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The stable free radical HO$_2$ has been the subject of numerous experimental[1,2] and theoretical[3-7] studies over the past ten years. The interest in HO$_2$ is due to its importance as an intermediate in combustion,[8] atmospheric,[9] and astrophysical[10] reactions. The purpose of this note is to calculate vibrational spacings for HO$_2$ and vibrational splittings for hydrogen atom exchange. In a previous study, Bunker and Howe[11] used a model HO$_2$ surface that was not intended to be quantitative. In this study we use an accurate HO$_2$ surface which is realistic for large amplitude hydrogen motion.

A summary of *ab initio* electronic structure calculations for the ground state of HO$_2$ has been given by Varandas, Brandao, and Quintales.[4] Melius and Blint[5] used a MCSCF CI calculation and defined a global HO$_2$ surface by fitting the calculated points to a generalized Morse functional form, which gave a barrier of about 800 cm^{-1} for the H + O$_2$ addition reaction. However, Langhoff and Jaffe[6] used a more extensive CI calculation and found no barrier for this reaction. Recently, Varandas and Brandao[3] reported a global HO$_2$ surface, henceforth called DMBE I, using the double many-body expansion method. The DMBE I surface conforms with the calculated points of Melius and Blint,[5] but shows no barrier for the H + O$_2$ addition reaction, and is therefore an improvement over previous global HO$_2$ surfaces. However, there are some unsatisfactory aspects of the DMBE I surface and, more recently, Varandas, Brandao, and Quintales[4] reported several other global HO$_2$ surfaces. Of these, the DMBE III surface considers the calculated points of Melius and Blint[5] and the available experimental force field data on an equal footing. These authors believe that the DMBE III surface may be the most realistic global HO$_2$ surface currently available (although we note that it may be possible to further improve this global HO$_2$ surface by incorporating the recently calculated points of Walch and Rohlfing[7]). As expected, there are two equivalent primary minima connected by a T-shaped saddle point. However, there is also a secondary potential minimum, corresponding to a weakly bound T-shaped HO$_2$ complex, which might provide an alternate pathway for hydrogen atom exchange.

In this note we calculate vibrational spacings for HO$_2$ and the vibrational splittings for hydrogen atom exchange, using the DMBE III surface of Varandas, Brandao, and Quintales.[4] For the O–O distance fixed at its equilibrium value, we calculate all vibrational spacings corresponding to bound vibrational levels; these would all be of potential interest in a study of the H + O$_2$ addition reaction. We use a combination of the discrete variable representation[12] (DVR) and distributed Gaussian basis[13] (DGB) methods. This DVR-DGB method, developed by Bacic and Light,[14] has been shown to be very efficient and accurate for variational calculations on triatomics such as LiCN and HCN. Our calculations are done at $r = 2.512\ a_0$, corresponding to

the primary potential minima. The primary potential minima are at $R = 2.469a_0$ and $\theta = 46.405°$ and $133.595°$ with energy 2332.4 cm^{-1} (since we report vibrational spacings only, we have not adjusted this energy to zero). The saddle point is at $R = 1.79a_0$ and $\theta = 90°$, with energy 8030 cm^{-1}. The secondary potential minimum is at $R = 4.74a_0$ and $\theta = 90°$, with energy 19 557 cm^{-1}. For $\theta = 90°$, the saddle point and the secondary potential minimum are separated by a 35 314 cm^{-1} potential barrier. The asymptotic H + O$_2$ energy is 22 095 cm^{-1}. The region of the potential surface on which basis functions were placed corresponds to energies below a total energy cutoff, E_{tot}. In addition, minimum and maximum values of R (dependent on θ) were specified to delineate the physical region of the potential surface. These range from $R = 2.48$–$4.4a_0$ for $\theta = 0°$ and $180°$ to $R = 1.33$–$9.0a_0$ for $\theta = 90°$.

We specified 35 Gauss–Legendre points with energy cutoffs of 0.161 a.u. for E_{tot} and 0.18 a.u. for E_{ray}, which give rise to 895 compact ray basis functions. The value of E_{tot} was chosen to be slightly larger than the potential barrier between the saddle point and the secondary potential minimum, which ensured that Gaussian basis functions were placed in the region of the potential surface corresponding to the weakly bound T-shaped HO$_2$ complex. The first vibrational level has energy 4638.8 cm^{-1}, so the zero point energy is 2306.4 cm^{-1}. All vibrational spacings below the asymptotic H + O$_2$ energy are included in Table I, and most of these are converged to within 10 cm^{-1}. The convergence of the higher vibrational spacings is briefly considered later below. In Table I, columns 1, 4, 6, 8, and 10 give the number of the vibrational spacing, and columns 3, 5, 7, 9, and 11 give the calculated vibrational spacings. Given in column 2 are zeroth-order assignments for some of the lower vibrational spacings. Note that because the O–O distance is fixed, only two vibrations are possible: the O–H stretch (first label) and the O–H bend (second label). It may be seen from Table I that the calculated stretch and bend fundamentals are 3211 and 1309 cm^{-1}, respectively, in reasonable agreement with the experimental values[1] of 3410 and 1389 cm^{-1}, respectively. It may also be seen from Table I that, as expected, the stretch and bend vibrations are highly anharmonic—for example, for the $(0,n)$ progressive, the first three successive spacings are 1309, 1214, and 1130 cm^{-1}, respectively.

The smallest meaningful calculated vibrational splitting is 0.6 cm^{-1}, for the $(0,3)$ levels, and this increases to 14 cm^{-1} for the $(0,4)$ levels. Note that, although it is higher in energy, the vibrational splitting for the $(2,0)$ levels is 0.9 cm^{-1}. This is expected, since motion for the stretching vibration has only a small component in the direction of hydrogen atom exchange. However, energy in the stretching vibration is important in promoting hydrogen atom exchange. For example, whereas the vibrational splitting is less

TABLE I. The number of the vibrational spacing (columns 1, 4, 6, 8, 10), the calculated vibrational spacings (columns 3, 5, 7, 9, 11) and the zeroth-order assignments for some of the lower vibrational spacings (column 2).

1	(0,0) −	0.0	31	8400	61	12 283	91	15 291	121	16 924
2	(0,1) +	1309.4	32	8646	62	12 489	92	15 439	122	16 934
3	(0,1) −	1309.4	33	8729	63	12 593	93	15 448	123	16 958
4	(0,2) +	2523.1	34	8872	64	12 700	94	15 482	124	17 003
5	(0,2) −	2523.1	35	9098	65	12 861	95	15 486	125	17 042
6	(1,0) +	3210.8	36	9 131	66	12 889	96	15 611	126	17 067
7	(1,0) −	3210.8	37	9 257	67	13 101	97	15 732	127	17 116
8	(0,3) +	3653.3	38	9 297	68	13 135	98	15 757	128	17 129
9	(0,3) −	3653.9	39	9 425	69	13 238	99	15 762	129	17 131
10	(1,1) +	4485.6	40	9 630	70	13 241	100	15 816	130	17 212
11	(1,1) −	4489.1	41	9 939	71	13 403	101	15 841	131	17 230
12	(0,4) +	4724.4	42	10 002	72	13 431	102	15 863	132	17 250
13	(0,4) −	4738.7	43	10 210	73	13 517	103	15 923	133	17 286
14		5371.7	44	10 282	74	13 679	104	15 982	134	17 319
15	(1,2) +	5498.1	45	10 512	75	13 758	105	16 128	135	17 324
16		5770.6	46	10 538	76	13 770	106	16 188	136	17 359
17	(1,2) −	5852.3	47	10 565	77	13 888	107	16 233	137	17 366
18		6091.8	48	10 568	78	13 967	108	16 272	138	17 400
19	(2,0) +	6273.6	49	10 763	79	14 111	109	16 320	139	17 410
20	(2,0) −	6274.5	50	10 926	80	14 212	110	16 469	140	17 438
21		6423	51	11 106	81	14 425	111	16 481		
22		6769	52	11 264	82	14 482	112	16 485		
23		6977	53	11 436	83	14 509	113	16 595		
24		7179	54	11 526	84	14 620	114	16 615		
25		7495	55	11 587	85	14 745	115	16 671		
26		7589	56	11 766	86	14 904	116	16 693		
27		7610	57	11 853	87	14 913	117	16 718		
28		7861	58	11 858	88	15 110	118	16 861		
29		8093	59	11 927	89	15 135	119	16 897		
30		8215	60	12 247	90	15 267	120	16 906		

than 0.1 cm^{-1} for the bend fundamentals, it is 3.5 cm^{-1} for the (1,1) levels. Although the 14th vibrational spacing could be assigned to the (0,5) + level, this does not correspond to a zeroth order eigenvalue, since its eigenvector has large components from DVR angles in the region of 90°. Neither, however, does this correspond to an eigenvalue of the weakly bound T-shaped HO$_2$ complex—the energy is much too small. Apparently then, this complex does not provide a significant pathway for hydrogen atom exchange at low energies, although it might, of course, be important close to the H–O$_2$ dissociation energy. We now briefly consider the convergence of the higher vibrational spacings, which was checked by changing E_{ray}. For the 100th vibrational spacing, with $E_{ray} = 0.12$, 0.14, and 0.16 a.u. this vibrational spacing is 15 982, 15 843, and 15 821 cm^{-1}, respectively. This is typical, but the convergence rate of vibrational spacings is nonuniform for higher vibrational levels—for example, the 129th is more slowly convergent while the 140th is more rapidly convergent. The 140th vibrational spacing corresponds to the highest bound vibrational level. Finally, we note that the vibrational spacings in Table I are for the ^{16}O isotope, which has a nuclear spin of zero. Consequently, due to nuclear spin statistics, the eigenvalues corresponding to eigenvectors that are antisymmetric with respect to oxygen atom exchange are missing for $J = 0$. Of course, in any experiment, $J > 0$ levels are populated, but nuclear spin statistics would influence the vibrational intensities.

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