

to relate the concentrations to each other absolutely. Accumulated uncertainties are therefore in excess of 10% even for examples where the molecular dipole moment (i.e., transition moment) is known with reasonable accuracy from microwave spectroscopy. Fortunately the determination of radical concentrations from LMR follows similar procedures developed over a decade ago for kinetic applications of gas-phase EPR and, although laborious, the determination of line shapes and areas is well understood.

Reactions of the important atmospheric species HO<sub>2</sub> have been particularly well studied by far-infrared LMR. The technique is advantageous for HO<sub>2</sub> kinetics due to its high sensitivity, 10<sup>9</sup> cm<sup>-3</sup> for the ground state, and capacity to detect related species such as OH simultaneously. For example, the reaction HO<sub>2</sub> + NO = OH + NO<sub>2</sub> has now been studied by LMR in three laboratories<sup>33,35,36</sup> with good agreement for the rate constant and with measurements by other techniques. The temperature dependence of this reaction has also been measured<sup>35</sup> by incorporating a heated flow reactor before the LMR detection region, again in an analogous fashion to earlier experiments using EPR. The majority of the kinetic results obtained so far have used the discharge laser sources but as the optically pumped lasers are developed for kinetics a much wider variety of radical reactions should be amenable to study. Pioneering results on the chemistry of the methoxy radical are an indication of future kinetic research with these

lasers.<sup>37</sup> Finally, it is interesting to note that all the kinetic applications so far have used far-infrared lasers and there appears to be no fundamental reason why mid-infrared spectrometers cannot be converted for kinetic studies also.

### Conclusion

The rapid and successful development of LMR is now manifested by the many instruments in use in more than a dozen laboratories throughout the world. The continuing discoveries of new laser lines in the far-infrared provides an almost continuous frequency coverage in the region and it is reasonable to postulate that "tuning" transitions from one laser line to the next across the 100-1000- $\mu$ m region should be possible in the near future. This is fortunate as in the far-infrared there are no narrow-band tunable laser sources for spectroscopy at zero field, and LMR is presently the only technique available for spectroscopy of free radicals in this region. Although discoveries of new laser lines in the mid-infrared have not been forthcoming there are alternative tunable sources, particularly the semiconductor diode laser, to cover this region for high-resolution free-radical spectroscopy.

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## ARTICLES

### Flexible d Basis Sets for Sc through Cu

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A prescription is presented and implemented for Sc through Cu that leads to practical-sized Gaussian d basis sets capable of accurate descriptions of the  $s^m d^{n-m}$  states of the atom. Optimized Gaussian basis sets containing four, five, and six primitives are given along with recommended double zeta, double zeta, and triple zeta contraction schemes, respectively. It is suggested that these basis sets be used for calculations on large, medium, and small transition metal complexes, respectively.

### Introduction

In molecular calculations involving transition metals, it is important to retain the smallest number of d basis functions consistent with accurate descriptions of the d orbitals of the atoms and molecules. The reasons are that integral calculations for d functions are costly and also that

each additional set of d primitives normally leads to six additional Cartesian Gaussians for SCF calculations. Based on atomic calculations, it has been concluded that five sets of d primitive Gaussians [denoted as (5d)] are required to accurately describe the shape of the atomic d orbitals. [For some applications a properly determined (4d) basis will be adequate.] For example, the total energy of the d<sup>10</sup> state of Ni drops by 5.99, 5.74, 1.57, and 0.14 eV upon going from three d's to four d's to five d's to six d's to seven d's, respectively. Of special concern in variational

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TABLE I: Atomic Excitation Energies (eV) Relative to the  $s^2d^{n-2}$  State<sup>a</sup>

atom	state	(5d) <sup>b</sup> opt. for $s^2d^{n-2}$	(4d) <sup>c</sup> opt. for $s^0d^n$	(5d) <sup>d</sup> augmented	(5d) <sup>c</sup> opt. for $s^0d^n$	(6d) <sup>d</sup> augmented	(6d) <sup>c</sup> opt. for $s^0d^n$	numerical HF
Sc	$s^1d^2$	1.54	1.25	1.08	1.08	1.03	1.02	1.01
	$d^3$	6.87	4.97	4.58	4.61	4.52	4.51	4.47
Ti	$s^1d^3$	1.17	0.73	0.60	0.61	0.54	0.55	0.54
	$d^4$	6.82	4.76	4.34	4.45	4.28	4.29	4.25
V	$s^1d^4$	0.85	0.29	0.16	0.17	0.15	0.13	0.12
	$d^5$	5.94	3.86	3.33	3.44	3.31	3.32	3.27
Cr	$s^1d^5$	-0.50	-1.11	-1.21	-1.22	-1.24	-1.25	-1.27
	$d^6$	9.10	6.44	5.82	5.97	5.79	5.81	5.75
Mn	$s^1d^6$	4.37	3.43	3.32	3.36	3.34	3.33	3.33
	$d^7$	13.04	9.98	9.15	9.37	9.18	9.21	9.15
Fe	$s^1d^7$	2.84	1.96	1.79	1.83	1.80	1.81	1.80
	$d^8$	11.43	8.49	7.44	7.77	7.47	7.51	7.46
Co	$s^1d^8$	2.63	1.71	1.51	1.57	1.53	1.52	1.53
	$d^9$	11.21	8.24	7.01	7.39	7.06	7.07	7.05
Ni	$s^1d^9$	2.44	1.53	1.25	1.32	1.27	1.29	1.28
	$d^{10}$	9.80	6.99	5.41	5.84	5.47	5.56	5.47
Cu	$s^1d^{10}$	0.85	-0.08	-0.42	-0.31	-0.38	-0.36	-0.37
	$d^{11}$	8.40	5.49	3.72	4.31	3.79	3.91	

<sup>a</sup> Uncontracted basis sets were used in all cases. <sup>b</sup> Wachter, ref 2. <sup>c</sup> This work. <sup>d</sup> Hay, ref 5.

TABLE II: Exponents and Contraction Coefficients for the (4d) d Basis Sets

$\alpha$	C	$\alpha$	C	$\alpha$	C
Sc		Ti		V	
8.614	6.40051723D-02	9.810	7.66199122D-02	12.02	7.74048182D-02
2.056	2.62705647D-01	2.433	2.94478935D-01	3.034	3.02137513D-01
0.5107	4.75394469D-01	0.6451	4.89296130D-01	0.8298	4.96182216D-01
0.1024	5.92246514D-01	0.1407	5.26968156D-01	0.1895	4.99744161D-01
Cr		Mn		Fe	
14.07	7.87628253D-02	16.18	7.98180297D-02	18.40	8.09367981D-02
3.587	3.08352315D-01	4.183	3.11699068D-01	4.772	3.17086631D-01
0.9899	4.99861905D-01	1.169	5.01003803D-01	1.342	5.02671338D-01
0.2237	4.89872992D-01	0.2662	4.81616287D-01	0.3071	4.72354408D-01
Co		Ni		Cu	
20.67	8.18823383D-02	23.15	8.22209743D-02	26.22	8.07285911D-02
5.399	3.20288911D-01	6.071	3.23241646D-01	6.857	3.23000241D-01
1.527	5.05192903D-01	1.725	5.05380400D-01	1.955	5.08297497D-01
0.3477	4.65718825D-01	0.3984	4.59207328D-01	0.4472	4.57658706D-01

calculations is that the primitive basis allows a compact contraction to reduce the number of independent functions. Previous studies<sup>1</sup> have shown that a five-Gaussian basis can be contracted to two functions, [5/2], often referred to as double zeta, without affecting calculations on molecules, whereas a six-Gaussian basis set cannot be acceptably contracted to two functions [6/2]. For these reasons, the (5d) basis has been considered an ideal one for molecular calculations of first-row transition metals.

Unfortunately the standard (5d) basis sets<sup>2,3</sup> are not sufficiently flexible to describe all the important states of transition metals. For example, they lead to an error of 4 eV in the  $s^2d^8$ - $d^{10}$  splitting of Ni. In this paper we report (4d), (5d), and (6d) basis sets for the first transition row (Sc-Cu) and double zeta, double zeta, and triple zeta contractions of the (4d), (5d), and (6d) basis sets, respectively, for these atoms.

### Method

In Table I we compare the separations of the  $s^2d^{n-2}$ ,  $s^1d^{n-1}$ ,  $s^0d^n$  states of Sc-Cu for Hartree-Fock (HF) calculations with various d basis sets. For Ni ( $^3F$ ,  $^3D$ , and  $^1S$

states) exact (numerical) HF calculations lead to an  $s^2d^8$ - $d^{10}$  splitting of 5.47 eV, whereas the Wachter basis (5d optimized for  $s^2d^8$ ) leads to 9.80 eV, an error of 4.3 eV! On the other hand, by optimizing the d basis for the  $s^0d^{10}$  state, we obtain  $s^2d^8$ - $d^{10}$  splittings of 6.99 (4d), 5.84 (5d), and 5.56 eV (6d), with errors of 1.52, 0.37, and 0.09 eV, respectively. The origin of this effect is as follows. The d orbitals are small in size compared with the s orbitals, so that an electron in the 4s orbital does not effectively shield a 3d electron from the nucleus. Thus in the  $d^{10}$  state each d electron is much more effectively shielded from the nucleus than in the  $s^2d^8$  state, leading to larger (more diffuse) orbitals. Consequently, the 5d basis from  $s^2d^8$  is not sufficiently diffuse to describe the d orbitals of the  $d^{10}$  state. On the other hand, the 5d basis from the  $d^{10}$  state can describe the tighter orbitals of the  $s^2d^8$  state by merely changing the linear coefficients. Further, the  $d^{10}$ -optimized basis provides a better description of the 3d-4s interactions, which is evidenced by improvement in the Koopmans' theorem ionization potentials for the 4s orbital of both the  $s^2d^8$  and  $s^1d^9$  states. The 4s orbital energies (hartrees) for the  $s^2d^8$  state are 0.27625 for numerical HF, 0.278483 for  $d^{10}$ -optimized (5d) basis, and 0.270857 for Wachter's (5d) basis. For the  $s^1d^9$  state, the 4s orbital energies are 0.23576 for numerical HF, 0.236990 for  $d^{10}$ -optimized basis, and 0.217732 for Wachter's basis. The

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TABLE III: Exponents and Contraction Coefficients for the (5d) d Basis Sets

$\alpha$	C	$\alpha$	C	$\alpha$	C
Sc		Ti		V	
15.19	2.89190492D-02	20.73	2.66517493D-02	21.18	3.35595342D-02
3.710	1.49174065D-01	5.090	1.46864218D-01	5.566	1.64567490D-01
1.084	3.34660015D-01	1.545	3.40392761D-01	1.753	3.65791138D-01
0.2974	4.60697426D-01	0.4585	4.56804981D-01	0.5256	4.58772599D-01
0.06936	4.65610383D-01	0.1102	4.46199540D-01	0.1336	3.87748639D-01
Cr		Mn		Fe	
28.00	2.82278486D-02	28.15	3.42869181D-02	31.78	3.54066628D-02
7.213	1.53903211D-01	7.564	1.70996105D-01	8.426	1.78115212D-01
2.241	3.68451130D-01	2.410	3.79828354D-01	2.719	3.8343646D-01
0.6612	4.68309376D-01	0.7282	4.58334035D-01	0.8335	4.51535378D-01
0.1620	3.91055232D-01	0.1799	3.68376780D-01	0.2113	3.59074071D-01
Co		Ni		Cu	
34.97	3.62293812D-02	39.49	3.55460797D-02	43.66	3.56934638D-02
9.463	1.81096242D-01	10.75	1.79996302D-01	11.97	1.80263235D-01
3.051	3.90134959D-01	3.475	3.92560290D-01	3.916	3.89610112D-01
0.9365	4.50939364D-01	1.065	4.54418307D-01	1.222	4.50798523D-01
0.2350	3.49816738D-01	0.2641	3.44670087D-01	0.3066	3.46402523D-01

TABLE IV: Exponents and Contraction Coefficients for the (6d) d Basis Sets

$\alpha$	C	$\alpha$	C	$\alpha$	C
Sc		Ti		V	
23.24	1.43632903D-02	28.11	1.53148419D-02	33.36	1.53978328D-02
6.143	7.80683128D-02	7.630	8.40269549D-02	9.331	8.46396181D-02
2.007	2.17559770D-01	2.528	2.38297448D-01	3.158	2.40000837D-01
0.6652	3.49798322D-01	0.8543	3.77444967D-01	1.113	3.79378333D-01
0.2021	4.25010943D-01	0.2673	4.12163691D-01	0.3608	4.08820800D-01
0.05454	3.72481407D-01	0.0743	3.17466802D-01	0.1007	3.01703363D-01
Cr		Mn		Fe	
37.89	1.61917253D-02	42.63	1.67152191D-02	47.10	1.76408791D-02
10.58	9.00714944D-02	11.97	9.40154390D-02	13.12	1.00782742D-01
3.603	2.52220408D-01	4.091	2.60779605D-01	4.478	2.74366978D-01
1.270	3.87985843D-01	1.450	3.93678761D-01	1.581	4.01473873D-01
0.4118	4.00116732D-01	0.4700	3.94443955D-01	0.5100	3.86216164D-01
0.1126	2.87349938D-01	0.1281	2.73536085D-01	0.1382	2.54090511D-01
Co		Ni		Cu	
51.69	1.78005661D-02	58.73	1.75292615D-02	65.80	1.70788632D-02
14.70	1.04596888D-01	16.71	1.00405051D-01	18.82	9.91554497D-02
4.851	2.97330161D-01	5.783	2.76091985D-01	6.538	2.74753795D-01
1.643	4.23527577D-01	2.064	4.03476707D-01	2.348	4.04008442D-01
0.5075	3.72830506D-01	0.6752	3.81219977D-01	0.7691	3.82620040D-01
0.1433	2.18673606D-01	0.1825	2.50255729D-01	0.2065	2.49008434D-01

improvement in the  $s^1d^9$  ionization is due to a better description of the tail region of the 3d orbital. From such considerations we conclude that d basis for transition metals should be optimized for the  $d^n$  configuration rather than for the ground-state configuration and that a (4d) basis optimized in this manner should yield adequate results for molecular calculations.

Using the (14s, 9p) primitive sets of Wachter (uncontracted), we optimized (5d) and (6d) basis sets for the  $d^n$  states of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu leading to the results in Tables II-IV. (For Cu the d basis was optimized for the  $d^{11}$  state. Although this state is not allowed by the Pauli principle, it leads to a basis consistent with the trends across the row.)

## Discussion

In all cases the reoptimized (5d) basis is considerably more diffuse than Wachter's, and the resulting energy separations are much improved. As shown in Table I, the

new (5d) basis gives energy splittings in reasonable agreement with numerical HF (considerably better than with the Wachter basis), and the new (6d) basis gives energy splittings in good agreement with numerical HF. For example, the Wachter's (5d) basis for Ni yields an  $s^1d^9 \rightarrow s^2d^8$  splitting of -2.44 eV, our reoptimized (5d) basis gives -1.32 eV, and our reoptimized (6d) basis yields -1.29 eV, compared with -1.28 eV for numerical HF. Further, if uncontracted primitives are used, the reoptimized basis sets apparently perform about as well as augmented basis sets.<sup>5,6</sup> For example, the augmented basis of Hay yields  $s^1d^9 \rightarrow s^2d^8$  splittings of -1.25 (5d) and -1.27 (6d).

There are two significant differences between the augmentation approach and the current technique. The

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TABLE V: Hartree-Fock Atomic Energies for Various d Orbital Basis Sets (in hartrees)

atom	state	$s^2d^{n-2}$		$s^0d^n$		$s^0d^n$	
		opt. (5d) <sup>b</sup>	augmented (5d) <sup>a</sup>	opt. (4d) <sup>c</sup>	opt. (5d) <sup>c</sup>	augmented (6d) <sup>a</sup>	opt. (6d) <sup>c</sup>
Sc	$s^2d^1$	-759.722 877	-759.719 586	-759.708 393	-759.720 942	-759.725 081	-759.724 870
	$s^1d^2$	-759.666 277	-759.679 887	-759.662 328	-759.681 142	-759.687 210	-759.687 207
	$d^3$	-759.470 540	-759.551 165	-759.525 599	-759.551 582	-759.558 873	-759.559 214
Ti	$s^2d^2$	-848.389 292	-848.379 808	-848.358 202	-848.385 713	-848.392 713	-848.392 637
	$s^1d^3$	-848.346 499	-848.357 829	-848.331 298	-848.363 335	-848.372 101	-848.372 335
	$d^4$	-848.138 608	-848.220 246	-848.183 448	-848.222 278	-848.234 826	-848.234 978
V	$s^2d^3$	-942.862 874	-942.845 727	-942.815 540	-942.857 312	-942.867 788	-942.868 703
	$s^1d^4$	-942.831 640	-942.839 757	-942.804 944	-942.851 168	-942.862 453	-942.863 776
	$d^5$	-942.644 716	-942.723 174	-942.673 704	-942.731 023	-942.746 332	-942.746 878
Cr	$s^2d^4$	-1043.282 630	-1043.256 202	-1043.210 758	-1043.272 889	-1043.289 092	-1043.290 634
	$s^1d^5$	-1043.301 167	-1043.300 676	-1043.251 598	-1043.317 776	-1043.334 813	-1043.336 700
	$d^6$	-1042.948 171	-1043.042 401	-1042.974 216	-1043.053 370	-1043.076 263	-1043.077 209
Mn	$s^2d^5$	-1149.832 454	-1149.794 112	-1149.734 035	-1149.818 974	-1149.840 173	-1149.842 561
	$s^1d^6$	-1149.671 881	-1149.672 122	-1149.607 819	-1149.695 588	-1149.717 585	-1149.720 018
	$d^7$	-1149.353 107	-1149.457 736	-1149.367 450	-1149.474 515	-1149.502 915	-1149.504 136
Fe	$s^2d^6$	-1262.401 375	-1262.348 502	-1262.276 115	-1262.386 692	-1262.411 565	-1262.415 316
	$s^1d^7$	-1262.296 914	-1262.282 798	-1262.204 266	-1262.319 432	-1262.345 366	-1262.348 980
	$d^8$	-1261.981 298	-1262.074 920	-1261.963 960	-1262.101 054	-1262.136 874	-1262.139 278
Co	$s^2d^7$	-1381.361 715	-1381.291 278	-1381.202 241	-1381.343 322	-1381.374 104	-1381.376 147
	$s^1d^8$	-1381.265 186	-1381.235 765	-1381.139 353	-1381.285 779	-1381.317 856	-1381.320 418
	$d^9$	-1380.949 590	-1381.033 643	-1380.899 584	-1381.071 922	-1381.114 835	-1381.116 288
Ni	$s^2d^8$	-1506.807 232	-1506.716 234	-1506.616 160	-1506.784 930	-1506.822 086	-1506.832 221
	$s\ d$	-1506.717 474	-1506.670 449	-1506.559 786	-1506.736 591	-1506.775 254	-1506.784 842
	$d^{10}$	-1506.447 106	-1506.517 245	-1506.359 442	-1506.570 219	-1506.620 980	-1506.627 784
Cu	$s^2d^9$	-1638.875 124	-1638.760 929	-1638.642 279	-1638.852 708	-1638.893 156	-1638.907 041
	$s^1d^{10}$	-1638.843 721	-1638.776 189	-1638.645 090	-1638.864 136	-1638.907 196	-1638.920 097
	$d^{11}$	-1638.566 483	-1638.624 108	-1638.440 407	-1638.694 281	-1638.753 923	-1638.763 533

<sup>a</sup> Hay (ref 5). <sup>b</sup> Wachters (ref 2). <sup>c</sup> This work.

TABLE VI: Total Energies (hartrees) and Errors (eV) for Various Contraction Schemes of Nickel

basis	contraction	$s^2d^8$		$s^1d^9$		$d^{10}$	
		TE	$\Delta$	TE	$\Delta$	TE	$\Delta$
current (4d)	(3,1) $s^2d^8$	-1506.616 160	0.0	-1506.559 708	0.002	-1506.359 439	0.000
	$s^1d^9$	-1506.616 083	0.002	-1506.559 786	0.0	-1506.359 375	0.002
	$d^{10}$	-1506.616 155	0.000	-1506.559 719	0.000	-1506.359 443	0.0
Hay (5d)	(4,1) $s^2d^8$	-1506.716 234	0.0	-1506.653 027	0.474	-1506.476 954	1.096
	$s^1d^9$	-1506.698 446	0.490	-1506.670 449	0.0	-1506.512 184	0.138
	$d^{10}$	-1506.673 713	1.157	-1506.665 198	0.143	-1506.517 245	0.0
current (5d)	(4,1) $s^2d^8$	-1506.784 930	0.0	-1506.734 236	0.064	-1506.566 259	0.108
	$s^1d^9$	-1506.782 602	0.063	-1506.736 591	0.0	-1506.570 002	0.006
	$d^{10}$	-1506.781 031	0.106	-1506.736 376	0.006	-1506.570 219	0.0
Hay (6d)	(5,1) $s^2d^8$	-1506.822 086	0.0	-1506.752 188	0.628	-1506.566 627	1.479
	$s^1d^9$	-1506.798 101	0.653	-1506.775 254	0.0	-1506.613 610	0.201
	$d^{10}$	-1506.762 230	1.629	-1506.767 389	0.214	-1506.620 980	0.0
current (6d)	(5,1) $s^2d^8$	-1506.832 221	0.0	-1506.774 662	0.277	-1506.606 164	0.588
	$s^1d^9$	-1506.821 850	0.282	-1506.784 842	0.0	-1506.625 536	0.061
	$d^{10}$	-1506.809 744	0.612	-1506.782 546	0.062	-1506.627 784	0.0
Hay (6d)	(4,1,1) $s^2d^8$	-1506.822 086	0.0	-1506.775 192	0.002	-1506.620 831	0.001
	$s^1d^9$	-1506.822 026	0.002	-1506.775 254	0.0	-1506.620 961	0.001
	$d^{10}$	-1506.821 940	0.004	-1506.775 235	0.001	-1506.620 980	0.0
current (6d)	(4,1,1) $s^2d^8$	-1506.832 221	0.0	-1506.784 837	0.000	-1506.627 781	0.000
	$s^1d^9$	-1506.832 216	0.000	-1506.784 842	0.0	-1506.627 777	0.000
	$d^{10}$	-1506.832 219	0.000	-1506.784 835	0.000	-1506.627 784	0.0

current (5d) basis is *easily* contractable to double zeta (vide infra), and the total energies (as shown in Table V) for *all* three states for each atom are as low (if not significantly lower) for the current basis as for the comparable augmented basis. The second point implies that the current basis sets are more "consistent" than those generated through augmentation. For example, for Ni the current (5d) basis has a total energy 1.87 eV lower than the (5d) augmented basis, and the current (6d) basis has a total energy 0.28 eV lower than the (6d) augmented basis. Another symptom of consistency is that in *all* cases our excitation energies are higher than numerical HF (the expected ordering for an incomplete basis) and the accuracy of the excitation energies increases as the size of the basis increases (as expected for an incomplete basis), whereas the augmented basis sets yield excitation energies

both low and high relative to numerical HF, indicating that in some cases the augmentation procedure leads to a differential bias against the  $s^2d^{n-2}$  state.

Because of the costs involved, nearly all molecular calculations with transition metals are carried out with contracted basis sets. We propose herein a (3,1) contraction of the reoptimized (4d) basis set, a (4,1) contraction of the reoptimized (5d) basis set, and a (4,1,1) contraction of the reoptimized (6d) basis. The contraction coefficients listed in Table II are based upon the  $3d^n$  states of the atoms. As shown in Table VI for Ni, various contraction schemes yield remarkably different results. As is apparent, the only double zeta contraction schemes that are truly acceptable are the (3,1) and (4,1) contractions of the reoptimized (4d) and (5d) basis sets. Both of the triple zeta contraction schemes are acceptable, though the cur-

rent (6d) basis yields the best total energy and hence is the basis of choice. A fundamental problem with double zeta contractions of the augmented basis sets is that they fix the ratio of coefficients between all original primitives and allow only the relative coefficients of the (slightly used) diffuse augmenting primitives to vary. While the contraction of this augmented basis by means of orbitals from the  $4s^1 3d^{n-1}$  state leads to perhaps acceptable atomic splittings [errors of 0.49 eV (5d) and 0.65 eV (6d)], it is not flexible enough to handle the general contraction or expansion of the 3d orbitals that result from a charge transfer to and from the ligands in molecules. For this reason we find the reoptimized (5d) basis contracted (4,1) to be the most suitable for routine molecular calculations. Further, we suggest that the (4d) basis for calculations on large transition metal complexes is a useful basis (errors

in excitation energies of less than 1.5 eV and no difficulty contracting to double zeta).

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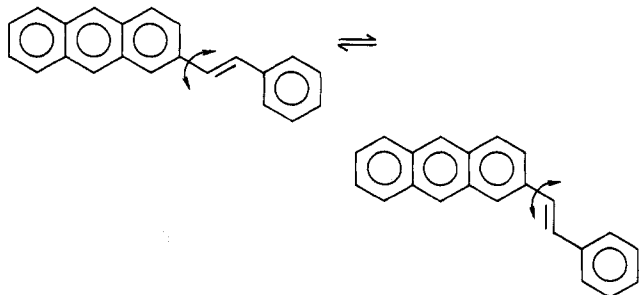
## Conformational Equilibria in *trans*-1,2-Diarylethylenes Manifested in Their Emission Spectra. 4.<sup>1</sup> 3-Anthryl and 3-Pyrenyl Derivatives

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The emission spectra of the title compounds vary with the wavelength of excitation. They can be described as superpositions of two spectra shifted 8–15 nm with respect to each other and contributing to the overall emission to an extent varying with the excitation wavelength. The phenomenon is ascribed to the existence, in solution, of an equilibrium mixture of two almost isoenergetic rotational conformers with slightly different absorption and emission spectra.

In earlier papers by us<sup>1</sup> and by Sheck et al.<sup>2</sup> emission-spectroscopic evidence was described for the existence of conformational equilibria in solutions of 2-naphthyl and 3-phenanthryl analogues of stilbene. In order to check



the generality of the underlying concepts, we have now investigated a number of 3-anthryl derivatives. As expected by analogy, we observed in all of them a variation of the emission spectra with the wavelength of the exciting light, which was most pronounced at long excitation wavelengths, in the tail of the absorption bands. In all

TABLE I: Emission Peaks (in nm) of the Two Modifications ↓ and ↑ of Various *trans*-(3-Anthryl)ethylenes under the Conditions Described in Figure 1<sup>a</sup>

compd				
1a	↓	413	436	462
	↑	426	452	482
1b	↓	407	(432)	(461)
	↑	416	444	474
1c	↓	414	438	(468)
	↑	424	451	482
1d	↓	423	448	(479)
	↑	430	458	(492)
2a	↓	422	450	480
	↑	431	460	490
2b	↓	415	442	470
	↑	423	457	488
2c	↓	426	450	(483)
	↑	433	459	(493)
2d	↓	423	450	479
	↑	433	462	497

<sup>a</sup> Values in parentheses are not well defined.

cases the emission spectra can be described by a superposition of two sets of peaks, shifted by 8–15 nm with respect to each other, and with the relative contributions of each set to the overall spectrum varying with the wavelength of excitation.

Figure 1 describes the results obtained at reduced temperatures, where the spectra are sharper, but qualitatively similar results were obtained also at room temperature.

(1) (a) Fischer, E. *J. Phys. Chem.* 1980, 84, 403–410. (b) *Bull. Soc. Chim. Belg.* 1979, 88, 889–895. (c) Haas, E.; Fischer, G.; Fischer, E. *J. Phys. Chem.* 1978, 82, 1638–43. (d) Fischer, G.; Fischer, E. Unpublished observations at 25 °C, not at reduced temperatures. (Improved experimental conditions have enabled us to make these observations recently.)

(2) Sheck, Yu. B.; Kovalenko, N. P.; Alfimov, M. V. *J. Lumin.* 1977, 15, 157.