PARAMETERS EMPLOYED IN ISM CALCULATIONS

Bond lengths, bond dissociation energies, stretching frequencies, ionization potentials and electron affinities employed in the calculation of atom and proton transfer rates. [a) b)]

	l_{eq} [a)] (Å)	D^0_{298} (kJ mol^{-1})	ω_e (cm^{-1})	I_P (eV)	E_A (eV)
H_2	0.74144	104.2	4161	13.598	0.75419
CH_4	1.0870	104.9	2917	9.843	0.08
CH_3CH_3	1.0940	101.1	2954	8.117	-0.26
$CH_3\mathbf{C}H_2CH_3$	1.107	97. 8	2887	7.37	-0.321
$(CH_3)_3\mathbf{C}H$	1.122	96.6	2890	6.70	-0.156
CH_3COCH_3	1.103	98.3	2939	9.703 [c)]	1.76
CH_3OCH_3	1.121	96.1	2817	6.90	-0.017
$\mathbf{C}H_3OH$	1.0936	96.0	2844	7.562	
$CH_3\mathbf{C}HO$	1.128	89.3	2822	7.00	0.423
$\mathbf{C}H_2O$	1.116	88.1	2783	8.14	0.313
$\mathbf{C}H_3C_6H_5$	1.111	89.8	2934	7.2488	0.912
$CH_2{=}CH_2$	1.087	111.2	3026	8.25	0.667
C_6H_6	1.101	113.1	3062	8.32	1.096
H**C**N	1.0655	126.1	3311	14.170	3.862
CH≡CH	1.060	132.9	3374	11.610	2.969
$\mathbf{C}H_3NO_2$	1.088	60.8	3048	11.08 [c)]	0.50 [c)]
$\mathbf{C}H_3NH_2$	1.099	93.3	2820	6.29	
$CH_3\mathbf{N}H_2$	1.010	100.0	3361		
$C_4H_4\mathbf{N}H$	0.996	93.9	3500	8.207 [c)]	2.145
$C_6H_5\mathbf{N}H_2$	0.998	88.0	3400	7.720 [c)]	
NH_3	1.012	108.2	3337	10.780	0.771
$(CH_3)_3\mathbf{Si}H$	1.485	90.3	2107	7.03	0.971
SiH_4	1.4798	91.8	2187	8.135	1.405
$(CH3)_3\mathbf{Sn}H$	1.700	77.0	1815	7.10	1.70

GeH_4	1.5251	83.4	2106	7.948	1.61
PH_3	1.4200	83.9	2323	9.824	1.25
AsH_3	1.511	76.3	2116	9.85	1.27
H_2O	0.9575	119.0	3657	13.017	1.8277
OH	0.96966	102.2	3737.76	13.618	1.4611
CH_3**O**H	0.9451	104.2	3681	10.720	1.57
CH_3CO**O**H	0.97	105.8	3583	10.65 [c)]	3.29
C_6H_5**O**H	0.956	86.5	3650	8.56	2.253
H_2S	1.3356	91.2	2615	10.422	2.317
H_2Se	1.47	80.0	2345	9.845	2.2125
CH_3**S**H	1.340	87.3	2610	9.262	1.867
C_6H_5**S**H	1.36	83.3	2597	8.6	2.26
HF	0.9169	136.2	3962	17.423	3.448
HCl	1.27455	103.2	2886	12.968	3.6144
HBr	1.41444	87.6	2559	11.814	3.3636
HI	1.60916	71.3	2230	10.451	3.059
CF_3H	1.098	107.4	3036	8.76	1.869
F_2	1.41193	38.0	892	17.423	3.448
Cl_2	1.988	58.0	557	12.968	3.6144
Br_2	2.281	46.1	317	11.814	3.3636
I_2	2.666	36.1	213	10.451	3.0590

[a)] The equilibrium stretching frequency (ω_e) has a small correction from the observed infrared stretching frequency ($\overline{\nu}_{BC}$) in the case of diatomic molecules. The ionization potentials and electron affinities are those of the radicals formed after the cleavage of the reactive bond, boldface letters indicate where the radical center is located in the cases where this could be ambiguous.

[b)] Data from L. G. Arnaut, A. A. C. C. Pais, S. J. Formosinho, M. Barroso, J. Am. Chem. Soc., 125 (2003) 5236, L. G. Arnaut, S. J. Formosinho, M. Barroso, *J. Mol. Struct.* **786** (2006) 207, and M. Barroso, L. G. Arnaut, S. J. Formosinho, submitted.

[c)] These data refer to the molecule and not to the radical, because the corresponding data is not available.