 ns), but longer than the value of 55.2 ns obtained by Schamps et al. (1992) and than the earlier experimental values of 24 ns and 51 ns (for the $v = 1$ level) reported by Price et al. (1974) and Davis et al. (1986), respectively. Because of the significant deviations between the data measured by different authors, is is difficult to estimate the accuracy of the theoretical results from comparing them to the experiment.

3.1.4. The $\gamma\prime(B^3\Pi - X^3\Delta)$ system

The TMF for the $B^3\Pi - X^3\Delta$ transition is similar to that of the $A^3\Phi - X^3\Delta$ (Table 3, Fig. 3), a finding in agreement with the results of Langhoff (1997). As in the case of the $A^3\Phi - X^3\Delta$ transition, our $B^3\Pi - X^3\Delta$ TMF deviates considerably from that of Langhoff at large distances ($R_{\mathrm{Ti-O}} > 3.0$ a.u.), where our TM is larger (Fig. 3). This leads to a larger f_{00} oscillator strength (0.1099) compared to the result of Langhoff (0.0781) (Table 2). The corresponding experimental value is 0.065 (Hedgecock et al. 1995). The oscillator strength of 0.1 for the $B^3\Pi - X^3\Delta$ transition reported by Davis et al. (1986) is close to our result. Our computed radiative lifetime of 41.9 ns for the $B^3\Pi$ state is shorter than the previous theoretical values

Table 5. Electronic transition moments for the triplet band systems of TiO

r(a.u.)	$E^3\Pi - D^3\Sigma^-$	$B^3\Pi - D^3\Sigma^-$	$E^3\Pi -^3 \Sigma^+$	$B^3\Pi -^3 \Sigma^+$
2.6	0.7587	1.1736	0.4007	0.2827
2.7	0.6927	1.0767	0.4335	0.3019
2.8	0.6329	0.9861	0.4508	0.3094
2.9	0.5703	0.9056	0.4581	0.3032
3.0	0.5090	0.8308	0.4617	0.2889
3.1	0.4566	0.7597	0.4998	0.2982
3.2	0.3989	0.7062	0.5334	0.2948
3.3	0.3420	0.6667	0.5865	0.2882
3.4	0.2838	0.6421	0.6589	0.2704
3.5	0.2161	0.6313	0.7383	0.2274
3.6	0.1288	0.5945	0.8105	0.1309

of Schamps et al. (1992) (56.2 ns) and Langhoff (61.6 ns). These theoretical lifetimes are close to the experimental values of 64.6 (Hedgecock et al. 1995) and 54.4 ns (Doverstall & Weijnitz 1992). Our theoretical lifetime is comparable with the other experimental values of 43 ns (Davis et al. 1986) and 44 ns (for the $v = 1$ level) (Carrette & Schamps 1992). This scatter in the experimental data does not allow for a reliable estimate of the accuracy of the theoretical lifetimes. Although Hedgecock et al. (1995) give very convincing arguments in favor of their measured lifetimes, independent laboratory studies are strongly required for all the states of the TiO molecule.

Interestingly, the $B^3\Pi - X^3\Delta$ TMF of Langhoff (1997) exhibits non monotonic behavior around $R_{\mathrm{Ti-O}} \sim 3.4$ a.u. (Fig. 3). Usually, such variations in the TMF occur due to avoided crossing between two states of the same symmetry. This feature indicates that there could be a $^3\Pi$ state which comes close in energy to the $B^3\Pi$ state at this interatomic distance according to Langhoff's calculations.

3.1.5. Other transitions

We have also calculated TMFs for the transitions involving the $D^3\Sigma^-$ and $^3\Sigma^+$ states. Because of the lack of the experimental data for these states we could not calculate accurate oscillator strengths. Thus, we just listed the TMFs in Table 5.

The $B^3\Pi - D^3\Sigma^-$ transition is besides the $B^3\Pi - X^3\Delta$ transition channel for radiative decay of the $B^3\Pi$ state. According to our estimates the electronic oscillator strength f_{e} for the $B^3\Pi - D^3\Sigma^-$ transition (0.012) is small compared to that for $B^3\Pi - X^3\Delta$ (0.1514). Therefore the $B^3\Pi - D^3\Sigma^-$ channel negligibly contributes to the radiative lifetime of the $B^3\Pi$ state.

3.2. Singlet transitions

The lowest excited singlet state in TiO is $a^1\Delta$ (Table 1). The electronic energy T_{e} obtained in the present work for this state is 3565 cm^{-1} which is close to the value of 3448.3 cm^{-1} recommended by Jørgensen (1994). For the $d^1\Sigma^+$ state our MRCI energy is 3435 cm^{-1} that is, about 2000 cm^{-1}, lower than of Jørgensen (1994) (5663.9 cm^{-1}) and of Schwenke (Schwenke 1998) (5559.070 cm^{-1}). The reason why the energy of the $d^1\Sigma^+$ state relative to the $X^3\Delta$ GS is too low in our MRCI calculations is that they are biased in favor of this state due to the choice of the $^1\Sigma^+$ reference SCF configuration, as we mentioned in Sect. 3.1. In this case the description of the $X^3\Delta$ GS is less accurate and therefore its energy is artificially too large compared to that of the excited $d^1\Sigma^+$ state. The MRCI energies of the $b^1\Pi$, $c^1\Phi$ and $f^1\Delta$ states are too high compared to the respective experimental data by ~3000 cm^{-1} (Table 1). Here we should note that the theoretical energies for the $d^1\Sigma^+$ and $b^1\Pi$ states, calculated by Langhoff (1997) also deviate by ~3000 cm^{-1} from the respective experimental values. In contrast to our MRCI result, where the energy of the $d^1\Sigma^+$ state is lower by ~2000 cm^{-1} than the experimental one, the SA-CASSCF/MRCI energy for this state (Langhoff 1997) is ~3000 cm^{-1} higher than the respective experimental value (Table 1). For the $a^1\Delta$, $d^1\Sigma^+$, $b^1\Pi$, $c^1\Phi$ and $f^1\Delta$ states the accuracy for the electronic energies and equilibrium interatomic distances obtained in our MRCI study is comparable with that of the SA-CASSCF/MRCI results of Langhoff (1997).

In Fig. 4 we compare our MRCI potentials for the $a^1\Delta$ and $f^1\Delta$ states with the RKR potentials obtained from the molecular constants recommended by Jørgensen (1994) and Schwenke (1998).

One can see that these two experimental potentials differ considerably. For the $a^1\Delta$ state our potential is closer to Jørgensen's one, whereas for the $f^1\Delta$ state our potential is closer to the potential of Schwenke. This difference between the two experimentally derived potentials leads to different Franck-Condon factors q_{00} and oscillator strengths f_{00}. For example, the oscillator strength f_{00} for the $f^1\Delta - a^1\Delta$ transition is 0.0787 when using Jørgensen's potentials and 0.0724 when using the potentials of Schwenke (Table 2). Here the uncertainty in the computed oscillator strengths amounts to ~9% due to the uncertainty in the experimental potentials.

The potentials for the $d^1\Sigma^+$, $h^1\Sigma^+$ and $g^1\Gamma$ states computed using the molecular data of Jørgensen (1994) and Schwenke (1998) are compared with our MRCI potentials in Fig. 5. One can see that our potential for the known $d^1\Sigma^+$ state agrees rather well with both Schwenke's and Jørgensen's potentials. For the $g^1\Gamma$ state the shape of our potential energy is close to that obtained from Schwenke's molecular constants, but the positions of the minima of these two potentials differ by ~0.04 a.u. Our MRCI potential for the $h^1\Sigma^+$ state strongly deviates from that of Schwenke. Here we should note that in the work of Schwenke (1998) the molecular constants for the $h^1\Sigma^+$ and $g^1\Gamma$ states have been determined indirectly, using a combination of ab initio calculations and available experimental data for the other states. These two states have not yet been detected experimentally. We surmise that

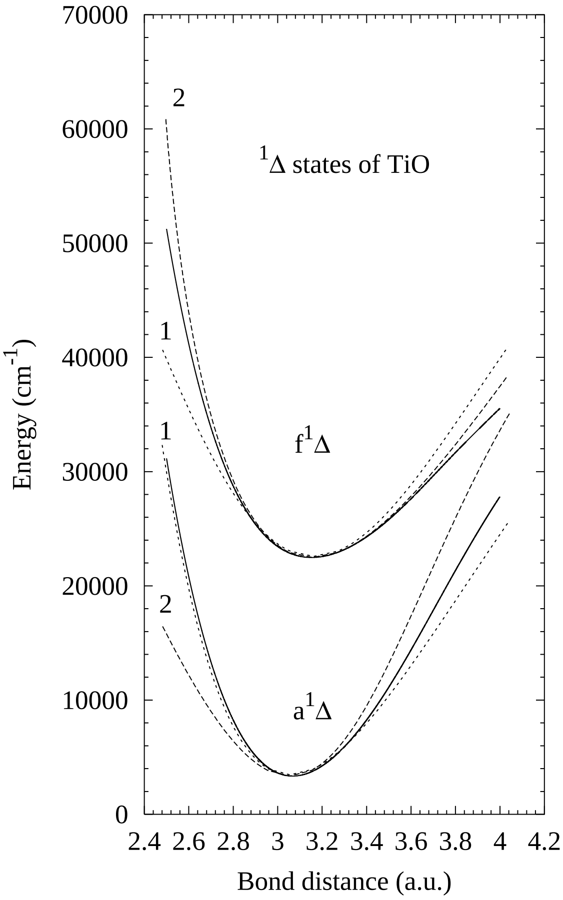

Fig. 4. The theoretical MRCI potentials (solid lines) for the $^1\Delta$ states of TiO in comparison with the RKR potentials obtained using the molecular spectroscopic constants of Jørgensen (1994) (1) and Schwenke (1998) (2)

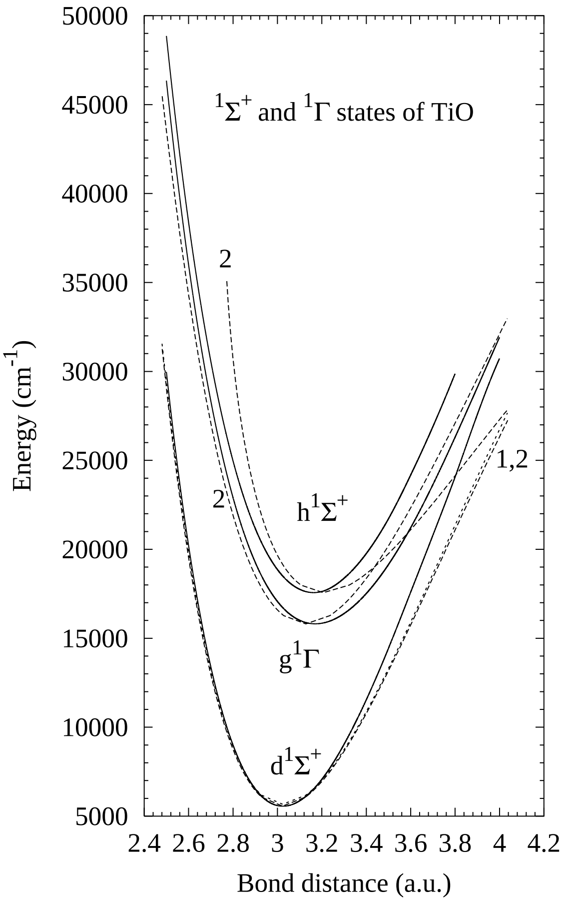

Fig. 5. The theoretical MRCI potentials (solid lines) for the $^1\Sigma^+$ and $^1\Gamma$ states of TiO in comparison with the RKR potentials obtained using the molecular spectroscopic constants of Jørgensen (1994) (1) and Schwenke (1998) (2)

one needs more direct (spectral) information on these two states to derive accurate molecular constants.

The MRCI potentials calculated for $^1\Pi$ states are presented in Fig. 6 together with the potentials of Jørgensen (1994) and Schwenke (1998). Our MRCI potential for the known $b^1\Pi$ state deviates considerably from both experimental potentials at large Ti-O distances.

In practice, MRCI calculations on the $^1\Pi$ states are very difficult because of numerous avoided crossings (Fig. 6). The regions of avoided crossings are encircled in the figure. We only succeeded to compute three $^1\Pi$ states, namely the $b^1\Pi$ state and two more states referred to as $i^1\Pi$ and $j^1\Pi$ which have not yet been observed. Because of the avoided crossings between the adiabatic electronic states the respective TMFs exhibit very non monotonic behavior in the vicinity of such the points.

The MRCI potentials for the known $c^1\Phi$ state and for the new $k^1\Phi$ state (found in the present study) are shown in Fig. 7 together with the experimental $c^1\Phi$ potentials of Jørgensen (1994) and Schwenke (1998).

For the $^1\Phi$ states our calculations reveal two avoided crossings at ~2.9 and 3.4 a.u. The first avoided crossing is of no relevance for our case because its energy is too high. The second one, however, strongly affects the transition moments involving the $c^1\Phi$ state leading to steps in the respective transition moments at ~3.4 a.u.

Because of the avoided crossings for the $^1\Pi$ and $^1\Phi$ states we replaced the adiabatic transition moments by the diabatic ones for the interatomic distances larger than 3.1 and 3.2 a.u., respectively. The diabatization procedure is described in the Appendix.

3.2.1. The $\beta(c^1\Phi - a^1\Delta)$ system

Our TMF for the $\beta(c^1\Phi - a^1\Delta)$ transition is shown in Fig. 8 in comparison with the result of Langhoff (1997) and tabulated in Table 6.

One can see that our MRCI TMF is rather close to that obtained by Langhoff at the level of SA-CASSCF/MRCI. The computed oscillator strength f_{00} of 0.1483 for this transition (Table 2) is smaller than the value of Langhoff (0.1609), but larger than the value of 0.11 reported by Hedgecock et al. (1995).

The respective value of Davis et al. (1986) (0.26) is considerably larger than both our and all the other values listed in Table 2. Our computed radiative lifetimes of 29.8 and 30.5 ns for the $c^1\Phi$ state (for the $v = 0$ and 1 levels,

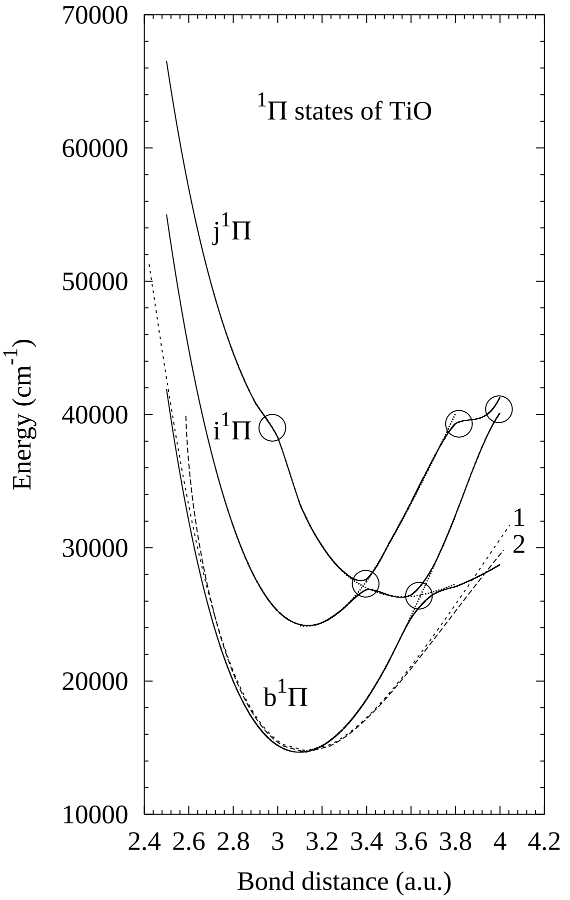

Fig. 6. The theoretical MRCI potentials (solid lines) for the $^1\Pi$ states of TiO in comparison with the RKR potentials obtained using the molecular spectroscopic constants of Jørgensen (1994) (1) and Schwenke (1998) (2). In the avoided crossing regions (encircled) the diabatic potentials are shown by the dashed lines

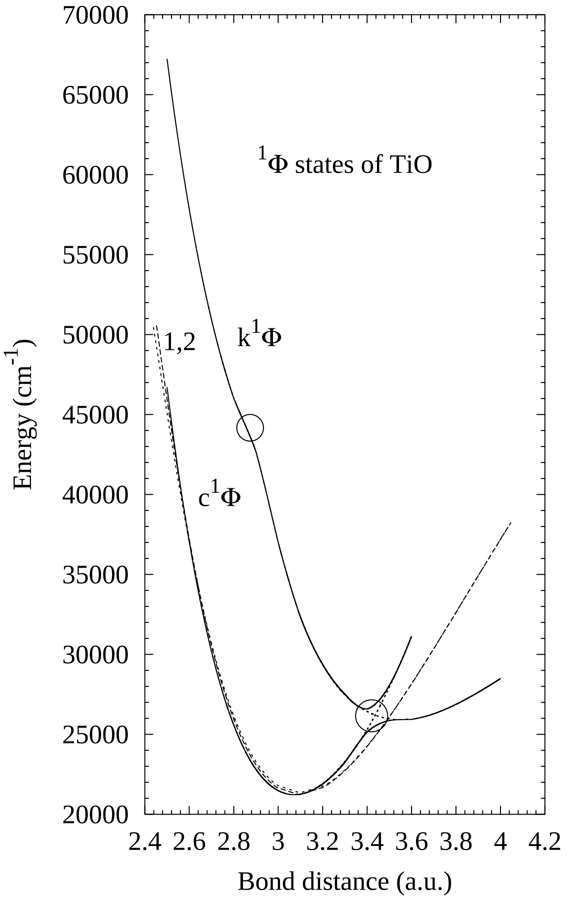

Fig. 7. The theoretical MRCI potentials (solid lines) for the $^1\Phi$ states of TiO in comparison with the RKR potentials obtained using the molecular spectroscopic constants of Jørgensen (1994) (1) and Schwenke (1998) (2). In the avoided crossing regions (encircled) the diabatic potentials are shown by the dashed lines

Table 6. Electronic transition moments for the singlet band systems of TiO

r(a.u.)	$\beta(c^1\Phi - a^1\Delta)$	$\delta(b^1\Pi - a^1\Delta)$	$\phi(b^1\Pi - d^1\Sigma^+)$	$f^1\Delta - a^1\Delta$
2.5	1.4643	1.2593	1.3583	1.8174
2.6	1.4225	1.2147	1.3191	1.7724
2.7	1.3799	1.1626	1.2800	1.7242
2.8	1.3378	1.1032	1.2395	1.6738
2.9	1.2960	1.0373	1.1945	1.6206
3.0	1.2590	0.9708	1.1440	1.5617
3.1	1.2168	0.9177	1.0936	1.4966
3.2	1.1678	0.8744	1.0429	1.4254
3.3	1.1330	0.8248	1.0147	1.3501
3.4	1.1017	0.8116	0.9842	1.2746
3.5	1.0902	0.7973	0.9739	1.2031
3.6	1.0868	0.7803	0.9799	1.1348
3.7		0.7864	0.9565	1.0581
3.8		0.7988	0.9357	0.9539

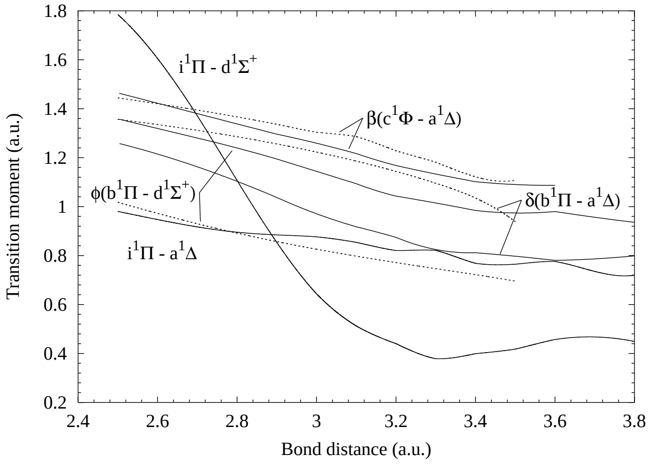

Fig. 8. MRCI transition moment functions (solid lines) for the singlet bands in TiO in comparison with those obtained by Langhoff (1997) (dashed lines). In the figure the adiabatic TMFs where the $^1\Pi$ and $^1\Phi$ states are involved are replaced with the diabatic ones for interatomic distances larger than 3.1 and 3.2 a.u., respectively

Table 7. Radiative lifetimes (ns) for the singlet electronic states of TiO. The values in parentheses have been obtained using Schwenke's potential (1998)

		Theory			Experiment
State	v	This work	L97[c]	S92[d]	
$b^1\Pi$	0	165.7(167.8)	119.7	455	
	1	164.4(169.0)	121.0		
$c^1\Phi$	0	29.8(29.9)	27.5	15.0	38.3[a], 17.5[b]
	1	30.5(30.9)	28.1		
$f^1\Delta$	0	36.0(36.8)	37.6	41.6	43.2[a]
	1	35.7(38.0)	37.3		

[a] Hedgecock et al. (1995). [b] Feinberg & Davis (1977, 1978). [c] Langhoff (1997). [d] Schamps et al. (1992).

respectively), are very close to those calculated by Langhoff (1997) (Table 7). The lifetime measured by Hedgecock et al. (1995) for the $v = 0$ level is 38.3 ns which is larger than all the theoretical values listed in Table 7.

The value of 17.5 ns measured by Feinberg & Davis (1977, 1978) is considerably smaller than all the lifetimes listed in Table 7, except of that calculated by Schamps et al. (1992) (15 ns). Our calculation and the calculation of Langhoff support the experimental value of 38.3 ns of Hedgecock et al. (1995).

3.2.2. The $\delta(b^1\Pi - a^1\Delta)$ and $\phi(b^1\Pi - d^1\Sigma^+)$ systems

The computed TMFs for the $\delta(b^1\Pi - a^1\Delta)$ and $\phi(b^1\Pi - d^1\Sigma^+)$ transitions are plotted in Fig. 8 and listed in Table 6. Comparing our TMFs and those of Langhoff (1997) (Fig. 8) one can see a remarkable difference between them. This results also in very different oscillator strengths and radiative lifetimes. Our MRCI values for the f_{00} oscillator strengths for the δ and ϕ transitions are 0.0455 and 0.0402, respectively, whereas Langhoff (1997) reported for these transitions f_{00} of 0.0753 and 0.0212, respectively. As described in the Introduction, the intensity of the δ band is supposedly overestimated if using the TMF of Langhoff. Schwenke (1998) supposed that the reason for this is an artificial influence of the state averaging used in the calculations of Langhoff (1997) on the relative weights of the $\sigma\pi$ and $\delta\pi$ configurations in the $b^1\Pi$ state. The principal configuration of the $b^1\Pi$ state is $8\sigma^2 3\pi^4 4\pi^1 1\delta^1$ ($\delta\pi$) with some admixture of the $8\sigma^2 9\sigma^1 3\pi^4 4\pi^1$ ($\sigma\pi$) configuration. The $a^1\Delta$ and $d^1\Sigma^+$ states are dominated by the $8\sigma^2 9\sigma^1 3\pi^4 1\delta^1$ and $8\sigma^2 9\sigma^2 3\pi^4$ configurations, respectively. In terms of one-electron (orbital) transitions the TMs for the $\delta(b^1\Pi - a^1\Delta)$ and $\phi(b^1\Pi - d^1\Sigma^+)$ systems can be expressed as follows

$$D_\delta \approx \chi(\delta\pi)\langle 9\sigma \mid \hat{d} \mid 4\pi\rangle + \chi(\sigma\pi)\langle 1\delta \mid \hat{d} \mid 4\pi\rangle \qquad (5)$$

and

$$D_\phi \approx \chi(\sigma\pi)\langle 9\sigma \mid \hat{d} \mid 4\pi\rangle \qquad (6)$$

where $\chi(\delta\pi)$ and $\chi(\sigma\pi)$ are the coefficients of the $\delta\pi$ and $\sigma\pi$ configurations in the MRCI vector of the $b^1\Pi$ state and $\hat{d}$ is the dipole operator. The dipole operator matrix element $\langle 9\sigma \mid \hat{d} \mid 4\pi\rangle$ is much larger than $\langle 1\delta \mid \hat{d} \mid 4\pi\rangle$ because it corresponds to the strong atomic 4s → 4p transition. The $\delta\pi$ and $\sigma\pi$ configurations are dominant in the $b^1\Pi$ state and thus, overestimating the contribution of one of them correlates to underestimating the contribution of the other. As a result, an overestimated $\chi(\delta\pi)$ coefficient leads to an overestimated D_δ but underestimated D_ϕ. This interrelation between the transition moments for the δ and ϕ bands is indeed observed when one compares our oscillator strengths with those of Langhoff (1997) (Table 2). Our oscillator strength f_{00} for the δ transition is 0.0455, whereas the corresponding value 0.0753 of Langhoff is considerably larger. Earlier Plez (1998) has shown that the intensity of the δ-band obtained with the use of Langhoff's (1997) transition moments should be divided by 2 to match Ramsey's observed $\delta(00)$-band head depression in the spectra of giant stars (Ramsey 1981). In contrast, for the ϕ transition our f_{00} is 0.0402 which is about two times larger than the value (0.0212) of Langhoff. The oscillator strength of 0.039 obtained for the δ transition from the measurements of Davis et al. (1986) is close to our computed value. For the ϕ transition our oscillator strength of 0.0402 is larger than the value of 0.03 measured by Davis et al. (1986). Our radiative lifetime of 165.7 ns computed for the $v = 0$ level of the $b^1\Pi$ state is longer by about 40% than that computed by Langhoff (1997) (119.7 ns). The lifetime of 455 ns calculated by Schamps et al. (1992) is too long compared to both our and Langhoff's values. There are two channels for radiative decay of the $b^1\Pi$ state: $b^1\Pi - a^1\Delta$ and $b^1\Pi - d^1\Sigma^+$. According to our calculations the radiative lifetime for the $v = 0$ level of the $b^1\Pi$ state is 221.6 ns if only the $b^1\Pi - a^1\Delta$ channel is considered, but it becomes much shorter (165.7 ns) when both the channels are taken into account. Thus, the δ/ϕ branching ratio is 2.9, that is, significantly smaller than the respective value of 9.3 reported by Langhoff (1997). In contrast to the results of Langhoff (1997), our computed lifetime decreases with increasing v. It should be noted that there are no direct measurements on the radiative lifetimes for the $b^1\Pi$ state. There is only an estimate of 192 ± 55 ns obtained from the oscillator strengths of Davis et al. (1986). This value is in qualitative agreement with our computed radiative lifetime.

3.2.3. The $f^1\Delta - a^1\Delta$ system

The transition moment function calculated for the $f^1\Delta - a^1\Delta$ system is listed in Table 6. Our computed oscillator strength f_{00} for this transition (0.0787) agrees rather well with the value of 0.062 reported by Langhoff (1997) (Table 2). The radiative lifetime of 36 ns calculated in the present study is very close to the value of Langhoff (Table 7) (37.6 ns). The respective experimental lifetime of Hedgecock et al. (1995) (43.2 ns) is slightly longer than our

Table 8. Electronic transition moments for the singlet band systems of TiO

r(a.u.)	$i^1\Pi - a^1\Delta$	$i^1\Pi - d^1\Sigma^+$	$b^1\Pi - h^1\Sigma^+$	$c^1\Phi - g^1\Gamma$
2.5	0.9804	1.7847	1.3806	1.8205
2.6	0.9470	1.6049	1.2588	1.7058
2.7	0.9170	1.3709	1.1346	1.5879
2.8	0.8953	1.1068	1.0097	1.4691
2.9	0.8843	0.8536	0.8871	1.3521
3.0	0.8765	0.6436	0.7710	1.2449
3.1	0.8539	0.5125	0.6714	1.1389
3.2	0.8205	0.4402	0.5754	1.0362
3.3	0.8213	0.3785	0.4775	0.9451
3.4	0.7683	0.3991	0.3959	0.8362
3.5	0.7646	0.4177	0.3015	0.7065
3.6	0.7758	0.4569	0.3660	0.7797
3.7	0.7352	0.4674	0.3998	
3.8	0.7195	0.4489	0.4134	

value. Here we should note that the $f^1\Delta - a^1\Delta$ transition is not the only radiative decay channel for the $f^1\Delta$ state. The $f^1\Delta - c^1\Phi$ and $f^1\Delta - b^1\Pi$ transitions are also dipole-allowed, but their contribution to the total radiative lifetime is negligible: f_{00} for these transitions are 0.00005 and 0.0001, respectively.

3.2.4. Other transitions

We have also calculated the TMFs where the $i^1\Pi$, $h^1\Sigma^+$ and $g^1\Gamma$ states are involved (Table 8, Fig. 8). The moments for the $i^1\Pi - a^1\Delta$, $i^1\Pi - d^1\Sigma^+$, $b^1\Pi - h^1\Sigma^+$ and $c^1\Phi - g^1\Gamma$ transitions are rather large (Table 8).

Unfortunately, our computed MRCI potentials for these states are not accurate enough to be used in the calculations of the oscillator strengths. The listed TMFs, however, can be useful for future calculations of TiO line lists when reliable experimental data on these states will be available.

4. Discussion

We have collected available literature data on the oscillator strengths f_{00} and electronic oscillator strengths f_e in Tables 2 and 9, respectively and compared them with our MRCI values.

First, we should note, that just due to uncertainties in the experimentally derived potentials the uncertainty in the oscillator strengths can amount to ∼10%. For example, from Table 2 one can see that the uncertainty in the f_{00} oscillator strengths for the γ, $\gamma\prime$, α and $f^1\Delta - a^1\Delta$ bands is 7%, 10%, 13% and 8%, respectively. Thus, for generating accurate TiO line lists the accuracy of the experimental spectroscopic parameters should be improved. At least there should be a convergence of the experimentally derived spectroscopic parameters. For the γ and $\gamma\prime$ transitions our f_{00} values are larger than the experimental data of Hedgecock et al. (1995) and the theoretical results of Langhoff (1997). The electronic oscillator strengths f_e for the $\gamma\prime$ transition obtained in our study is close to that reported earlier by Davis et al. (1986) and adopted by Jørgensen (1994). We surmise that f_e value of 0.06 for this transition used by Schiavon & Barbuy (1999) is too small. Our f_e for the γ transition is between that of Davis et al. (1986) and Hedgecock et al. (1995). According to our calculations the ϵ transition is rather weak ($f_e = 0.0025$) which is in accord with the experimental estimates $f_e < 0.0056$ of Hedgecock et al. (1995) and theoretical result of Langhoff (1997) (0.002). For the α system our electronic oscillator strength is larger than the value of Hedgecock et al. (1995). Here we should note that the theoretical f_e of Langhoff (1997) listed in Table 9 for the α transition has been computed at the level of SA CASSCF. We have shown in Sect. 3.1 that f_e should increase and become close to our result if a subsequent MRCI is performed.

In general, we consider the theoretical TMFs for the $\gamma(A^3\Phi - X^3\Delta)$ and $\gamma\prime(B^3\Pi - X^3\Delta)$ transitions obtained by Langhoff (1997) as more accurate than ours. The reason for the deviation between our TMFs for the γ and $\gamma\prime$ transitions and those of Langhoff may be that Langhoff used the $X^3\Delta$ reference SCF configuration. It means that the calculations were biased in favor of the $X^3\Delta$ state and, in general, in favor of the triplet states. Our reference SCF configuration was $d^1\Sigma^+$ and thus, our calculations were biased in favor of singlet states. We believe that our results on the singlet transitions are more reliable than those of Langhoff (1997). In particular, the TMFs obtained by Langhoff seem to result in a too large oscillator strength for the $\delta(b^1\Pi - a^1\Delta)$ transition and a too small oscillator strength for the $\phi(b^1\Pi - d^1\Sigma^+)$ transition. In his TiO line list, which has been generated using Langhoff's TMFs, Plez (1998) imposed a scaling on the intensity of the δ band (the intensity has been divided by 2). According to our calculations and the analysis in Sect. 3.2.2 one should scale accordingly also the intensity of the ϕ band. This means that in Plez's line list the intensity of the ϕ band should be multiplied by a factor of 2.

The most recent measured oscillator strengths (Hedgecock et al. 1995) are smaller than our theoretical MRCI results and the SA-CASSCF/MRCI values of Langhoff (1997) (Tables 2 and 9). There is no clear dependence of the magnitude of the theoretical oscillator strengths on the level of the electron correlation treatment. Indeed, the theoretical electronic oscillator strengths for the $\gamma\prime$, α, ϵ and $f^1\Delta - a^1\Delta$ transitions calculated by Schamps et al. (1992) are very close to the measured values of Hedgecock et al. (1995), despite the fact that these calculations have been performed at a rather low level of the electron correlation treatment (single reference singles and doubles CI). Our results and those of Langhoff (1997) have been obtained at a much higher level of the electron correlation treatment, but the agreement with the experimental results of Hedgecock et al. (1995)

Table 9. MRCI electronic oscillator strengths f_e for the transitions in TiO in comparison with the literature data

System	D86[a]	B90[b]	S92[c]	J94[d]	H95[e]	L97[f]	AP98[g]	SB99[h]	This Work
$\gamma'(B^3\Pi - X^3\Delta)$	0.138	...	0.101	0.14	0.093	0.108	0.0935	0.06	0.1514
$\gamma(A^3\Phi - X^3\Delta)$	0.154	0.22	0.135	0.15	0.079	0.092	0.0786	0.12	0.1195
$\epsilon(E^3\Pi - X^3\Delta)$	...	0.006	0.005	0.014	<0.0056	0.002	0.0023	...	0.0025
$\alpha(C^3\Delta - X^3\Delta)$	0.176	...	0.102	0.17	0.106	0.105*	0.106	...	0.1288
$\beta(c^1\Phi - a^1\Delta)$	0.278	...	0.268	0.28	0.120	0.176	0.125	...	0.1621
$\delta(b^1\Pi - a^1\Delta)$	0.048	0.05	0.0004	0.048	...	0.096	0.048	0.05	0.0581
$\phi(b^1\Pi - d^1\Sigma^+)$	0.049	0.05	0.020	0.052	...	0.036	0.0178	0.01	0.0668
$f^1\Delta - a^1\Delta$	...	...	0.098	...	0.103	0.123	0.098	...	0.1282

[a]Davis et al. (1986). [b]Brett (1990). [c]Schamps et al. (1992). [d]Jørgensen (1994). [e]Hedgecock et al. (1995). [f]Langhoff (1997). [g]Alvarez & Plez (1998). [h]Schiavon & Barbuy (1999). *This value has been obtained at the SA-CASSCF level.

for the γ', α, ϵ and $f^1\Delta - a^1\Delta$ transitions is better in the later case. Because of this it is of great importance to have highly reliable independent measurements on the oscillator strengths (radiative lifetimes) for the electronic transitions in TiO.

Our MRCI calculations have revealed avoided crossings between the known $b^1\Pi$ and the new $i^1\Pi$ and $j^1\Pi$ electronic states and between the $c^1\Phi$ and $k^1\Phi$ states (Figs. 6 and 7). The accuracy of our MRCI calculations for the energies of the electronic states is not very good and, therefore, the computed positions of the avoided crossings can differ from the actual positions. Since the avoided crossings can influence the rotational-vibrational progressions in the respective spectra it is important to take them into account when analyzing spectra. We did not make a thorough analysis of possible nonadiabatic perturbations in the spectra of TiO because the accuracy of our calculation is not high enough. The problem is additionally complicated by the presence of high lying electronic states which should be included in the calculations in such a case. In practice, however, such calculations are presently hardly possible due to technical limitations and due to convergence problems. We can only very roughly estimate that levels with $v'' \sim 12$ and $v'' \sim 6$ of the $b^1\Pi$ and $c^1\Phi$ states, respectively may be appreciably perturbed by the nonadiabatic couplings.

5. Conclusion

The IC MRCI calculations have been performed for the singlet and triplet electronic states of the TiO molecule. Comparison with the previous calculations and available in the literature measurements shows that our transition moments for the singlet transitions are more accurate than the most recent theoretical results of Langhoff (1997). According to our calculations, the transition moments calculated by Langhoff for the $\delta(b^1\Pi - a^1\Delta)$ band is largely overestimated, whereas that for the $\phi(b^1\Pi - d^1\Sigma^+)$ is largely underestimated. The latter is in accord with the values recommended by most authors for this transition (Davis et al. 1986; Brett 1990; Jørgensen 1994; Plez 1998; Schiavon & Barbuy 1999). Our results on the triplet $\gamma'(B^3\Pi - X^3\Delta)$ and $\gamma(A^3\Phi - X^3\Delta)$ transitions are less accurate than those of Langhoff (1997). For other triplet transitions our TMFs agree well with those previously computed by Langhoff (1997). We have calculated several new singlet electronic states of Π and Φ symmetries. These states exhibit avoided crossings with the known $b^1\Pi$ and $c^1\Phi$ states that can affect the rotational-vibrational progressions in the $\beta(c^1\Phi - a^1\Delta)$ and $\phi(b^1\Pi - d^1\Sigma^+)$ bands for high excitations.

The transition moments functions for the transitions involving the $i^1\Pi$, $h^1\Sigma^+$, $g^1\Gamma$, $D^3\Sigma^-$ and $^3\Sigma^+$ states have been computed and tabulated. These transitions can be relevant for generating accurate TiO line lists.

Comparison of our results with the available theoretical data and laboratory measurements shows that further accurate measurements on the radiative lifetimes and spectroscopic parameters for the low-lying states of TiO are urgently needed.

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Appendix A: Diabatization

In the present work for diabatization we used a block-diagonalization technique proposed by Cederbaum et al. (1989).

The unitary transformation F which brings the Hamiltonian matrix H in the basis of the adiabatic states (diagonal matrix) into a block-diagonal matrix H^d in the basis of the diabatic states (strictly speaking quasiadiabatic) is defined for each block n as follows (Cederbaum et al. 1989):

$$\mathrm{H}^{\mathrm{d}}_{nn} = \mathrm{F}^{\dagger}_{nn}\Lambda_{nn}\mathrm{F}_{nn}, \qquad (\mathrm{A.1})$$

$$\mathrm{F}_{nn} = \mathrm{S}^{\dagger}_{nn}(\mathrm{S}_{nn}\mathrm{S}^{\dagger}_{nn})^{-1/2}, \tag{A.2}$$

where the Λ_{nn} is the respective block of the diagonal matrix of eigenvalues and S_{nn} is the respective block of the matrix of eigenvectors of the Hamiltonian H. In practice, the transformation F is constructed in the following way. First, one defines a set of m adiabatic electronic states which should be diabatized. Then, m leading configurations in the eigenvectors of these states are chosen and the block of the matrix of eigenvectors S_{nn} is defined. The final result is the $(m \times m)$ matrix H^{d}. The diagonal elements of this matrix are the energies of the respective diabatic (quasiadiabatic) states and the nondiagonal elements are the respective potential nonadiabatic couplings.

When passing to the diabatic basis one should also transform the electronic transition moments for the considered states. It is convenient to consider the parallel ($\hat{d}_z$ dipole transition moment operator) and perpendicular ($\hat{d}_x$ and $\hat{d}_y$) transitions separately. In this case the desired diabatic transition moments are obtained from Eqs. (A.1) and (A.2) where the diagonal matrix of the eigenvalues Λ_{nn} is replaced by a matrix of adiabatic transition moments D_{nn}. For perpendicular transitions the matrix D_{nn} has the following form:

$$\mathrm{D}_{nn} = \begin{pmatrix} d_{11} & d_{12} & \cdots & d_{1l} \\ d_{21} & 0 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ d_{l1} & 0 & \cdots & 0 \end{pmatrix} \tag{A.3}$$

where $l = m + 1$. In this case one of the states does not belong to the set of states being diabatized because it has a different symmetry. The S_{nn} matrix in this case is the following

$$\mathrm{S}_{kk} = \begin{pmatrix} 1 & 0 \\ 0 & \mathrm{S}_{nn} \end{pmatrix} \tag{A.4}$$

where the S_{nn} is the $(m \times m)$ block of the matrix of eigenvectors.

For parallel transitions the matrix D_{nn} has the following form:

$$\mathrm{D}_{nn} = \begin{pmatrix} d_{11} & d_{12} & \cdots & d_{1l} \\ d_{21} & d_{22} & \cdots & d_{2l} \\ \vdots & \vdots & \ddots & \vdots \\ d_{l1} & d_{l2} & \cdots & d_{ll} \end{pmatrix} \tag{A.5}$$

here l can be equal to m (if all the states involved in the transitions are the subject of diabatization) or equal to $m + 1$ (if one of the states should not be diabatized). The matrix S in this case is S_{nn} or S_{kk} (Eq. (A.4)), respectively. The diagonal elements of the matrix (A.5) are just the respective adiabatic dipole moments for the states considered.

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