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## Potential Energy Curves for OH\*

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Potential energy curves for four of the bound states of OH have been calculated by the Rydberg-Klein-Rees method. Various mechanisms to explain the anomalously high population of the  $v'=2$  and 3 levels of the  $A\ ^2\Sigma^+$  state are discussed.

## INTRODUCTION

THIS is one of a series of papers dealing with the potential energies of interaction of diatomic species existing in flames. A knowledge of the reliable potential energy curves for these species can sometimes lead to the elucidation of the possible kinetics of the reactions that occur.<sup>1-3</sup>

Four of the bound states of OH have been calculated by the Rydberg-Klein-Rees (RKR) method<sup>4-8</sup>:  $X\ ^2\Pi$ ,  $A\ ^2\Sigma^+$ ,  $B\ ^2\Sigma^+$ , and  $C\ ^2\Sigma^+$ . Of these, only the  $X\ ^2\Pi$  dissociates to ground-state atoms. According to the Wigner-Witmer rules the interaction of an oxygen atom and a hydrogen atom, both in their ground states, gives rise, in addition to a  $^2\Pi$ , to three other electronic states:  $^4\Pi$ ,  $^4\Sigma^-$ , and  $^2\Sigma^-$ . Mulliken<sup>9</sup> has predicted that these three are all repulsive and for a given internuclear distance the order written above is also the order of increasing energy.

TABLE I. Potential energy of the  $X\ ^2\Pi_i$  state of OH.<sup>a</sup>

$v$	$V(\text{cm}^{-1})$	$V(\text{ev})$	$r_{\text{max}}(\text{\AA})$	$r_{\text{min}}(\text{\AA})$
0	1848	0.2291	1.081	0.884
1	5418	0.6717	1.179	0.831
2	8822	1.0937	1.257	0.800
3	12062	1.4954	1.329	0.777
4	15139	1.8769	1.399	0.758
5	18055	2.2384	1.468	0.743
6	20806	2.5795	1.538	0.731
7	23392	2.9000	1.610	0.720
8	25808	3.1996	1.683	0.710
9	28051	3.4777	1.760	0.702

<sup>a</sup> Data from footnotes 14, 15, and 16.

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<sup>1</sup> R. J. Fallon, J. T. Vanderslice, and E. A. Mason, *J. Phys. Chem.* **63**, 2082 (1959).

<sup>2</sup> R. J. Fallon, J. T. Vanderslice, and E. A. Mason, *J. Phys. Chem.* **64**, 505 (1960).

<sup>3</sup> R. J. Fallon, I. Tobias, J. T. Vanderslice, and W. G. Maisch, *Can. J. Chem.* **38**, 743 (1960).

<sup>4</sup> R. Rydberg, *Z. Physik* **73**, 376 (1931); **80**, 514 (1933).

<sup>5</sup> O. Klein, *Z. Physik* **76**, 226 (1932).

<sup>6</sup> A. L. G. Rees, *Proc. Phys. Soc. (London)* **59**, 998 (1947).

<sup>7</sup> J. T. Vanderslice, E. A. Mason, W. G. Maisch, and E. R. Lippincott, *J. Mol. Spectroscopy* **3**, 17 (1959).

<sup>8</sup> F. Gilmore (Rand Corporation, Santa Monica, California) has corrected the formulas of reference 7. The corrections have appeared as errata [*J. Mol. Spectroscopy* **5**, 83 (1960) and *J. Chem. Phys.* **33**, 614 (1960)].

<sup>9</sup> R. S. Mulliken, *Revs. Modern Phys.* **4**, 1 (1932).

## CALCULATION OF CURVES

The results of the RKR procedure for the different bound states of OH are listed in Tables I to IV and are shown as solid lines in Fig. 1. Mulliken's prediction for the three other states dissociating to ground state atoms are indicated by the dotted lines.

The RKR method, a semiclassical procedure for determining potential energy curves from the measured vibrational and rotational energy levels, is both rapid and accurate. It has been sufficiently described in recent articles<sup>4-8,10-12</sup> so that no further details will be given here. In our calculations we have used the spectroscopic data of Barrow,<sup>13</sup> Michel,<sup>14</sup> Herman and Hornbeck,<sup>15</sup> and Dieke and Crosswhite.<sup>16</sup> From the data of Chamberlain and Roesler,<sup>17</sup> which is practically identical to that we used, Jarmain<sup>18</sup> has obtained a potential curve for the  $X\ ^2\Pi$  ground state of OH up to  $v=6$ . His results up to that point agree with ours to  $\pm 0.001$  Å.

Jarmain<sup>18</sup> has used his own modification of the RKR

TABLE II. Potential energy of the  $A\ ^2\Sigma^+$  state of OH.<sup>a</sup>

$v$	$V(\text{cm}^{-1})$	$V(\text{ev})$	$T_e + V(\text{ev})^b$	$r_{\text{max}}(\text{\AA})$	$r_{\text{min}}(\text{\AA})$
0	1566	0.1941	4.2462	1.131	0.917
1	4555	0.5647	4.6168	1.244	0.863
2	7348	0.9110	4.9631	1.338	0.832
3	9941	1.2325	5.2846	1.428	0.809
4	12327	1.5283	5.5804	1.518	0.792
5	14491	1.7966	5.8487	1.614	0.777
6	16407	2.0341	6.0862	1.722	0.766
7	18032	2.2356	6.2877	1.856	0.758
8	19306	2.3935	6.4456	2.038	0.752

<sup>a</sup> Data from footnotes 13, and 14.

<sup>b</sup>  $T_e$  is the energy difference between the bottom of the potential curve in question and the bottom of the  $X\ ^2\Pi_i$  state.

<sup>10</sup> J. T. Vanderslice, E. A. Mason, and E. R. Lippincott, *J. Chem. Phys.* **30**, 129 (1959).

<sup>11</sup> J. T. Vanderslice, E. A. Mason, and W. G. Maisch, *J. Chem. Phys.* **31**, 738 (1959).

<sup>12</sup> J. T. Vanderslice, E. A. Mason, and W. G. Maisch, *J. Chem. Phys.* **32**, 515 (1960).

<sup>13</sup> R. F. Barrow, *Arkiv Fysik* **11**, 281 (1956).

<sup>14</sup> A. Michel, *Z. Naturforsch.* **12a**, 887 (1957).

<sup>15</sup> R. C. Herman and G. A. Hornbeck, *Astrophys. J.* **118**, 214 (1953).

<sup>16</sup> S. H. Dieke and H. M. Crosswhite, "The Ultraviolet Bands of OH Fundamental Data," Bumblebee Report No. 86, The Johns Hopkins University (1948).

<sup>17</sup> J. W. Chamberlain and F. L. Roesler, *Astrophys. J.* **121**, 541 (1955).

<sup>18</sup> W. R. Jarmain, *Can. J. Phys.* **38**, 217 (1960).

procedure which involves expressing the classical turning points in a power series in  $v + \frac{1}{2}$ , where  $v$  is the vibrational quantum number. Since the series starts to diverge for large  $v$ , Jarman has arbitrarily limited himself to the calculation of potential curves up to one half of the dissociation limit. In some cases, he finds that the series diverges even at small values of  $v$ .<sup>18</sup> Therefore, we have continued to use the original formulation of the RKR procedure<sup>6-8</sup> which does not appear to suffer from this disadvantage except very close to the dissociation limit.<sup>12</sup>

### DISCUSSION

The hydroxyl radical is present in a number of flames and there has been much discussion concerning the kinetics of its formation in the  $A^2\Sigma^+$  state.<sup>19-21</sup> The intensity measurements first made by Kondratiev and Ziskin<sup>22</sup> and later confirmed by other workers<sup>23,24</sup> suggest that the  $v'=2$  and 3 levels of the OH  $A^2\Sigma^+$  state have a greater relative population than that expected under conditions of thermal equilibrium. This has led Gaydon and Wolfhard<sup>23</sup> to propose an inverse predissociation of the  $A^2\Sigma^+$  state by the  $2\Sigma^-$

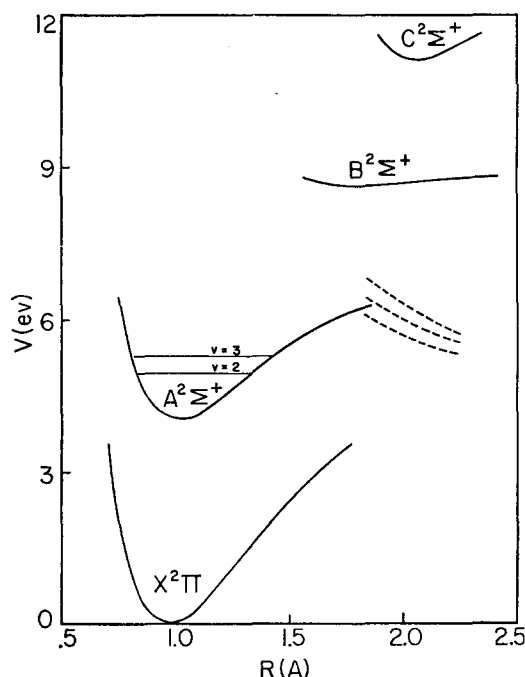


FIG. 1. Potential energy curves for OH. The solid curves were calculated by the RKR method. The dashed curves are those predicted by Mulliken. In order of increasing energy, these are  $^4\Pi < ^4\Sigma^- < ^2\Sigma^-$ .

<sup>19</sup> M. Charton and A. G. Gaydon, Proc. Roy. Soc. (London) **A245**, 84 (1958).

<sup>20</sup> K. J. Laidler, *The Chemical Kinetics of Excited States* (Oxford University Press, London, 1955).

<sup>21</sup> K. E. Shuler, J. Chem. Phys. **21**, 624 (1953).

<sup>22</sup> V. Kondratiev and M. Ziskin, Acta. Physiochim. U.S.S.R. **7**, 65 (1937).

<sup>23</sup> A. G. Gaydon and H. G. Wolfhard, Proc. Roy. Soc. (London) **A208**, 63 (1951).

<sup>24</sup> H. P. Broida and K. E. Shuler, J. Chem. Phys. **20**, 168 (1952).

TABLE III. Potential energy of the  $B^2\Sigma^+$  state of OH.<sup>a</sup>

$v$	$V(\text{cm}^{-1})$	$V(\text{ev})$	$T_e + V(\text{ev})$	$r_{\text{max}}(\text{\AA})$	$r_{\text{min}}(\text{\AA})$
0	441	0.0547	8.7053	2.041	1.627
1	1101	0.1365	8.7871	2.426	1.569

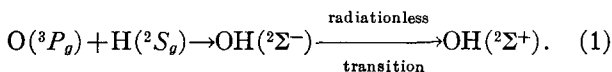
<sup>a</sup> Data from footnote 13.

TABLE IV. Potential energy of the  $C^2\Sigma^+$  state of OH.<sup>a</sup>

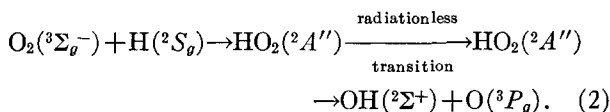
$v$	$V(\text{cm}^{-1})$	$V(\text{ev})$	$T_e + V(\text{ev})$	$r_{\text{max}}(\text{\AA})$	$r_{\text{min}}(\text{\AA})$
0	1090	0.1351	11.3151	2.193	1.953
1	3364	0.4171	11.5971	2.328	1.893

<sup>a</sup> Data from footnote 14.

state,



Shuler<sup>21</sup> mentioned that this inverse predissociation reaction should be very weak since it violates selection rules<sup>25</sup> and instead proposes a reaction involving a triatomic complex which should be more efficient than (1),



This reaction, however, is not consistent with the more recent finding that the intensity of emission is approximately proportional to the square of the free-atom concentration, which indicates that an inverse predissociation reaction mechanism contributes a substantial part to the formation of  $\text{OH}(^2\Sigma^+)$  in the  $v'=2$  level.<sup>19,26,27</sup> Also, the anomalously strong excitation of OH bands with  $v'=2$  and 3 is accompanied by selective excitation of the  $f_1$  spin levels of the  $2\Sigma^+$  state which again suggests an inverse predissociation.<sup>4</sup>

On the basis of this new information, Charton and Gaydon<sup>19</sup> have again proposed that the  $2\Sigma^-$  state is responsible for this predissociation. Predissociation by the  $2\Sigma^-$  state as well as by either the  $4\Sigma^-$  or the  $4\Pi$  state violates Kronig's selection rules. Therefore, it does not seem possible, on the basis of existing information, to rule out the other two excited states, the  $4\Sigma^-$  and the  $4\Pi$ . Indeed, as Fig. 1 shows, Mulliken's predictions of the relative positions of the excited states would favor the  $4\Pi$  state as causing the predissociation. Further investigation of the exact position of these excited states and the details of their interaction with the  $2\Sigma^+$  state is necessary before anything more definite can be said.

<sup>25</sup> G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), pp. 416 ff.

<sup>26</sup> E. M. Balewicz, C. G. James, and T. M. Sugden, Proc. Roy. Soc. (London) **A235**, 89 (1956).

<sup>27</sup> W. E. Kaskan, J. Chem. Phys. **31**, 944 (1959).