

Transition Moments among $^3\Sigma$ and $^3\Pi$ States of the H₂ Molecule

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Explicitly correlated wavefunctions are used to compute adiabatic potential energy curves and electronic dipole transition moments for a number of triplet Σ and Π states of the hydrogen molecule in a wide range of internuclear distances. The potential energy curves are more accurate and complete than any earlier results. The character of the wavefunctions at large internuclear distances is investigated and the variational energies smoothly approach asymptotic interaction energies predicted by perturbation theory. © 1999 Academic Press

1. INTRODUCTION

Dipole transition moments between several triplet states of the hydrogen molecule have been computed more than once (1–3). However, the accuracy of the results is not uniform because wavefunctions of different complexity were used by different authors. Also, results for some states of interest are missing in the literature. Therefore, having in mind future, nonadiabatic computations, we decided to recompute the potentials of the lowest states and to determine the transition moments with uniform accuracy in a wide range of internuclear distances.

In this work, we consider the three lowest states of $^3\Sigma_g$, $^3\Sigma_u$, and $^3\Pi_u$ symmetry, and two lowest $^3\Pi_g$ states. This leads to 30 possible dipole transitions and far too many numbers for a publication in print. Therefore, in this paper, we give numerical results only for illustration and comparison with earlier work. Otherwise, the results are presented just graphically. Full tables, containing Born–Oppenheimer energies, adiabatic corrections, and transition moments are available as supplementary data in the form of an ASCII file. The tables can be also acquired from the authors through anonymous ftp (Ftp to <ftp://phys.uni.torun.pl>. The file name is /pub/publications/ifiz/luwo/h2trans.99).

In this work, atomic units are used throughout, unless explicitly stated otherwise.

2. DETAILS OF THE COMPUTATIONS

2.1. Wavefunctions and Energies

Explicitly correlated variational electronic wavefunctions are used in the form of expansions in elliptic coordinates as described earlier (see e.g., (4)). The convergence of the Born–

Supplementary data for this article is available on the journal home page (<http://www.academicpress.com/jms>) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).

Oppenheimer energies with increasing expansion length, in general, deteriorates with the excitation and therefore, longer expansions must be used for higher excited states. In our case, the expansion lengths varied from 247 terms in the case of the $b^3\Sigma_u$ state to 447 terms in the case of the $r^3\Pi_g$ state.

The first and second excited $^3\Sigma_g$ states are named differently by different authors. This point is discussed in some detail by Schins *et al.* (5). In this work, we use h and g to denote the first and second adiabatic excited state, respectively.

In the case of the $h^3\Sigma_g$ and $e^3\Sigma_u$ states, we use the electronic functions obtained earlier (6). The remaining Born–Oppenheimer potential energy curves, computed in this work, are lower than any other reported results. We compare our energies with the best existing data. For the two lowest Σ states, $b^3\Sigma_u$ and $a^3\Sigma_g$, our curves are lower than those of (7) and (8) by about 0.01 and 0.02 cm⁻¹. However, at two internuclear distances, better results do exist: In an attempt to get benchmark results for the Born–Oppenheimer energies, Cencek *et al.* (9), using 600 term expansions in explicitly correlated Gaussian functions, obtained for the $b^3\Sigma_u$ state at $R = 2$ and for the $a^3\Sigma_g$ state at $R = 1.8683$ energies that are lower than ours by 0.014 and 0.0016 cm⁻¹, respectively. This shows that our a and b state potentials are accurate to about 10⁻⁸ a.u., because in the computations the same variational expansion is used for all internuclear distances. For the remaining Σ states, g and f , the improvements over (10, 11) amount to 0.3–0.4 cm⁻¹ and for the $c^3\Pi_u$ and $i^3\Pi_g$ states, when compared with (12), to 0.5 and 1.0 cm⁻¹. In the case of the $r^3\Pi_g$, $d^3\Pi_u$, and $k^3\Pi_u$ states, our energies seem to be the first accurate potential curves. We computed the Born–Oppenheimer energies and adiabatic corrections for internuclear distances up to $R = 44$. At this separation, the variational energies are almost identical with the asymptotic energies of Stephens and Dalgarno (13) obtained by the perturbation method. We thus get a smooth transition from intermediate to large internuclear distances.

The phases of our variational functions are chosen, similarly as in (14), relative to the corresponding, large R , asymptotic



TABLE 1
Asymptotic Behavior of 1s2l States

State	R	$\langle 2s \Psi \rangle$	$\langle 2p \Psi \rangle$	$V(R)^a$	ΔV^b
$a^3\Sigma$	12.0	0.171	0.985	-124.2125	43.9572
	15.0	-0.005	1.000	-74.7046	3.1673
	20.0	-0.014	1.000	-31.3311	-0.0559
	30.0			-9.0845	-0.0015
	40.0			-3.8163	-0.0001
$h^3\Sigma$	12.0	0.985	-0.169	19.9228	38.3946
	15.0	1.000	0.005	-1.6688	2.5363
	20.0	1.000	0.014	-0.6749	-0.0259
	30.0			-0.0514	-0.0011
	40.0			-0.0086	-0.0001
$e^3\Sigma_u$	12.0	0.989	0.151	9.6222	36.2730
	15.0	1.000	-0.015	-2.9993	2.7591
	20.0	1.000	-0.018	-0.9122	-0.0364
	30.0			-0.0694	-0.0011
	40.0			-0.0117	-0.0001
$f^3\Sigma_u$	12.0	-0.149	0.988	166.0343	52.4614
	15.0	0.016	1.000	69.2242	2.9872
	20.0	0.018	1.000	29.5250	-0.0597
	30.0			8.9570	-0.0017
	40.0			3.7956	0.0000
$c^3\Pi_u$	12.0		1.000	-79.4452	-1.4806
	15.0		1.000	-38.0643	-0.0670
	20.0			-15.5584	-0.0013
	30.0			-4.5397	-0.0001
$i^3\Pi_g$	12.0		1.000	62.8168	0.1063
	15.0		1.000	34.0838	-0.0439
	20.0			14.8843	-0.0020
	30.0			4.4818	-0.0001

^a $V(R) = -D(R)$ is the variational interaction energy in cm⁻¹.

^b ΔV is the difference between the previous column and the long range energies from [13].

molecular functions. For an asymptotic (1s, nlm) state, with $n > 1$, these functions are

$$|nlm\rangle = \frac{1}{2} \{ \psi_{nlm}(\mathbf{r}_{1a})\psi_{100}(\mathbf{r}_{2b}) \pm \psi_{nlm}(\mathbf{r}_{2a})\psi_{100}(\mathbf{r}_{1b}) \\ + (-1)^{l+p} [\psi_{nlm}(\mathbf{r}_{1b})\psi_{100}(\mathbf{r}_{2a}) \pm \psi_{nlm}(\mathbf{r}_{2b})\psi_{100}(\mathbf{r}_{1a})] \}, \quad [1]$$

where \mathbf{r}_{ia} , \mathbf{r}_{ib} are electronic coordinates relative to the nuclei, the \pm signs correspond to singlet and triplet states, and $p = 0$, 1 for the g and u symmetry, respectively. If $n = 1$, an additional factor, $1/\sqrt{2}$, is obviously required in Eq. [1] for normalization. The atomic functions $\psi_{nlm}(\mathbf{r})$ are defined as in (14), i.e.,

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}, \quad [2]$$

with R_{nl} being the familiar hydrogen atom radial function ($R_{nl}(r) > 0$ for $r \approx 0$) and Y_{lm} a spherical harmonic with the phase convention of Condon and Shortley (15). Thus, our

atomic functions differ from those of Landau and Lifshitz (16). To get the latter, one has to multiply our atomic functions by i^l .

In all cases, we assume m , the angular momentum projection quantum number, to be nonnegative, i.e., $m = 0$ and $m = 1$ for the Σ and Π states, respectively, and we omit this index below. The phases of the variational wavefunctions, Ψ , are chosen such that a function of a state dissociating to 1snl has the asymptotic form $|nl\rangle$ given by Eq. [1]. We illustrate the asymptotic behavior of our wavefunctions in Tables 1 and 2 where overlaps of the variational functions and asymptotic functions, $|nl\rangle$, are listed for the 1s2l and 1s3l states. Also, we have included in the tables the interaction energy, $V(R)$, of the two atoms, computed in this work, and the difference between our interaction energy and the asymptotic interaction energy computed from the formulas given by Stephens and Dalgarno (13). It is seen from Table 1 that the wavefunctions of the 1s2l states attain their asymptotic character already at $R = 15$. However, the last column shows that larger distances are required to get a smooth transition to the asymptotic long-range energies. The convergence to the 1s3l limit, as seen in Table 2, is less rapid, but $R = 44$ suffices to allow the use of the perturbational asymptotic energies (13). This is true even in the case of the g state which has still mixed character at this

TABLE 2
Asymptotic Behavior of 1s3l States

State	R	$\langle 3s \Psi \rangle$	$\langle 3p \Psi \rangle$	$\langle 3d \Psi \rangle$	$V(R)^a$	ΔV^b
$g^3\Sigma_g$	12.0	-0.279	0.420	0.619	-58.3667	737.2261
	15.0	-0.041	0.483	0.643	-16.7745	136.8899
	20.0	0.175	0.525	0.554	-4.7389	15.7500
	30.0	-0.204	0.689	-0.065	-1.9694	0.1675
	40.0	-0.057	0.720	0.006	-0.7169	-0.0134
$d^3\Pi_u$	44.0	-0.037	0.721	0.027	-0.5130	-0.0047
	12.0		0.503	-0.863	-129.9583	47.6611
	15.0		0.565	-0.825	-40.1241	-3.0381
	20.0		0.755	-0.656	-6.7052	-0.9604
	30.0		1.000	-0.013	-0.9281	0.0028
$k^3\Pi_u$	40.0		0.998	0.066	-0.3415	0.0030
	44.0		0.997	0.071	-0.2501	0.0023
	12.0		0.864	0.504	-28.6472	9.4222
	15.0		0.825	0.565	-10.4378	1.6901
	20.0		0.653	0.757	-2.9947	0.0579
$r^3\Pi_g$	30.0		0.013	1.000	-0.2827	-0.0094
	40.0		-0.066	0.998	-0.0442	-0.0005
	44.0		-0.071	0.997	-0.0241	-0.0001
	12.0		-0.418	0.907	-118.8233	58.3424
	15.0		-0.481	0.876	-38.5456	-2.4117
$r^3\Pi_g$	20.0		-0.463	0.886	-5.8393	-1.0603
	30.0		-0.264	0.965	-0.3053	-0.0158
	40.0		-0.155	0.988	-0.0435	-0.0006
	44.0		-0.132	0.991	-0.0233	-0.0002

^a $V(R) = -D(R)$ is the variational interaction energy in cm⁻¹.

^b ΔV is the difference between the previous column and the long range energies from [13].

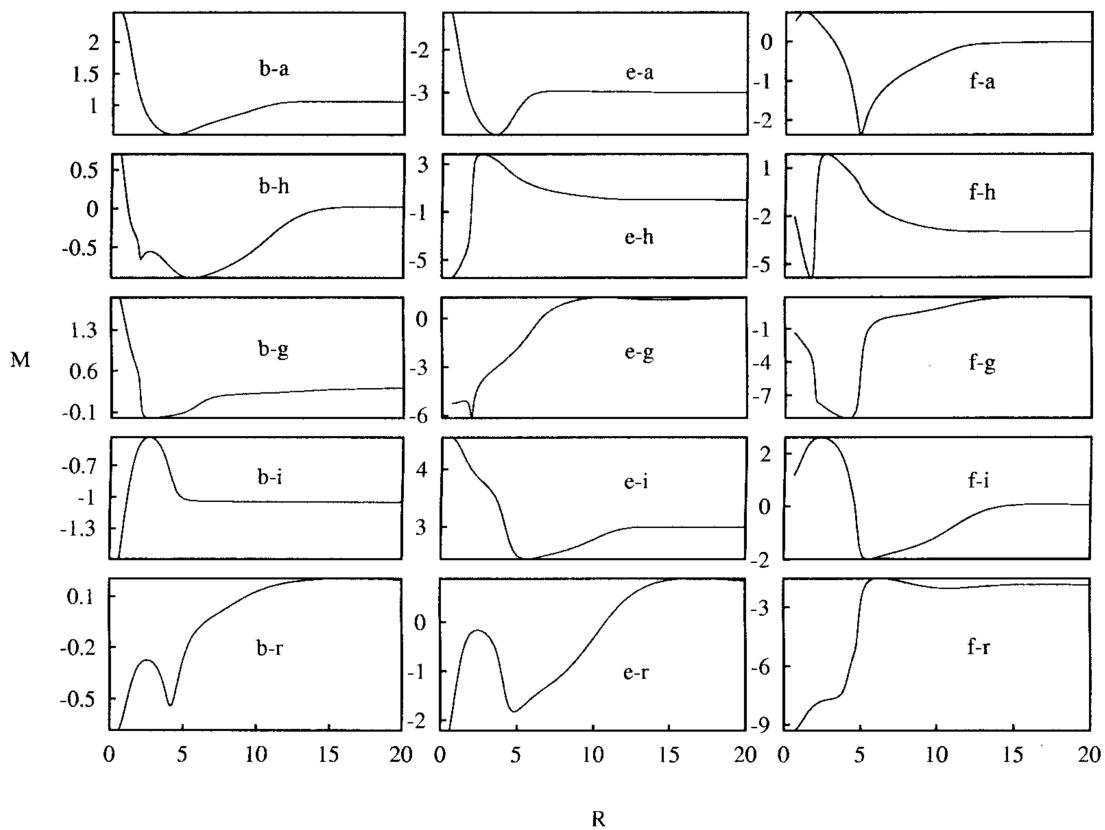


FIG. 1. Transition moments involving ${}^3\Sigma_u$ states.

separation; the probability of finding the $1s3p$ configuration being only $|\langle 3p|\Psi \rangle|^2 = 0.52$.

2.2. Transition Moments

Previous experience has shown (14) that, when our wavefunctions are used, the dipole and velocity formulas for the transition moments yield in most cases practically the same results, and, if the energy differences of the two corresponding states are small, the dipole formula is superior. Therefore, in this work, the transition moment, M , between states Ψ and Φ is computed from the dipole formula:

$$M = \langle \Psi | \mathbf{r}_1 + \mathbf{r}_2 | \Phi \rangle. \quad [3]$$

In the case of $\Sigma \rightarrow \Pi$ transitions, we assume the Π state function to be on the left in Eq. [3]. Thus, since we use wavefunctions corresponding to nonnegative angular momentum projections onto the molecular axis, the nonvanishing components of the transition moments are $M_+ = (M_x + iM_y)/\sqrt{2}$ for the $\Sigma \rightarrow \Pi$ transitions and M_z otherwise.

As was mentioned in the introduction, full tables containing all numerical results obtained in this work are deposited as JMS supplementary material. In this material we have also included, for completeness, the e and h state energies computed in (6). Here we present the transition moments graphically, in Fig. 1 for transitions involving ${}^3\Sigma_u$ states and in Fig.

2 for those involving ${}^3\Pi_u$ states. The rather irregular behavior of the moments is due to rapid changes in the character of the molecular states due to avoided crossings. These changes are most clearly seen in the adiabatic corrections as was demonstrated by Kołos and Rychlewski, who found unusually large corrections for the h , g , and f states (10, 11) at about $R = 2$ and $R = 5$. We summarize the corrections, for all states considered in this work, in Fig. 3. It is seen that in the case of the $k{}^3\Pi_u$ state there is a very narrow maximum, much more pronounced than in the case of the Σ states, and the adiabatic correction amounts to over $52\,000\text{ cm}^{-1}$ at $R = 2.85$. It is clear that the adiabatic approximation must fail in the description of such states. There are also maxima for other states but neither as high nor as narrow. Since our Born–Oppenheimer energies are most probably accurate to about 10^{-8} a.u. , we believe that the moments computed in this work are accurate to 10^{-4} a.u. or better, though it is impossible to give rigorous error bounds.

Some of the transitions, considered here, have been investigated before. These are compared with our results in Tables 3–5. In general, although less accurate functions were used by Rychlewski (1), the agreement in Table 3 is quite good. The exceptionally large discrepancies for the $c \rightarrow h$ and $c \rightarrow g$ at $R = 5$ must be due to an accidental error in the c -state function used by Rychlewski. In Table 4, our $b \rightarrow i$ and $c \rightarrow i$ transition moments are compared with those of Koch (1), and

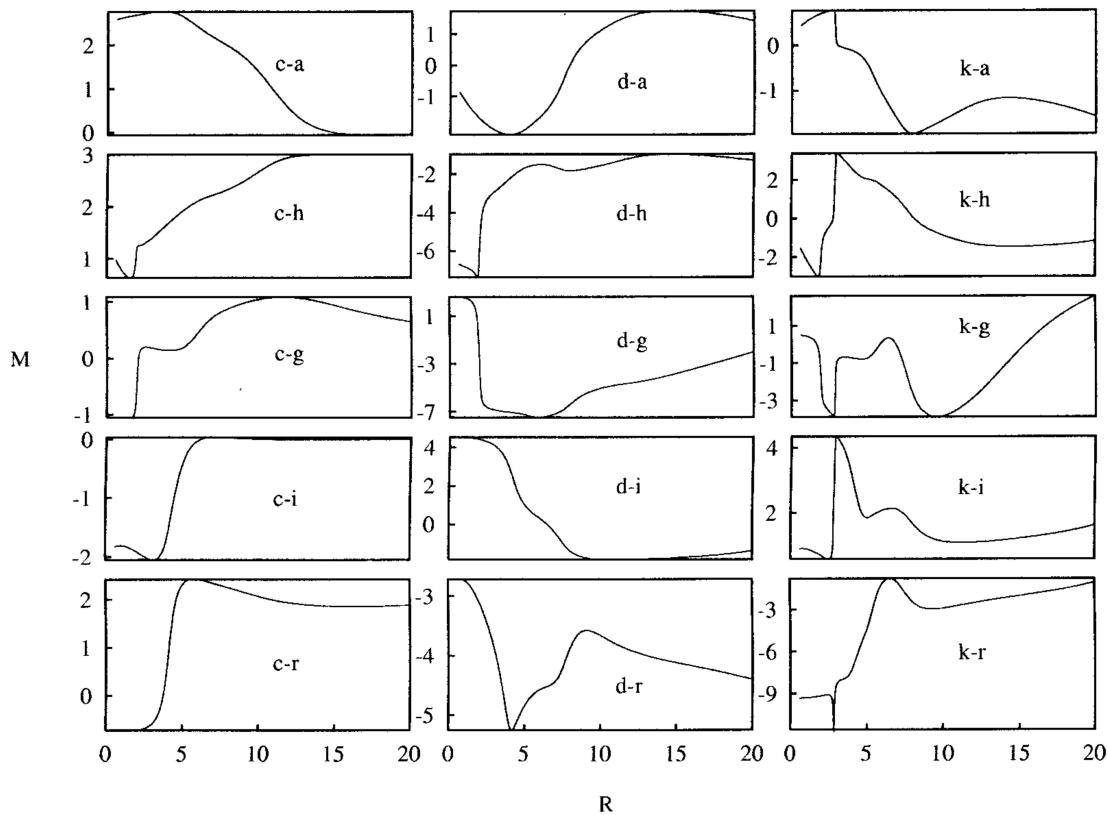
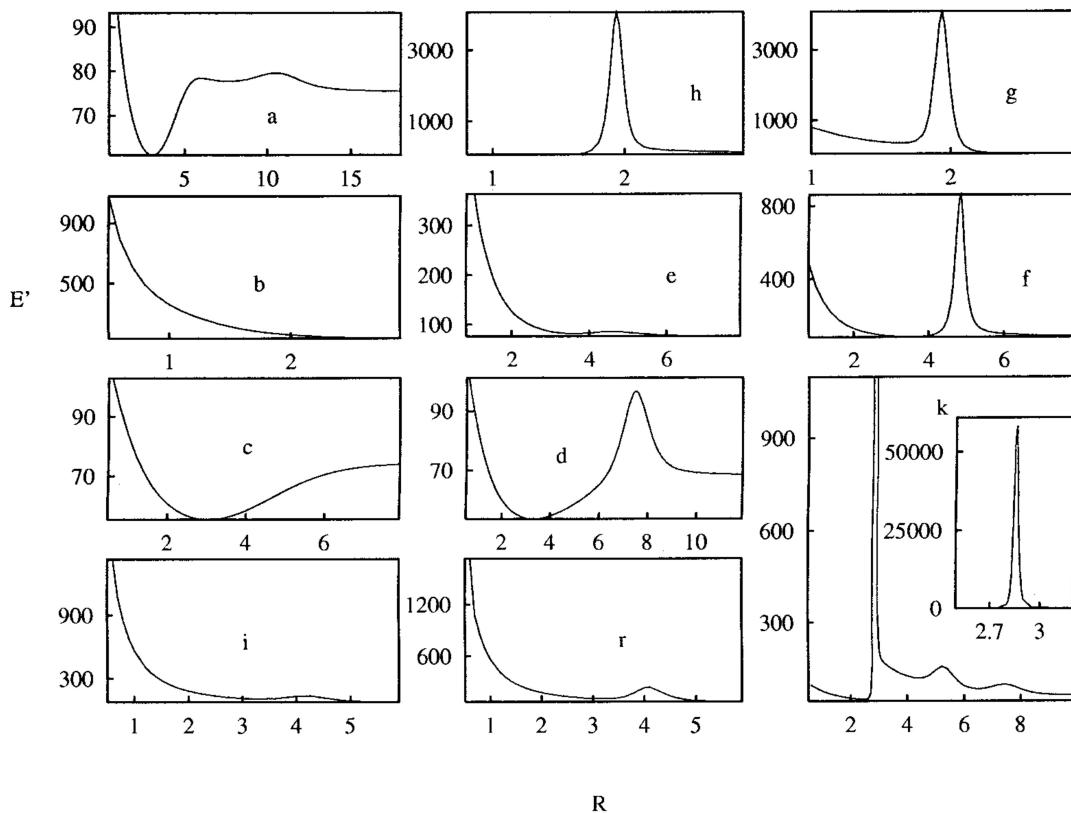
FIG. 2. Transition moments involving $^3\Pi_u$ states.FIG. 3. Total adiabatic corrections in cm^{-1} .

TABLE 3
Comparison of Transition Moments Involving *g* and *h* States

R	<i>b</i> → <i>h</i>			<i>b</i> → <i>g</i>			<i>c</i> → <i>h</i>			<i>c</i> → <i>g</i>		
	<i>M</i> _z	ΔM^a	<i>M</i> _z	ΔM	<i>M</i> ₊	ΔM	<i>M</i> ₊	ΔM	<i>M</i> ₊	ΔM		
1.00	0.1279	0.0072	1.3673	0.0024	0.7694	-0.0090	-1.0476	0.0031				
1.20	-0.0889	0.0036	1.1175	0.0026	0.6952	-0.0065						
1.40	-0.2344	0.0006	0.9033	0.0005	0.6435	-0.0054	-1.0555	0.0020				
1.50	-0.2845	0.0037	0.8141	-0.0001	0.6296	-0.0052	-1.0562	0.0018				
1.80	-0.4326	0.0013	0.5718	0.0016	0.7356	-0.0048	-0.9838	0.0008				
1.90	-0.5629	0.0010	0.3896	0.0017	0.9744	0.0042	-0.7565	-0.0079				
2.00	-0.6566	-0.0004	0.0458	0.0016	1.2240	-0.0037	-0.2031	-0.0030				
2.05		-0.0557	0.0013				-0.0319	-0.0034				
2.10	-0.6271	-0.0007	-0.1123	0.0011			0.0626	-0.0035				
2.20	-0.5978	-0.0006	-0.1662	0.0008			0.1494	-0.0036				
2.50	-0.5574	-0.0004	-0.2033	-0.0001	1.2932	-0.0021	0.1992	-0.0034				
3.00	-0.5736	-0.0002	-0.1965	0.0003	1.4048	-0.0014	0.1776	-0.0032				
3.50	-0.6481	-0.0001	-0.1801	0.0002	1.5404	-0.0013	0.1500	-0.0024				
4.00	-0.7469	-0.0001	-0.1627		1.6781	-0.0008	0.1351	-0.0019				
5.00	-0.8800	0.0000	-0.1055	-0.0001	1.9280	-0.0222	0.1910	-0.0450				
6.00					2.1201	-0.0002	0.4712	-0.0037				
8.00					2.3424	-0.0002	0.8875	-0.0012				

^a ΔM is the difference between the previous column and the result of Rychlewski as given in [1]

Guberman and Dalgarno (2), and the *e* → *i* moments with the results of Stolyarov and Child (3). The *c* → *i* transition moment changes sign at about *R* = 6.15 and *R* = 12.0. This fact was overlooked both by Koch, and by Guberman and Dalgarno. Therefore, for the comparison, we changed the signs of the moments of (1) and (2) in order to bring them in agreement with our signs. The last two columns in Table 4 contain WKB and quantum defect theory results (3). In view of the somewhat approximate nature of the computations in (3), the agreement with our results must be considered as very good. This is especially true for the WKB approximation which, except for *R* > 4, gives results accurate to better than

TABLE 4
Comparison of Transition Moments Involving the *f*³*Π_g* State

R	<i>b</i> → <i>i</i>			<i>c</i> → <i>i</i>			<i>e</i> → <i>i</i>		
	<i>M</i> ₊	ΔM^a	ΔM^b	<i>M</i> _z	ΔM^a	ΔM^b	<i>M</i> ₊	ΔM^c	ΔM^d
1.0	-1.177		0.003	-1.811		0.020	4.461	-0.030	0.128
1.3	-0.865		0.004	-1.824	-0.024	0.017	4.316	-0.052	0.123
1.4	-0.779	-0.006	0.004	-1.832	-0.025	0.016	4.261	-0.058	0.118
1.5	-0.706	-0.005	0.004	-1.841	-0.026	0.016	4.206	-0.063	0.112
2.0	-0.492	0.001	0.002	-1.909		0.015	3.979	-0.072	0.087
2.5	-0.430			-1.990	-0.039	0.017	3.829	-0.065	0.071
3.5	-0.553		-0.002	-2.016	-0.043	0.016	3.541	-0.024	0.050
4.0	-0.752		-0.006	-1.683	-0.040	0.002	3.228	0.007	0.037
4.5	-0.946		-0.004	-0.971	-0.030	-0.007	2.763	-0.111	-0.036
5.0	-1.019		-0.001	-0.410	-0.026	0.003	2.500	-0.525	-0.258
5.5				-0.136	-0.024				
6.0	-1.042		0.000	-0.019	-0.017	0.014			
6.1				-0.006	0.008				
6.2				0.005	-0.019				
8.0	-1.045		-0.001	0.025		0.010			
10.0	-1.048		-0.002	0.005		0.007			
15.0	-1.052		-0.001	-0.001		0.000			

^a The difference between present results (previous column) and the results of Koch as given in [1]

^b The difference between present results and [2]

^c The difference between present and the WKB results of [3]

^d The difference between present and the quantum defect theory results of [3]

TABLE 5
Comparison of *a* → *c* Transition Moments

<i>R</i>	<i>M</i> ₊	ΔM^a	<i>R</i>	<i>M</i> ₊	ΔM
1.0	2.634	-0.015	5.0	2.645	-0.001
1.5	2.670	-0.014	6.0	2.392	-0.005
1.9	2.696	-0.016	7.0	2.162	-0.012
2.0	2.703	-0.016	8.0	1.955	-0.024
2.5	2.736	-0.017	9.0	1.702	-0.043
3.5	2.781	-0.012	10.0	1.349	-0.071
4.0	2.775	-0.006	15.0	-0.014	0.037
4.5	2.732	-0.003	20.0	-0.042	-0.019

^a The difference between present results (previous column) and [2].

2%. This is comparable with the accuracy of the *ab initio* results of Koch (1), and Guberman and Dalgarno (2). The latter authors computed also the *a* → *c* transition moments with similar accuracy. The comparison with our results is performed in Table 5. Again, in the comparison, we corrected the signs of the moments of (2) for *R* > 10 to account for the change of sign neglected in (2).

In conclusion, transition moments computed in this work, where earlier results exist, differ from the latter by amounts on the order of 0.0001–0.01 a.u. These differences cannot influence transition probabilities of strong lines but can be significant in the case of weak lines. However, for many states considered here, transition probabilities between adiabatic vibrational levels are not very meaningful. Adiabatic corrections are large and this indicates strong nonadiabatic interactions. Therefore, nonadiabatic computations are desirable and are in preparation in this laboratory. This work is just one step in this direction.

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