

A Method for Testing and Improving Molecular Constants of Diatomic Molecules with Special Reference to $\text{Br}_2 \ ^1(\Sigma_g^+)$ *

ROBERT J. LEROY[†] AND GEORGE BURNS

Lash Miller Chemical Laboratory, University of Toronto, Toronto, Ontario, Canada

The common procedure of constructing RKR potentials from known spectroscopic data has been reversed in the present work. Instead, spectroscopic constants, which had often been obtained by approximate methods, were tested to determine whether they agree with the expected shape of the RKR potential. For a special case, the $^{79,81}\text{Br}_2 \ (^1\Sigma_g^+)$ molecule, it was found that no spectroscopic constants available in the literature could generate a RKR potential which is reasonable at all energies, and that some reported constants yield a highly erroneous potential. A new set of spectroscopic constants has been calculated. These constants agree with the experimental results and, at the same time, yield a reasonable RKR potential. They are (in cm^{-1}): $\omega_e = 324.24$, $\omega_e x_e = 1.172$, $\omega_e y_e = 0.342 \times 10^{-2}$, $\omega_e z_e = -0.101 \times 10^{-3}$, $B_e = 0.081079$, $\alpha_e = 0.30405 \times 10^{-3}$, and $\gamma_e = -0.40 \times 10^{-5}$. The term values generated from these constants predict that there are eighty vibrational levels in $\text{Br}_2 \ (^1\Sigma_g^+)$. The RKR turning points for the lowest thirty-seven vibrational levels of $\text{Br}_2 \ (^1\Sigma_g^+)$ are given.

I. INTRODUCTION

Although it is possible to approximate the internuclear potential of a diatomic molecule by analytic functions, such functions have limited use, because they only reproduce the experimental data over a narrow energy range. Rees (1), Klein (2), and Rydberg (3, 4) developed a method of constructing a numerical, rather than an analytic, potential which is free from this disadvantage. Their potential, usually referred to as the RKR potential, is obtained directly from the experimental vibrational and rotational spectroscopic term values, and its accuracy depends mainly on the accuracy of experimental results. The RKR potential consists of a finite number of pairs of internuclear distances, the "turning points," at which the total energy of the diatomic molecule is equal to its classical potential energy. An interpolation between turning points is necessary to

* This work was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, grant No. AF AFOSR 506-66.

[†] Present address: Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin 53706.

generate the continuous potential. Using the RKR potential, the eigenfunctions and eigenvalues of the radial Schrödinger equation can be obtained numerically with a high degree of accuracy. On the other hand, the eigenvalues obtained by solution of the radial Schrödinger equation using analytic potential functions, agree with the experimental eigenvalues only in the case of the lower vibrational levels. For these reasons, Steele, Lippincott, and Vanderslice (5) pointed out that agreement with the RKR potential is a good quantitative test of any analytic potential.

The main limitation in the calculation of RKR potentials is the lack of sufficient spectroscopic data to define the whole potential. These data are usually expressed in terms of a set of vibrational and rotational constants ω_e , B_e , $\omega_e x_e$, α_e , \dots , etc. Their values are chosen in such a way as to generate energies from the polynomial

$$T(v, J) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \dots \\ + J(J + 1)(B_e - \alpha_e(v + \frac{1}{2}) + \dots) \quad (1)$$

which best approximate the observed rotational and vibrational levels. The vibrational and rotational terms are often separated, using formulas defined elsewhere (6).

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \dots, \quad (2)$$

$$\Delta G_{v+1/2} = G(v + 1) - G(v), \quad (3)$$

and

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2 \dots \quad (4)$$

The calculation of the RKR turning points is involved, and hence these potentials have not been extensively used in the past. However, with the advent of large digital computers, this problem has become relatively simple. There are now programs available both for calculating the RKR turning points of diatomic molecules, and for solving the radial Schrödinger equations for these systems (7).

The relative ease with which RKR potentials can be generated now allows us to turn the problem around. We are now able to test whether spectroscopic constants are compatible with the expected shape of an RKR potential. This approach tests the approximations which sometimes are used to obtain spectroscopic constants in the absence of sufficient experimental data. Moreover, it may yield approximate values of new higher order spectroscopic constants.

It is the purpose of the present paper to demonstrate the usefulness of such an approach.

II. METHOD

In the calculation of an RKR potential, the vibrational constants determine the distance between the two turning points for a given vibrational level. On the

other hand, the rotational constants determine the internuclear distance corresponding to the average of the turning points for a given vibrational level. Therefore, an error in the vibrational constants affects the shape of the calculated RKR potential in a different way than does an error in the rotational constants. More specifically, if the $\Delta G_{v+1/2}$ value for a given energy is too small, the two turning points will be too far apart. Analogously, if the rotational constants yield too large a B_v for a given vibrational level, the values of both turning points will be too large, although their difference may be correct.

The method described here tests whether the spectroscopic constants yield an RKR potential which satisfies the following requirements:

(1) The outer turning points should asymptotically approach the known dissociation limit of the given electronic state. This is equivalent to the requirement that in equations (2) and (3) $\Delta G_{v+1/2} = 0$ and $G(v) = D$, for the same value of v , where D is the known dissociation energy.

(2) The slope of the inner portion of the RKR potential must be negative.

(3) Over the range of the inner turning points, the RKR potential must become steeper with decreasing internuclear distance. In other words, the second derivative of the potential with respect to internuclear distance, $d^2U(r)/dr^2$, must be positive in this region.

In order to satisfy these requirements, the values of the vibrational and rotational constants reported in literature may need to be changed. However, the adjusted constants must also be consistent with the existing spectroscopic data. The lower order rotational and vibrational constants are usually fairly accurately determined by the readily available vibrational energies and B_v 's for the lowest few vibrational levels. On the other hand, accurate values of the higher order constants can only be experimentally determined if the energies and B_v values are known for a large number of vibrational levels. In the absence of this data, the present method may not only improve the existing values of the constants, but may also yield values of new higher order constants.

The methods of deriving these constants are similar for both rotational and vibrational cases. First, a trial value of the highest order constant is selected. The term value equation [(2) or (4)] which includes the new constant must yield the best possible least squares fit to the experimental data. This requirement defines new values of all lower order constants. The new set of constants is tested to determine whether it abides by the requirements (1)–(3). If a number of such trial values are used, the best combination of constants can be found. It should be emphasized that for an arbitrary choice of the new higher order constant, all the others are uniquely determined by the experimental data.

When testing the existing constants, the vibrational constants should be considered first. This is because their compliance with requirement (1) is relatively independent of the choice of rotational constants, while the latter's fulfillment of requirements (2) and (3) depends on the values of the vibrational constants.

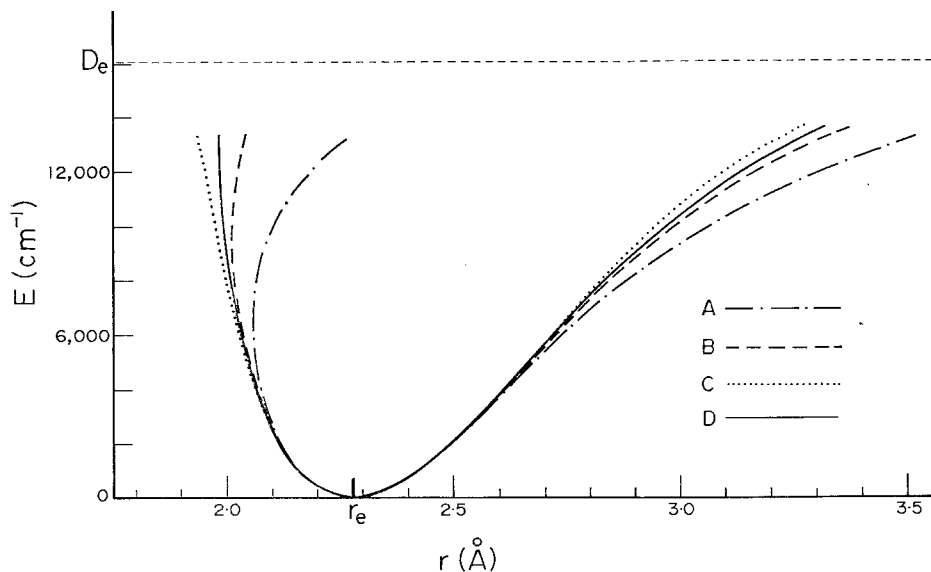


Fig. 1. RKR potentials calculated for ground-state $^{79,81}\text{Br}_2$ using different sets of spectroscopic constants. The curves were generated from the constants in Table I. Curve A was obtained from the R&V constants and Curve D from our derived best constants. Curves B and C illustrate the effect of variation in the rotational constants on the potential.

Any given set of vibrational constants is tested by calculating $\Delta G_{v+1/2}$ for increasing v , until it becomes zero or negative. If this occurs when $G(v)$ is less than 2 cm^{-1} smaller than the dissociation energy, we consider the constants to be satisfactory. In most cases it is necessary to change the existing constants before this requirement can be satisfied. In general, this requires the introduction of an additional higher order vibrational constant. For each trial value of the highest order constant, the corresponding lower order constants were defined by a fit to the experimental data, as described above. A judicious choice of trial values will make this iteration converge very quickly.

The first step in the testing of any given set of rotational constants is the construction of an RKR potential by combining the rotational constants with the best set of vibrational constants. If the first and second derivatives of the inner portion of this potential satisfy requirements (2) and (3) at all energies up to the dissociation limit, the original constants are satisfactory. If the existing rotational constants are found to be inadequate, a new higher order constant usually needs to be introduced. RKR potentials are constructed and tested for several trial values of the highest order constant until its best value is found. At low energies, there will be a relatively wide range of acceptable values of the highest order rotational constant, but this range becomes progressively more restricted at higher energies.

TABLE I
 VIBRATIONAL AND ROTATIONAL CONSTANTS USED TO GENERATE RKR POTENTIALS IN
 FIG. 1. ALL CONSTANTS ARE EXPRESSED IN WAVE NUMBERS. COLUMN A ARE THE
 R&V CONSTANTS AND COLUMN D ARE OUR DERIVED CONSTANTS

Constant	Curve			
	A	B	C	D
ω_e	323.21	324.24	324.24	324.24
$\omega_e x_e$	1.0282	1.172	1.172	1.172
$\omega_e y_e$	-0.97×10^{-3}	0.342×10^{-3}	0.342×10^{-2}	0.342×10^{-2}
$\omega_e z_e$	-0.417×10^{-4}	-0.101×10^{-3}	-0.101×10^{-3}	-0.101×10^{-3}
B_e	0.08106	0.081074	0.081085	0.081079
α_e	0.265×10^{-3}	0.29605×10^{-3}	0.31205×10^{-3}	0.30405×10^{-3}
γ_e	-1.394×10^{-5}	-0.60×10^{-5}	-0.20×10^{-5}	-0.40×10^{-5}

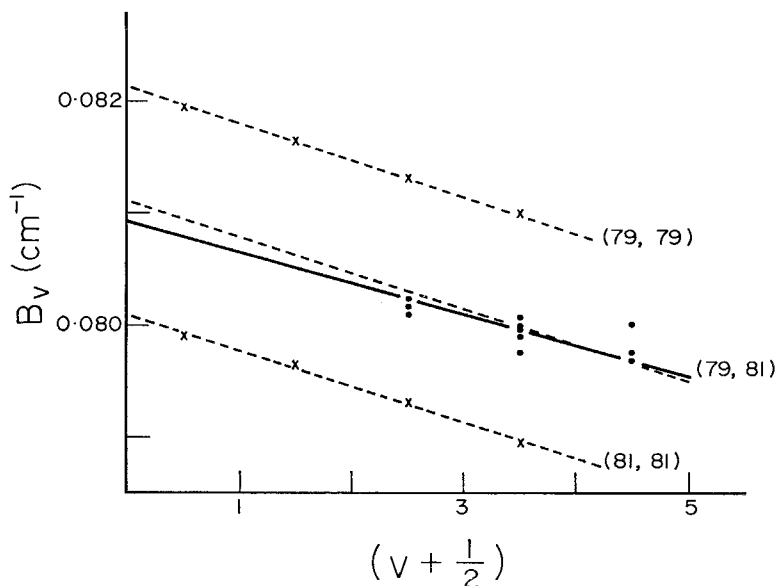


FIG. 2. B_v values for the three isotopic forms of ground-state Br_2 ($^1\Sigma_g^+$). ● Results of Brown (10). × Results of Horsley and Barrow (11).

III. SPECTROSCOPIC CONSTANTS FOR GROUND STATE OF $^{79,81}\text{Br}_2$ ($^1\Sigma_g^+$)

In our work, all RKR turning points were calculated using the computer program recently developed by Zare (7, 8). The Fortran IV version of his program was modified slightly for use in the present calculations. This program can yield turning points for all values of the vibrational quantum number v . The calculation of the turning points for one hundred levels required less than 0.3 minute execution of an IBM 7094 II. The first and second derivatives of the inner portion of the potential at the energy of a given vibrational level v were obtained

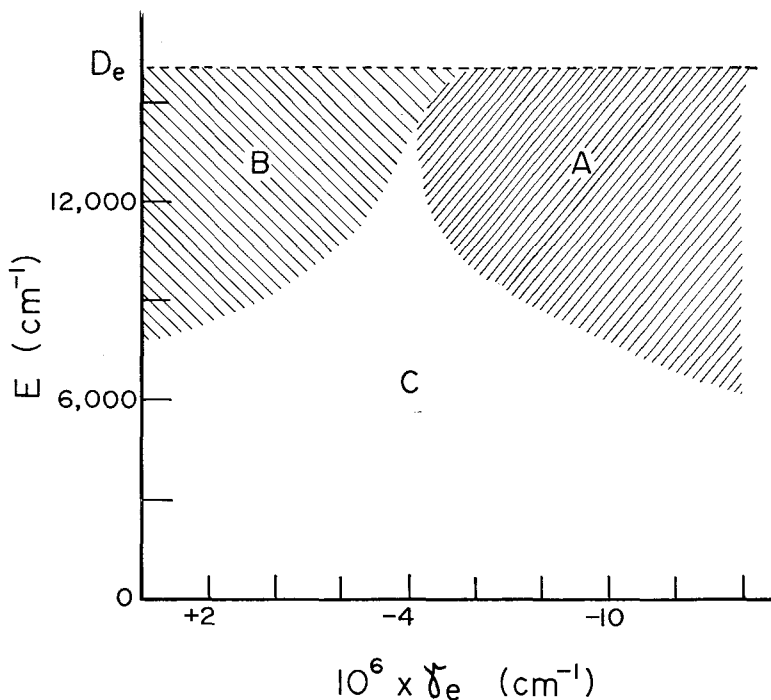


FIG. 3. Effect of γ_e on the derivatives of the inner portion of RKR potentials calculated for ground-state $^{79,81}\text{Br}_2$. The ordinate is energy above the potential minimum. In region A, the first derivative is positive, contradicting condition (2). In region B, the second derivative is negative, contradicting condition (3). In region C, both conditions (2) and (3) are satisfied. The vibrational constants from column D in Table I were used in obtaining the data shown here.

numerically from the turning points at $(v - 1)$, v , and $(v + 1)$. Any other choice of the two nearby points should yield equivalent results. However, due to the limited precision of our computer program, the use of smaller increments, such as 0.2, sometimes yields erroneous derivatives.

In this work, RKR potentials for the ground electronic state of Br_2 were calculated using a number of different sets of rotational and vibrational constants. Some of these potentials are shown in Fig. 1, and the corresponding constants are listed in Table I. The values of all necessary constants not listed in the table were taken from Herzberg (6).

The most recent literature values of the spectroscopic constants for ground-state $^{79,81}\text{Br}_2$ are those obtained by Horsley and Barrow (9) by interpolation of their absorption data for isotopically pure $^{79,79}\text{Br}_2$ and $^{81,81}\text{Br}_2$. They measured B_v values for the first four vibrational levels of the two isotopically pure species. When their B_v 's for each level of the two species were mass-corrected and aver-

TABLE II
RKR TURNING POINTS FOR GROUND-STATE $^{79,81}\text{Br}_2$ ($^1\Sigma_u^+$). E IS GIVEN IN cm^{-1} , r IN \AA

v	E	r (in)	r (out)	v	E	r (in)	r (out)
0	161.8	2.2324	2.3345	19	5887.8	2.0375	2.7150
1	483.7	2.1988	2.3763	20	6166.0	2.0336	2.7306
2	803.3	2.1768	2.4066	21	6441.8	2.0299	2.7463
3	1120.6	2.1595	2.4323	22	6715.1	2.0265	2.7619
4	1435.6	2.1451	2.4554	23	6986.0	2.0232	2.7776
5	1748.3	2.1326	2.4767	24	7254.3	2.0202	2.7933
6	2058.8	2.1216	2.4968	25	7520.0	2.0173	2.8091
7	2367.0	2.1117	2.5159	26	7783.2	2.0147	2.8249
8	2672.9	2.1026	2.5343	27	8043.6	2.0122	2.8409
9	2976.6	2.0943	2.5521	28	8301.4	2.0098	2.8569
10	3278.0	2.0867	2.5694	29	8556.5	2.0076	2.8731
11	3577.2	2.0796	2.5864	30	8808.7	2.0056	2.8893
12	3874.1	2.0731	2.6031	31	9058.1	2.0037	2.9057
13	4168.7	2.0670	2.6195	32	9304.6	2.0020	2.9223
14	4461.0	2.0612	2.6357	33	9548.1	2.0004	2.9391
15	4751.1	2.0559	2.6518	34	9788.7	1.9989	2.9560
16	5038.8	2.0508	2.6677	35	10026.1	1.9975	2.9732
17	5324.1	2.0461	2.6835	36	10260.4	1.9963	2.9905
18	5607.1	2.0417	2.6993				

aged, we obtained four empirical values which are considerably more accurate than the earlier results (10) (see Fig. 2). Previously, Rao and Venkateswarlu (11) (hereafter referred to as R&V) had measured a long series of band progressions in the ultraviolet, and determined approximate values of the first four vibrational constants (ω_e , $\omega_e x_e$, $\omega_e y_e$, and $\omega_e z_e$). However, B_v values could not be obtained directly from their experimental data. Therefore, they derived rotational constants from their vibrational constants using an approximate Pekeris equation which was derived for a Morse potential through the use of perturbation methods. The rotational constants obtained in this way were then corrected to make them consistent with the empirical B_v values reported by Brown (10) for a few of the lowest vibrational levels. The details of this procedure are discussed by Rao and Venkateswarlu (12). The RKR potential we constructed from these workers' constants is curve A in Fig. 1. It shows that the R&V rotational constants are inadequate, since the slope of the inner turning points is positive above 6000 cm^{-1} , contradicting our requirement (2). In addition, the values of $\Delta G_{v+1/2}$ generated from the R&V constants did not go to zero until $G(v)$ was approximately 1000 cm^{-1} above the known (9) dissociation limit, and this contradicts our first requirement for a reasonable set of constants.

In general, condition (1) may require the introduction of one more vibrational constant than is warranted by the experimental $G(v)$ data. However, in the special case considered here this happened to be unnecessary. For the rotational

constant, on the other hand, our method requires the evaluation of one more constant than was reported by Horsley and Barrow (9).

Our improved spectroscopic constants for the ground state of $^{79,81}\text{Br}_2$ were obtained in the following way. First Horsley and Barrow's (9) two rotational constants were applied to the raw R&V data to yield $G(v)$ values. From these we then obtained a set of vibrational constants consistent with requirement (1). Next, RKR potentials were generated from these vibrational constants and a number of trial values of γ_e . For each potential, the first and second derivatives of the inner turning points were calculated over a wide energy range. Figure 3 shows how we found the set of rotational constants which satisfy requirements (2) and (3) over the widest possible energy range. These new constants were then applied to the R&V data to yield an improved set of $G(v)$ values, and hence better vibrational constants. When this cycle was repeated two more times, the following self-consistent molecular constants were obtained, all in cm^{-1} :

$$\begin{aligned} \omega_e &= 324.24, & \omega_e x_e &= 1.172, & \omega_e y_e &= 0.342 \times 10^{-2}, \\ \omega_e z_e &= -0.101 \times 10^{-3}, \\ B_e &= 0.081079, & \alpha_e &= 0.30405 \times 10^{-3}, & \gamma_e &= -0.40 \times 10^{-5}, \text{ and} \\ r_e &= 2.2814 \text{ \AA}. \end{aligned}$$

These constants predict the existence of eighty vibrational levels for ground-state $^{79,81}\text{Br}_2$ ($^1\Sigma_g^+$). The potential generated from these constants is curve D in Fig. 1, and the turning points for the first 37 levels are given in Table II.

The standard deviation between the emission frequencies predicted by our constants and those observed by R&V is $\pm 1.0 \text{ cm}^{-1}$. This is quite acceptable, since R&V estimated an accuracy of $\pm 0.7 \text{ cm}^{-1}$ for only strong sharp lines.

CONCLUSIONS

For diatomic molecules in a given electronic state, the spectroscopic constants must produce an RKR potential which satisfies at least the following three requirements:

- (1) The outer turning points should approach the known dissociation limit asymptotically.
- (2) The slope of the inner portion of the RKR potential must be negative.
- (3) The second derivative of the inner portion of the potential must always be positive.

The conditions may be used in conjunction with experimental data to improve the existing vibrational and rotational constants.

The above requirements were applied to the ground state of $^{79,81}\text{Br}_2$ ($^1\Sigma_g^+$) and an improved set of four vibrational and three rotational constants were generated. Turning points are reported for 37 vibrational levels within the range of the existing experimental data (9, 11).

ACKNOWLEDGMENTS

One of us (R.J.L.) is indebted to the Province of Ontario for a Graduate Fellowship. We are grateful to the Institute of Computer Science of the University of Toronto for use of their facilities.

RECEIVED: March 4, 1967

REFERENCES

1. A. L. G. REES, *Proc. Roy. Soc.* **59**, 998 (1947).
2. O. KLEIN, *Z. Physik.* **76**, 226 (1932).
3. R. RYDBERG, *Z. Physik.* **73**, 376 (1931).
4. R. RYDBERG, *Z. Physik.* **80**, 514 (1933).
5. D. STEELE, E. R. LIPPINCOTT, AND J. T. VANDERSTICE, *Rev. Mod. Phys.* **34**, 239 (1962).
6. G. HERZBERG, "Spectra of Diatomic Molecules." Van Nostrand, Princeton, New Jersey, 1963.
7. R. N. ZARE, University of California Radiation Laboratory Report UCRL-10925 (1963).
8. R. N. ZARE, *J. Chem. Phys.* **40**, 1934 (1964).
9. J. A. HORSLEY AND R. F. BARROW, *Trans. Faraday Soc.* **63**, 32 (1967).
10. W. G. BROWN, *Phys. Rev.* **39**, 777 (1932).
11. Y. V. RAO AND P. VENKATESWARLU, *J. Mol. Spectry.* **13**, 288 (1964).
12. Y. V. RAO AND P. VENKATESWARLU, *J. Mol. Spectry.* **9**, 173 (1962).