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PARTITION FUNCTIONS AND THERMODYNAMIC PROPERTIES TO HIGH TEMPERATURES FOR H_3^+ AND H_2^+

by R. W. Patch and Bonnie J. McBride

Lewis Research Center
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CONTENTS

APPENDICES

PARTITION FUNCTIONS AND THERMODYNAMIC PROPERTIES TO HIGH TEMPERATURES FOR H_3^+ AND H_2^+

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Lewis Research Center

SUMMARY

Tables of partition functions were compiled for H_3^+ and H_2^+ at temperatures from 298.15° to 56 000° K. Tables of thermodynamic properties were compiled at temperatures from 298.15° to 10 000° K. The latter tables give the following thermodynamic functions for ideal gases: heat capacity at constant pressure C_p/R, sensible enthalpy $(H_T - H_O)/RT$, entropy at 1 atmosphere S_T^o/R, sensible free energy at 1 atmosphere $-(G_T^o - H_O)/RT$, enthalpy H_T/RT, and free energy at 1 atmosphere $-G_T^o/RT$. The heats of formation at 298.15° K are also given. Since no band spectra have been observed for either ion, all calculations were based on ab initio potential energy calculations found in or derived from the literature. All results for H_2^+ are reliable up to 15 000° K, but results for H_3^+ are tentative at all temperatures.

A digital computer program to calculate Wentzel-Kramers-Brillouin rotational energies from the potential energy of a diatomic molecule or molecular ion is also included. The program is in FORTRAN IV.

INTRODUCTION

In very-high-temperature propulsion devices such as gaseous nuclear rockets, the dominant mechanism of heat transfer is radiant energy exchange between volumes of plasma, and between plasma and the wall. To calculate such heat transfer, it is necessary to know the opacity of the plasma. For a hydrogen plasma under many conditions, minor species make major contributions to the opacity, either directly or by their influence on the composition. Two such minor species are the hydrogen triatomic molecular ion H_3^+ and the hydrogen diatomic molecular ion H_2^+. The partition functions of these two molecular ions are needed to calculate the composition of a hydrogen plasma at high pressures and low degrees of ionization, and the thermodynamic properties are needed to interpret data from some experimental investigations of the opacity of hydrogen.

The existence of H_3^+ and H_2^+ has been well established by investigations using mass spectrometers, but no band spectrum of either ion has been observed. There have been no published calculations of the partition function or thermodynamic properties of H_3^+, and only one such calculation for H_2^+ (ref. 1) has come to the authors' attention.

The purpose of the present work was to calculate the partition function for temperatures between 298.15° and $56\,000^\circ$ K and thermodynamic properties for temperatures between 298.15° and $10\,000^\circ$ K for H_3^+ and H_2^+. This presented two principal difficulties: (1) complete sets of spectroscopic constants were not available because no band spectra have been observed, and (2) the usual approximations used in calculating partition functions are not accurate at high temperatures.

The solution was to utilize existing ab initio calculations for the potential energy of both molecular ions. For H_3^+ the potential energy was used to obtain both low- and high-temperature approximations to the partition function; the two approximations were then faired together. For H_2^+ the rotational term values were calculated from the potential energy by the Wentzel-Kramers-Brillouin (WKB) approximation, and the vibrational term values were obtained from more accurate existing calculations. The partition function was then found by direct summation over the vibration-rotation states.

The present work was limited to ideal gases with no excited electronic states.

TRIATOMIC MOLECULAR ION H_3^+

The calculations in this section are divided into two sections, the Analysis and the Results and Discussion. The latter of these contains numerical results for the partition function and thermodynamic properties and a discussion of the accuracy of the partition function.

Analysis

Assumptions and restrictions. - The assumptions and restrictions utilized in the analysis are listed here for convenience. They are the following:

(1) The Born-Oppenheimer approximation (ref. 2) is assumed to be applicable.

(2) The equilibrium configuration is an equilateral triangle.

(3) There are no excited electronic states (this is a good assumption, since the lowest excited electronic state is about 75 000 centimeters^{-1} above the ground state and appears to be a repulsive state (ref. 3).

(4) Differences in nuclear spin degeneracy are neglected in computing the thermodynamic properties.

(5) An ideal gas is assumed.

Potential energy. - A number of ab initio calculations (refs. 3, 4, 5, 6, and 7) and one semitheoretical calculation (ref. 8) have been made of the potential energy of H_3^+. It is now generally agreed that the equilibrium configuration is an equilateral triangle with a proton at each vertex. The results of these calculations are given in table I. All but the earliest (ref. 3) ab initio calculations give about the same equilibrium internuclear distance r_e, but there is considerable disagreement about the equilibrium potential energy V_e. (All symbols are defined in appendix A.)

There are no experimental values for the dissociation energy or potential energy of H_3^+ or any of its isotopic modifications, but Stevenson and Schissler (ref. 9) measured the rate of the reaction

$$D_2^+ + D_2 \rightarrow D_3^+ + D$$

where D_2^+ is the deuterium diatomic molecular ion, D_2 is the deuterium molecule, D_3^+ is the deuterium triatomic molecular ion, and D is the dueterium atom. It was concluded that the rate of this reaction was so high that the reaction was unlikely to have any activation energy (private communication from David P. Stevenson, Shell Development Company, Emeryville, California). An activation energy of zero gives a lower limit to the dissociation energy of D_3^+ (into $D + D + D^+$ where D^+ is the deuterium atomic ion) of 58 456 centimeters^{-1}. In the Born-Oppenheimer approximation the potential energies of H_3^+ and D_3^+ are the same. If a D_3^+ zero-point energy of 3684 centimeter^{-1} calculated from Conroy's (ref. 5) H_3^+ potential energy is assumed, the equilibrium potential energy of D_3^+ (and hence H_3^+) is thus -6.214×10^4 centimeter^{-1} or less. This value is consistent with all calculations for H_3^+ except Hoyland's (ref. 6).

Conroy's equilibrium potential energy (ref. 5) is generally considered to be the most reliable for three reasons: (1) Conroy used a 26-term wave function, (2) Christoffersen (ref. 4) estimated that if he included more terms in his calculation, he would get an equilibrium potential energy of -7.68×10^4 centimeter^{-1}, which is close to Conroy's value, and (3) Conroy and Bruner (ref. 10) calculated the potential energy of the linear hydrogen triatomic molecule H_3 by a development of the method used for H_3^+ and found the rim of the potential energy basin of H_3 to be 2.17×10^3 centimeter^{-1} above the energy of $H_2 + H$ where H_2 is the hydrogen diatomic molecule and H is the hydrogen atom. This is in good agreement with the experimental activation energy (ref. 11) for the exchange reaction

$$H + H_2 \rightarrow H_2 + H$$

Consequently, Conroy's H_3^+ potential energy was used in this report.

As explained in appendix B, it was necessary to make a least-squares fit to Conroy's H_3^+ potential for use in the low-temperature approximation. This resulted in slightly different values of r_e and V_e which are also given in table I and which for consistency were used in calculating the partition function and thermodynamic properties in the low-temperature approximation.

Partition function. - The energy of the rotationless ground vibrational state was used as the reference for the internal partition function $q_{H_3^+}$, which was obtained by two different approximations. For low temperatures it was computed from the calculated spectroscopic constants (eq. (B39)) by means of Woolley's approximation (ref. 12). For high temperatures a classical partition function with vibrational quantum corrections (eq. (C21)) was used (see appendix C).

Thermodynamic properties. - The thermodynamic functions C_p/R, $(H_T - H_0)/RT$, $-(G_T^o - H_0)/RT$, and S_T^o/R for ideal gases were calculated on a digital computer. Equations for evaluating the thermodynamic functions from the logarithm of the partition function and its derivatives are as follows (ref. 13, ch. V):

$$\frac{C_p}{R} = T^2 \frac{d^2(\ln q)}{dT^2} + 2T \frac{d(\ln q)}{dT} + \frac{5}{2} \tag{1}$$

$$\frac{H_T - H_0}{RT} = T \frac{d(\ln q)}{dT} + \frac{5}{2} \tag{2}$$

$$\frac{S_T^o}{R} = T \frac{d(\ln q)}{dT} + \ln q + \frac{3}{2} \ln M + \frac{5}{2} \ln T - 1.164953 \tag{3}$$

$$\frac{-(G_T^o - H_0)}{RT} = \frac{S_T^o}{R} - \frac{H_T - H_0}{RT} = \ln q + \frac{3}{2} \ln M + \frac{5}{2} \ln T - 3.664953 \tag{4}$$

where M is the molecular weight or 3.02336 grams per mole for H_3^+. Physical constants have been taken from reference 14.

Results and Discussion

Partition function. - The low-temperature partition-function approximation with first-order corrections (ref. 12) and with both first- and second-order corrections are shown in figure 1. Above 7000° K the second-order correction was appreciable compared to the first-order correction, causing one to suspect that higher-order corrections should be included. In addition, at high temperatures the least-squares fit (eqs. (B15) and (B17)) used to calculate the spectroscopic constants is inadequate: it does not fit Conroy's potential energy at the high energies corresponding to some of the energy levels which contribute significantly to the partition function.

The high-temperature approximation to the partition function $q_{H_3^+}$ is also shown in figure 1. For low temperatures, it gave about twice the values that the low-temperature approximation did. The principal reason for this is the crude but necessary assumption in the high-temperature approximation that the potential energy V is the sum of three two-atom potential energies U (eq. (C5)) coupled with the assumption that U is one-third of Conroy's (ref. 5) V for the equilateral triangle configuration. This results in constant-V lines that tend to fall outside Conroy's constant-V lines (fig. 2) for isosceles triangles, except, of course, along the line Q corresponding to equilateral triangles. Similar discrepancies would undoubtedly occur for many scalene triangles if Conroy had calculated V for scalene triangles. Hence, the high-temperature approximation to the partition function gave values that were too large at low temperatures.

At temperatures of the order of 40 000° K the high-temperature approximation contains at least two significant inaccuracies in addition to the one mentioned in the preceding paragraph: (1) all metastable rotational states are omitted and (2) the approximation yields the following identical heats of reaction:

$$H_3^+ \rightarrow H_2^+ + H \qquad \Delta H_0 = 52\ 200\ \text{cm}^{-1}$$

$$H_3^+ \rightarrow H_2 + H^+ \qquad \Delta H_0 = 52\ 200\ \text{cm}^{-1}$$

(using potential energy for H_3^+ from ref. 5) whereas the best available information (refs. 5, 15, 16, and 17) used directly gives

$$H_3^+ \rightarrow H_2^+ + H \qquad \Delta H_0 = 55\ 800\ \text{cm}^{-1}$$

$$H_3^+ \rightarrow H_2 + H^+ \qquad \Delta H_0 = 40\ 100\ \text{cm}^{-1}$$

(zero-point energies have been neglected in all four equations). Inaccuracy (1) tends to make $q_{H_3^+}$ too low whereas inaccuracy (2) and the inaccuracy in the preceding paragraph tend to make $q_{H_3^+}$ too high. Thus at temperatures of the order of 40 000° K the inaccuracies in the high-temperature approximation tend to cancel.

Taking the inaccuracies mentioned in the preceding three paragraphs into consideration, a smooth curve (fig. 1) was used to fair the low-temperature approximation into the high-temperature approximation. This curve extended from 7000° to 26 000° K and had the formula

$$\ln q_{H_3^+} = 3.1705 + 1.03824\times10^{-3}\ T - 3.2449\times10^{-8}\ T^2 + 5.2127\times10^{-13}\ T^3 - 4.077\times10^{-18}\ T^4 \qquad (5)$$

The resulting $q_{H_3^+}$ is shown in figure 3 and is tabulated in table II.

Thermodynamic properties. - The thermodynamic functions C_p/R, $(H_T - H_0)/RT$, S_T^0/R, $-(G_T^0 - H_0)/RT$, H_T/RT, and $-G_T^0/RT$ for H_3^+ are tabulated in table III. The functions are given for temperatures ranging from 298.15° to 10 000° K at 100° K intervals from 300° K. The absolute values, H_T/RT and $-G_T^0/RT$, are relative to an assigned enthalpy base of $H_{298.15} = 0$ for H_2 and e.

The following heats of reaction ΔH_0 were used to obtain the heat of formation of H_3^+ from H_2(g) and electron gas e:

$H_3^+ \rightarrow 2H + H^+$ $\quad \Delta H_0 = 72\ 707\ \text{cm}^{-1}$ (appendix B)

$H_2 \rightarrow 2H$ $\quad \Delta H_0 = 36\ 113.6\ \text{cm}^{-1}$ (refs. 16 and 18)

$H \rightarrow H^+ + e$ $\quad \Delta H_0 = 109\ 678.76\ \text{cm}^{-1}$ (ref. 19)

where H^+ is the hydrogen atomic ion. At 298.15° K the following values of $(H_{298.15} - H_0)/RT$ were used: 3.41561 for H_2 (ref. 20), 2.5 for e, and 3.9745 for H_3^+ (table III). The heat of formation at 298.15° K was calculated to be:

$$\frac{3}{2} H_2 \rightarrow H_3^+ + e \qquad \Delta H_{298.15} = 1\ 093\ 640\ \text{J/mole} = 261\ 386\ \text{cal/mole}$$

Accuracy. - The estimated accuracy of $q_{H_3^+}$ (table II) is different at different temperatures. Assuming Conroy's V is exact, $q_{H_3^+}$ should be accurate to within 20 percent from 298.15° to 8000° K. From 8000° to 15 000° K, $q_{H_3^+}$ should be accurate to within a factor of 2. Above 15 000° K, $q_{H_3^+}$ is an order of magnitude estimate. However, at 1000-atmospheres pressure and above about 8000° K there is less H_3^+ than H_2^+ or H^+ in a hydrogen plasma. (Below about 8000° K there is more H_3^+ than H_2^+ and at still lower temperatures there is more H_3^+ than H_2^+ or H^+). At lower pressures, the temperature where the concentrations of H_3^+ and H_2^+ are equal will be less than 8000° K. Hence, errors in $q_{H_3^+}$ at high temperatures are not of much practical importance. Considering the almost complete lack of experimental data on H_3^+, a more sophisticated calculation of $q_{H_3^+}$ than is contained in this report is not warranted.

DIATOMIC MOLECULAR ION H_2^+

The calculations in this section are divided into two parts, the Analysis and the Results and Discussion. The latter of these contains numerical results for the rotational term values, partition function, and thermodynamic properties, comparison with other investigators, and a discussion of the accuracy of the results for H_2^+.

Analysis

Assumptions and restrictions. - The assumptions and restrictions utilized in the analysis are listed here for convenience; they are the following:

(1) There are no excited electronic states (this is a good assumption below 15 000° K because the lowest electronically excited state is repulsive and the next excited state is about 92 600 centimeters^{-1} above the ground state and only has a shallow potential well (ref. 21)).

(2) Differences in nuclear spin degeneracy were neglected in computing the thermodynamic properties.

(3) An ideal gas was assumed.

Potential energy and energy levels. - Experiments and various ab initio calculations of the constants of H_2^+ have resulted in the values listed in table IV. The experimental values of r_e and ω' have some uncertainty because no band spectra of H_2^+ have ever been observed. Obviously, the small differences in the various values for the constants in table IV would have negligible effect on the partition function and thermodynamic properties, and it can be safely assumed that the potential energies used by Cohen, et al. (ref. 22) and by Wind (ref. 15) are essentially correct.

The best potential energy that could be obtained from the literature was found by adding Wind's electron energy (ref. 23) to the nuclear repulsion potential energy. Rotational term values were obtained from this potential energy by the WKB connection formula for Hund's coupling case (b) (eq. (D10)) with the help of equations (D11), (D12), and (D16). The second term on the right hand side of equation (D12) was assumed to be zero. The computer program used for this calculation is described in appendix D. Vibration-rotation term values $\mathscr{F}(v, K)$ were obtained by adding vibration term values from Wind (ref. 15) to the rotational term values obtained from the computer program.

Partition function. - The energy of the rotationless ground vibrational state was used as the reference for the internal partition function $q_{H_2^+}$, which was obtained from the relation

$$q_{H_2^+} = \frac{g_e}{\sigma} \sum_{v} \sum_{K} (2K+1) e^{-hc\mathscr{F}(v, K)/kT} \tag{6}$$

where g_e is the electronic statistical weight, σ is the symmetry number, v is the vibrational quantum number, K is the quantum number for total angular momentum apart from spin, h is Planck's constant, c is the velocity of light, k is Boltzmann's constant, and T is temperature. Metastable rotational levels were included in the summation in equation (6). The quantities g_e and σ are both equal to 2. In equation (6) the difference in statistical weights of ortho and para states is neglected as was done for H_3^+. This is a good approximation at 298.15° K and above.

Thermodynamic properties. - The thermodynamic functions C_p/R, $(H_T - H_0)/RT$, $-(G_T^o - H_0)/RT$, and S_T^o/R for H_2^+ were calculated on a digital computer using equations (1) to (4). The molecular weight was taken to be 2.01539 grams per mole.

Results and Discussion

Rotational term values. - The calculated rotational term values are given in table V. Note that these rotational term values are not the same as obtained in the sample problem (tables VI and VII) because many more potential energy points with internuclear distance r as great as 25×10^{-8} centimeter were provided as input to the program when table V was calculated. Where no value is given in table V, the state is nonexistent. The rotational term values in table V agree within 0.85 centimeter^{-1} with rotational term values calculated from Wind's energy levels (ref. 15) and within 0.12 centimeter^{-1} with term values from reference 24.

Partition function. - The partition function calculated from equation (6) is given in table II and figure 3. It agrees within 38 percent with the less accurate values of Vardya (labeled $r_{\infty\infty}$ (n_J = 40) in table III of ref. 1), who made calculations for 3000° to $25\,000^\circ$ K.

Thermodynamic properties. - The thermodynamic functions C_p/R, $(H_T - H_0)/RT$, S_T^o/R, $-(G_T^o - H_0)/RT$, H_T/RT, and $-G_T^o/RT$ for H_2^+ are tabulated in table VIII. The functions are given for temperatures ranging from 298.15° to 10 000° K at 100°K intervals from 300° K. The absolute values, H_T/RT and $-G^0_T/RT$, are relative to an assigned enthalpy base of $H_{298.15} = 0$ for H_2 and e.

The following heats of reaction ΔH_0 were used to obtain the heat of formation of H_2^+ from H_2(g) and electron gas e:

$$H_2 \rightarrow 2H \qquad \Delta H_0 = 36\ 113.6\ \mathrm{cm}^{-1} \qquad \text{(refs. 16 and 18)}$$

$$H \rightarrow H^+ + e \qquad \Delta H_0 = 109\ 678.76\ \mathrm{cm}^{-1} \qquad \text{(ref. 19)}$$

$$H_2^+ \rightarrow H + H^+ \qquad \Delta H_0 = 21\ 379.36\ \mathrm{cm}^{-1} \qquad \text{(ref. 15)}$$

Using $(H_{298.15} - H_0)/RT$ values of 3.41561 for H_2 (ref. 20), 2.5 for e, and 3.4623 for H_2^+ (table VIII) results in the heat of formation at 298.15° K becoming

$$H_2 \rightarrow H_2^+ + e \qquad \Delta H_{298.15} = 1\ 494\ 610\ \mathrm{J/mole}$$

$$= 357\ 220\ \mathrm{cal/mole}$$

Accuracy. - The estimated accuracy of $q_{H_2^+}$ (table II) is different at different temperatures. The contribution of the ground electronic state is given to within 1 percent by equation (6) for 298.15° to 56 000° K. However, at temperatures above 15 000° K there are contributions of 1/2 percent or more due to electronically excited states with potential wells (ref. 21) which are not included in equation (6). At 56 000° K the value of $q_{H_2^+}$ in table II is consequently about 70 percent too low. The large error at high temperatures is of little practical importance since at 1000-atmospheres pressure and 15 000° K there is only about 4 percent as much H_2^+ as H^+ in a hydrogen plasma and even less at higher temperature or lower pressure.

CONCLUDING REMARKS

In this report the partition function and thermodynamic properties of H_2^+ and H_3^+ were calculated for ideal gases. Because no band spectra have been observed for H_2^+ or H_3^+, potential energies had to be obtained from ab initio calculations found in the literature.

The partition function and thermodynamic properties of the ground electronic state of H_2^+ are based on reliable potential energies and other calculations and are unlikely to change appreciably if the calculations are carried to higher degrees of approximation or if more experimental information becomes available. However, if excited electronic states of H_2^+ were included, the partition function for H_2^+ would be appreciably higher at temperatures in excess of 15 000° K.

The partition function and thermodynamic properties of H_3^+ are based on the most reliable potential energies available from ab initio calculations, but there is very little published experimental information.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, December 18, 1967,
122-28-02-17-22.

APPENDIX A

SYMBOLS

A_1'	nondegenerate totally symmetric symmetry species for point group D_{3h} (ref. 25)
B	$h^2/8\pi^2\mu r^2$
B_e, C_e	rotational constants for equilibrium separation of atoms
$B_i(i=1, 2, \ldots, 7)$	constants in expression for H_3^+ potential energy in terms of $\mathscr{S}$
B_v, C_v	rotational constants for vibrational state v_1, v_2
C_p	heat capacity at constant pressure
c	velocity of light
D_J, D_{JK}, D_K, ρ	rotational stretching constants
D_o	energy to dissociate rotationless ground vibrational state
E	energy
E'	doubly degenerate symmetry species for point group D_{3h} (ref. 25)
E_F	vibration-rotation energy eigenvalue
E_o	unevaluated constant term in H_3^+ energy
$F(r_{ij})$	ratio of incomplete gamma function to complete gamma function defined in ref. 26
$\mathscr{F}(v, j)$	vibration-rotation term value for actual potential (an eigenvalue if corresponding v has the value 0 or is a positive integer)
$\mathscr{F}_t(v, j)$	vibration-rotation term value for Morse potential
$f(v, j)$	rotational term value
$\underline{G}$	kinetic energy matrix (ref. 25)
$\underline{G}^{-1}$	inverse of kinetic energy matrix (ref. 25)
G_T	Gibbs free energy at temperature T
g_e	electronic degeneracy
H_T	sum of sensible enthalpy at temperature T and chemical energy at 0° K
$H_T - H_0$	sensible enthalpy

ΔH_T	heat of reaction at temperature T
H_0	chemical energy at 0° K
$\mathcal{H}$	Hamiltonian of H_3^+ with reference energy of infinitely separated $H + H + H^+$ in ground states
h	Planck's constant
$I_{ii}^{(e)}$	equilibrium moment of inertia about principal axis i
I_1	integral due to two-bond states of H_3^+ in expression for Z'
I_2	integral due to three-bond states of H_3^+ in expression for Z'
J	total angular momentum quantum number
j	generalized rotation quantum number
K	quantum number for total angular momentum apart from electron spin
k	Boltzmann constant
$k_{111}, k_{122}, k_{1111}, k_{1122}, k_{2222}$	force constants
$\vec{L}$	electronic orbital angular momentum vector
$\underline{L}^{-1}$	matrix for orthogonal transformation from mass-weighted Cartesian coordinates to normal coordinates (ref. 25)
l_2	vibrational angular momentum integral number
M	molecular weight
m	mass of proton plus two-thirds of mass of electron
P(r)	radial wave function of diatomic molecule or molecular ion
$\vec{p}_1, \vec{p}_2, \vec{p}_3$	momentum of atoms 1, 2, and 3, respectively
$\underline{Q}$	normal coordinate column vector for H_3^+
$Q_i (i=4, 5, \ldots, 9)$	normal coordinates for rotation and translation of H_3^+
Q_1, Q_{21}, Q_{22}	normal coordinates for H_3^+ vibration
q	internal partition function
q_c	classical internal partition function of H_3^+ including only bound states and with reference energy of rotationless ground vibrational state of H_3^+

q'_c	classical internal partition function of H_3^+ including only bound states and with reference energy of infinitely separated $H + H + H^+$ in ground states
q'_{ct}	classical partition function of H_3^+ including translation of the molecular ion and only bound states and with reference energy of infinitely separated $H + H + H^+$ in ground states
q''_{ct}	classical partition function of H_3^+ including translation of the atoms, bound and unbound states, and with reference energy of infinitely separated $H + H + H^+$ in ground states
R	universal gas constant
R, R'	internuclear distances (fig. 2 only)
$\mathcal{R}_l, \mathcal{R}_1, \mathcal{R}_2$	ratios of quantum-mechanical harmonic-oscillator partition function to classical harmonic-oscillator partition function
$r, r_{ij}, r_{12}, r_{13}, r_{23}$	internuclear distances
r_e	equilibrium internuclear distance
r_{max}	internuclear distance of far turning point
r_{min}	internuclear distance of near turning point
r_{01}, r_{02}	internuclear distances of inflection points in U'' (fig. 6)
r_{03}	internuclear distance of minimum of U'' (fig. 6)
r_{04}	internuclear distance of maximum of U'' (fig. 6)
$\vec{r}_1, \vec{r}_2, \vec{r}_3$	position vectors of atoms 1, 2, and 3, respectively, relative to fixed axes
S	total electron spin quantum number
S_T	entropy at temperature T
$\underline{\mathcal{S}}$	$\mathcal{S}$ column vector
$\underline{\tilde{\mathcal{S}}}$	$\mathcal{S}$ row vector
$\mathcal{S}_1, \mathcal{S}_2, \mathcal{S}_3$	changes in internuclear distances of H_3^+
s_1, s_{21}, s_{22}	symmetry coordinates of H_3^+
T	absolute temperature
U, U_a, U_b, U_σ	diatomic potential such as obtained from RKR approximation
U'_a, U'_b, U'_σ	diatomic electronic potential (including nuclear repulsion)

$U'', U''_a, U''_b, U''_\sigma$	effective diatomic potential
U_t	diatomic Morse potential
U_{12}, U_{13}, U_{23}	two-atom potential energies of H_3^+ with reference energy of infinitely separated $H + H + H^+$ in ground states
u_l	dimensionless energy of fundamental vibration l of H_3^+
V	three-atom potential energy of H_3^+ with reference energy of infinitely separated $H + H + H^+$ in ground states
V'	three-atom potential energy of H_3^+ (zero for equilibrium internuclear distances)
V_e	three-atom equilibrium potential energy of H_3^+ with reference energy of infinitely separated $H + H + H^+$ in ground states
v, v_1, v_2	vibrational quantum number if integer; vibration number if noninteger
v_{max}	maximum value of v
W	volume of container
W'_a	diatomic electronic potential energy for Hund's coupling case (a)
x	Cartesian coordinate
$x_{l_2 l_2}$	vibrational angular momentum constant
$\Delta x_1, \Delta x_2, \Delta x_3$	displacements of protons 1, 2, and 3, respectively, in x-direction
$x_{11}, x_{12}, x_{21}, x_{22}$	anharmonicity constants
y	Cartesian coordinate
$\Delta y_1, \Delta y_2, \Delta y_3$	displacements of protons 1, 2, and 3 respectively, in y-direction
Z'	H_3^+ configuration integral including only bound states
Z''	H_3^+ configuration integral including bound and unbound states
z	Cartesian coordinate
z'	Cartesian coordinate with origin at proton 1
$\Delta z_1, \Delta z_2, \Delta z_3$	displacements of protons 1, 2, and 3, respectively, in z-direction
$\alpha_0, \alpha_1, \alpha_2,$ $\gamma_0, \gamma_1, \gamma_2$	vibration-rotation interaction constants for H_3^+
$\Gamma(s)$	representation

ζ_2	Coriolis splitting constant for H_3^+
$\underline{\eta}$	η column vector
$\eta_i (i=1,2,\ldots,9)$	mass-weighted Cartesian displacement coordinates of H_3^+
θ_1,θ_2	polar angles of H_3^+ (fig. 5)
κ	quantum number for component of total angular momentum along z axis for H_3^+
Λ	quantum number for component of orbital angular momentum along internuclear axis
$\lambda_m,\lambda_1,\lambda_2$	squares of angular velocities of normal vibrations of H_3^+
μ	reduced mass of two atoms in diatomic molecule or molecular ion
Σ	quantum number for component of electron spin angular momentum along internuclear axis for diatomic molecule or molecular ion
σ	symmetry number
φ_1,φ_2	aximuthal angles of H_3^+ (fig. 5)
ψ	vibrational wave function of diatomic molecule or molecular ion
Ω	quantum number for component of total electronic angular momentum along internuclear axis for diatomic molecule or molecular ion
ω_1,ω_2	zero-order vibrational frequencies of H_3^+
$\omega',\omega_1',\omega_2',\omega_l'$	fundamental vibrational frequencies
Subscripts:	
H_2^+	hydrogen diatomic molecular ion
H_3^+	hydrogen triatomic molecular ion
j	proton j of H_3^+
k	vibrational kinetic
T	temperature given as table argument
Superscripts:	
.	time derivative
o	standard state (1-atm pressure)
*	effective value for unbound atoms
‡	effective value for bound atoms

APPENDIX B

SPECTROSCOPIC CONSTANTS AND DISSOCIATION ENERGY OF H_3^+

Since the spectrum of H_3^+ has never been observed, it is necessary to obtain the spectroscopic constants and dissociation energy from theoretical calculations. This is done in this appendix, using the H_3^+ potential computed by Conroy (ref. 5).

The procedure consists of three parts: (1) The vibration of the molecular ion is analyzed assuming that the potential energy V contains only terms that are quadratic in the symmetry coordinates or normal coordinates. This is known as the harmonic oscillator approximation and gives zero-order frequencies of vibration, which are the frequencies which the molecule would exhibit if the anharmonic terms in V were all zero. (2) The symmetry of the molecular ion is used to find the form of the anharmonic terms in V, and a least-squares fit to the potential computed by Conroy is made. (3) The anharmonic terms in V are treated as perturbations to the harmonic oscillators. With the exception of the least-squares fit, this procedure has been well established for molecules (refs. 25 and 27) and requires no modification for molecular ions, so only important steps and results are given in this appendix.

Harmonic Oscillator Approximation

There is general agreement (refs. 4, 5, 6, 7, 8, and 28) that the equilibrium configuration of H_3^+ is an equilateral triangle with a proton at each vertex. Hence, H_3^+ belongs to point group D_{3h}. It follows by the methods of Wilson, Decius, and Cross (ref. 25) that the structure of the symmetry coordinate representation is

$$\Gamma(s) = A_1' + E' \tag{B1}$$

where s stands for the three symmetry coordinates (ref. 25). The normal coordinates have the same structure of their representation as the symmetry coordinates do. There is one zero-order frequency associated with the normal coordinate of symmetry species A_1' and another zero-order frequency associated with the pair of normal coordinates of symmetry species E'. In the following paragraphs, the zero-order frequencies of vibration will be found by setting up and solving the secular equation (ref. 25) in terms of the symmetry coordinates.

The lengths of the three sides of the triangle with protons at the vertexes are called internuclear distances. The changes in these internuclear distances from the equilibrium value r_e are designated $\mathcal{S}_1$, $\mathcal{S}_2$, and $\mathcal{S}_3$, coresponding to sides 1, 2, and 3 of the triangle, respectively. With the aid of equation (B1), the symmetry coordinates s are related to the changes in internuclear distances by the matrix equation

$$\begin{bmatrix} s_1 \\ s_{21} \\ s_{22} \end{bmatrix} = \begin{bmatrix} 1/3^{1/2} & 1/3^{1/2} & 1/3^{1/2} \\ 2/6^{1/2} & -1/6^{1/2} & -1/6^{1/2} \\ 0 & 1/2^{1/2} & -1/2^{1/2} \end{bmatrix} \begin{bmatrix} \mathcal{S}_1 \\ \mathcal{S}_2 \\ \mathcal{S}_3 \end{bmatrix} \tag{B2}$$

where s_1 is of species A_1' and s_{21} and s_{22} are of species E'. (The subscripts of s were chosen to conform to Nielsen's notation in ref. 27.)

The potential energy V and vibrational kinetic energy E_k are also needed in setting up the secular equation. The symmetry of H_3^+ requires that, in the harmonic oscillator approximation, the potential energy (referred to the equilibrium value) be of the form

$$2V' = B_1\left(\mathcal{S}_1^2 + \mathcal{S}_2^2 + \mathcal{S}_3^2\right) + B_2\left(\mathcal{S}_1\mathcal{S}_2 + \mathcal{S}_1\mathcal{S}_3 + \mathcal{S}_2\mathcal{S}_3\right) \tag{B3}$$

where B_1 and B_2 are constants. Combining equations (B2) and (B3) gives

$$2V' = B_1\left(s_1^2 + s_{21}^2 + s_{22}^2\right) + B_2\left(s_1^2 - \frac{1}{2}s_{21}^2 - \frac{1}{2}s_{22}^2\right) \tag{B4}$$

The kinetic energy is given by the matrix equation

$$2E_k = \underline{\dot{\tilde{\mathcal{S}}}}\,\underline{G}^{-1}\,\underline{\dot{\mathcal{S}}} \tag{B5}$$

where $\underline{G}^{-1}$ is the inverse of the $\underline{G}$ matrix (ref. 25) and the dots indicate derivatives with respect to time. Using the method in reference 25 results in

$$\underline{G} = \begin{bmatrix} 2/m & 1/2m & 1/2m \\ 1/2m & 2/m & 1/2m \\ 1/2m & 1/2m & 2/m \end{bmatrix} \tag{B6}$$

where m is the mass of a proton plus two-thirds the mass of an electron. From equations (B2), (B5) and (B6), the following is obtained:

$$2E_k = m\left(\frac{1}{3}\dot{s}_1^2 + \frac{2}{3}\dot{s}_{21}^2 + \frac{2}{3}\dot{s}_{22}^2\right) \tag{B7}$$

From equation (B4) and (B7), the secular equation is

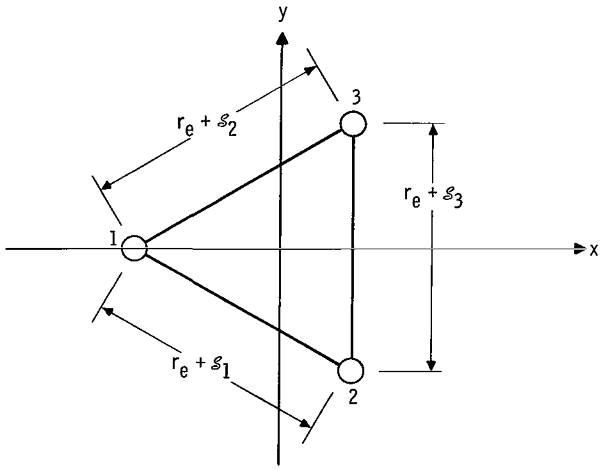
$$\begin{vmatrix} B_1 + B_2 - m\lambda/3 & 0 & 0 \\ 0 & B_1 - (B_2/2) - 2m\lambda/3 & 0 \\ 0 & 0 & B_1 - (B_2/2) - 2m\lambda/3 \end{vmatrix} = 0 \tag{B8}$$

where the zero-order frequencies are given by $\lambda_m^{1/2}/2\pi$. The solutions of equation (B8) are

$$\left.\begin{aligned} \lambda_1 &= \frac{3(B_1 + B_2)}{m} \\ \lambda_2 &= \frac{3(B_1 - B_2/2)}{2m} \end{aligned}\right\} \tag{B9}$$

the second solution occurring twice.

The next problem is to obtain the $\underline{L}^{-1}$ matrix (ref. 25), which is needed in the perturbation solution for the spectroscopic constants contained in a following section. Assume the molecular ion is in the x-y plane, with the axes passing through the center of mass as shown in the following sketch:



where the protons are represented by circles and r_e is the equilibrium internuclear distance. Let Δx_j, Δy_j, and Δz_j be the components of the displacement of the j^{th} proton from equilibrium. Mass-weighted Cartesian displacement coordinates are defined by

$$\left.\begin{array}{lll} \eta_1 \equiv m^{1/2}\,\Delta x_1, & \eta_2 \equiv m^{1/2}\,\Delta y_1, & \eta_3 \equiv m^{1/2}\,\Delta z_1 \\ \eta_4 \equiv m^{1/2}\,\Delta x_2, & \eta_5 \equiv m^{1/2}\,\Delta y_2, & \eta_6 \equiv m^{1/2}\,\Delta z_2 \\ \eta_7 \equiv m^{1/2}\,\Delta x_3, & \eta_8 \equiv m^{1/2}\,\Delta y_3, & \eta_9 \equiv m^{1/2}\,\Delta z_3 \end{array}\right\} \tag{B10}$$

so that a matrix which appears later in the analysis will be orthogonal. For small displacements

$$\left.\begin{array}{l} \mathcal{S}_1 = \dfrac{1}{m^{1/2}}\left(-\dfrac{3^{1/2}}{2}\,\eta_1 + \dfrac{1}{2}\,\eta_2 + \dfrac{3^{1/2}}{2}\,\eta_4 - \dfrac{1}{2}\,\eta_5\right) \\ \mathcal{S}_2 = \dfrac{1}{m^{1/2}}\left(-\dfrac{3^{1/2}}{2}\,\eta_1 - \dfrac{1}{2}\,\eta_2 + \dfrac{3^{1/2}}{2}\,\eta_7 + \dfrac{1}{2}\,\eta_8\right) \\ \mathcal{S}_3 = \dfrac{1}{m^{1/2}}\,(\eta_8 - \eta_5) \end{array}\right\} \tag{B11}$$

A set of coordinates such as s_1, s_{21}, s_{22} in which the potential energy (eq. (B4)) and the vibrational kinetic energy (eq. (B7)) involve no cross terms (such as $s_1 s_{21}$) are always coordinates which differ from normal coordinates Q_1, Q_{21}, and Q_{22} only by a constant for each coordinate or do not differ at all. The constants can be found from the matrix equation

$$\underline{Q} = \underline{L}^{-1}\underline{\eta} \tag{B12}$$

by noting that $\underline{L}^{-1}$ must be an orthogonal matrix. From equations (B2) and (B11) and the proportionality between s_1 and Q_1, s_{21} and Q_{21}, and s_{22} and Q_{22}, equation (B12) becomes

$$\begin{bmatrix} Q_1 \\ Q_{21} \\ Q_{22} \\ Q_4 \\ Q_5 \\ Q_6 \\ Q_7 \\ Q_8 \\ Q_9 \end{bmatrix} = \begin{bmatrix} -3^{1/2}/3 & 0 & 0 & 3^{1/2}/6 & -1/2 & 0 & 3^{1/2}/6 & 1/2 & 0 \\ -3^{1/2}/6 & 1/2 & 0 & 3^{1/2}/3 & 0 & 0 & -3^{1/2}/6 & -1/2 & 0 \\ -1/2 & -3^{1/2}/6 & 0 & 0 & 3^{1/2}/3 & 0 & 1/2 & -3^{1/2}/6 & 0 \\ \text{-------} & \text{-------} & \text{-} & \text{------} & \text{------} & \text{-} & \text{-------} & \text{-------} & \text{-} \\ \text{-------} & \text{-------} & \text{-} & \text{------} & \text{------} & \text{-} & \text{-------} & \text{-------} & \text{-} \\ \text{-------} & \text{-------} & \text{-} & \text{------} & \text{------} & \text{-} & \text{-------} & \text{-------} & \text{-} \\ \text{-------} & \text{-------} & \text{-} & \text{------} & \text{------} & \text{-} & \text{-------} & \text{-------} & \text{-} \\ \text{-------} & \text{-------} & \text{-} & \text{------} & \text{------} & \text{-} & \text{-------} & \text{-------} & \text{-} \\ \text{-------} & \text{-------} & \text{-} & \text{------} & \text{------} & \text{-} & \text{-------} & \text{-------} & \text{-} \end{bmatrix} \begin{bmatrix} \eta_1 \\ \eta_2 \\ \eta_3 \\ \eta_4 \\ \eta_5 \\ \eta_6 \\ \eta_7 \\ \eta_8 \\ \eta_9 \end{bmatrix} \tag{B13}$$

where Q_4 to Q_9 are normal coordinates for rotation and translation. The elements of $\underline{L}^{-1}$ in equation (B13) that are pertinent to rotation and translation have been indicated by dashes since they are not relevant to finding spectroscopic constants. Thus the $\underline{L}^{-1}$ matrix has been determined to the extent necessary in the following calculations.

Evaluation of Potential Energy

To obtain additional spectroscopic constants by the perturbation method of Nielsen (ref. 27), the cubic and quartic terms in the potential energy are needed in addition to the quadratic terms. All these terms are obtained by deducing the correct form of the potential energy and then selecting the constants to fit Conroy's calculated potential (ref. 5). This is explained in more detail in the following paragraphs.

The correct form for the potential energy is obtained by noting that the potential energy must be invariant for all symmetry operations permitted by point group D_{3h} even when H_3^+ is vibrating. By application of group theory (refs. 13 and 25) this yields

$$\begin{aligned} V = V_e + \frac{1}{2}\left[\lambda_1 Q_1^2 + \lambda_2\left(Q_{21}^2 + Q_{22}^2\right)\right] + k_{111}Q_1^3 + k_{122}Q_1\left(Q_{21}^2 + Q_{22}^2\right) + k_{1111}Q_1^4 \\ + k_{1122}Q_1^2\left(Q_{21}^2 + Q_{22}^2\right) + k_{2222}\left(Q_{21}^2 + Q_{22}^2\right)^2 + \text{higher order terms} \end{aligned} \tag{B14}$$

where V_e is the potential energy at equilibrium, and k_{111}, k_{122}, k_{1111}, k_{1122}, and

k_{2222} are force constants. Expressing equation (B14) in terms of changes in bond lengths and omitting higher order terms gives

$$\begin{aligned}
V = V_e &+ \frac{B_1}{2}\left(\mathcal{S}_1^2 + \mathcal{S}_2^2 + \mathcal{S}_3^2\right) + \frac{B_2}{2}\left(\mathcal{S}_1\mathcal{S}_2 + \mathcal{S}_1\mathcal{S}_3 + \mathcal{S}_2\mathcal{S}_3\right) + (B_3 + B_4)\left(\mathcal{S}_1^3 + \mathcal{S}_2^3 + \mathcal{S}_3^3\right) \\
&+ (6B_3 - 3B_4)\, \mathcal{S}_1\mathcal{S}_2\mathcal{S}_3 + 3B_3\left(\mathcal{S}_1^2\mathcal{S}_2 + \mathcal{S}_1\mathcal{S}_2^2 + \mathcal{S}_2^2\mathcal{S}_3 + \mathcal{S}_2\mathcal{S}_3^2 + \mathcal{S}_3^2\mathcal{S}_1 + \mathcal{S}_3\mathcal{S}_1^2\right) \\
&+ (B_5 + B_6 + B_7)\left(\mathcal{S}_1^4 + \mathcal{S}_2^4 + \mathcal{S}_3^4\right) + (4B_5 + B_6 - 2B_7)\left(\mathcal{S}_1^3\mathcal{S}_2 + \mathcal{S}_1^3\mathcal{S}_3 + \mathcal{S}_2^3\mathcal{S}_1\right. \\
&\left. + \mathcal{S}_2^3\mathcal{S}_3 + \mathcal{S}_3^3\mathcal{S}_1 + \mathcal{S}_3^3\mathcal{S}_2\right) + (6B_5 + 3B_7)\left(\mathcal{S}_1^2\mathcal{S}_2^2 + \mathcal{S}_1^2\mathcal{S}_3^2 + \mathcal{S}_2^2\mathcal{S}_3^2\right) \\
&+ (12B_5 - 3B_6)\left(\mathcal{S}_1^2\mathcal{S}_2\mathcal{S}_3 + \mathcal{S}_2^2\mathcal{S}_1\mathcal{S}_3 + \mathcal{S}_3^2\mathcal{S}_1\mathcal{S}_2\right)
\end{aligned} \tag{B15}$$

where B_3 to B_7 are given by

$$\left.\begin{aligned}
B_3 &\equiv m^{3/2}\,\frac{k_{111}}{27} \\
B_4 &\equiv m^{3/2}\,\frac{4k_{122}}{27} \\
B_5 &\equiv m^{2}\,\frac{k_{1111}}{81} \\
B_6 &\equiv m^{2}\,\frac{4k_{1122}}{81} \\
B_7 &\equiv m^{2}\,\frac{16k_{2222}}{81}
\end{aligned}\right\} \tag{B16}$$

Conroy's computed H_3^+ potential is shown in figure 2. He obtained an equilibrium internuclear distance r_e of 1.68 Bohrs (8.8900×10^{-9} cm) and a potential energy V_e at equilibrium of -0.357 Hartree (-7.835×10^{4} cm^{-1}). Conroy very kindly furnished large graphs similar to figure 2 of this report and to figure 8 of reference 5. Potential energies and internuclear distances were read from these two graphs by means of an optical comparitor. Points along lines J, Q, and S (fig. 2) with potentials of -0.29 Hartree (-6.36×10^{4} cm^{-1}) or less were used in fitting V (eq. (B15)) to Conroy's potential by minimizing the sum of the squares of the deviations. It was impossible to get a realistic fit by holding r_e and V_e at the values recommended by Conroy and varying B_1 to B_7. Instead, the nine quantities r_e, V_e, and B_1 to B_7 were all varied simultaneously. The resulting least-squares fit gave

$$\left.\begin{aligned}
r_e &= 1.66597 \text{ Bohrs } (0.88158\times10^{-8} \text{ cm})\\
V_e &= -0.354771 \text{ Hartree } (-7.7863\times10^{4} \text{ cm}^{-1})\\
B_1 &= 0.2709 \text{ Hartree/Bohr}^2 \; (2.123\times10^{21} \text{ cm}^{-1}/\text{cm}^2)\\
B_2 &= -0.11736 \text{ Hartree/Bohr}^2 \; (-9.198\times10^{20} \text{ cm}^{-1}/\text{cm}^2)\\
B_3 &= -0.008914 \text{ Hartree/Bohr}^3 \; (-1.3203\times10^{28} \text{ cm}^{-1}/\text{cm}^3)\\
B_4 &= -0.06664 \text{ Hartree/Bohr}^3 \; (-9.870\times10^{28} \text{ cm}^{-1}/\text{cm}^3)\\
B_5 &= 0.0016468 \text{ Hartree/Bohr}^4 \; (4.609\times10^{35} \text{ cm}^{-1}/\text{cm}^4)\\
B_6 &= 0.012395 \text{ Hartree/Bohr}^4 \; (3.469\times10^{36} \text{ cm}^{-1}/\text{cm}^4)\\
B_7 &= -0.016949 \text{ Hartree/Bohr}^4 \; (-4.744\times10^{36} \text{ cm}^{-1}/\text{cm}^4)
\end{aligned}\right\} \qquad \text{(B17)}$$

Attempts to include points with larger potential energies in the fit were unsuccessful for some unknown reason. The reason was probably either lack of higher order terms in equation (B15) or inaccuracies in figure 2 of this report and figure 8 of reference 5.

As might be expected, equation (B15) with constants from equation (B17) fit Conroy's potential (fig. 2) near the bottom of the potential well, as shown in figure 4, but not at higher potential energies. However, this was considered satisfactory because the fit is only used to calculate partition functions at temperatures low enough that most of the H_3^+ ions occupy states near the bottom of the potential energy well.

Perturbation Calculation and Final Results

Nielsen (ref. 27) has carried out a second-order perturbation calculation to get the vibration-rotation energies of any polyatomic molecule except those with tetrahedral symmetry or internal rotation. In this section Nielsen's equations are applied to H_3^+ to obtain its vibration-rotation energies and spectroscopic constants. Before doing this, it was necessary to correct a number of typographical errors in reference 27 in addition to the errors in reference 27 subsequently corrected by Nielsen (ref. 29). The necessary force constants and equilibrium internuclear distance for H_3^+ were obtained from the least-squares fit in the preceding section.

It is customary in spectroscopic work to use term values rather than energy levels. A term value is defined as E/hc where E is the energy level, h is Planck's constant, and c is the speed of light. Based on Nielsen's equations and on the results of the section Harmonic Oscillator Approximation, the term values of H_3^+ are

$$\begin{aligned}\frac{E}{hc} = \frac{E_o}{hc} &+ \omega_1\left(v_1 + \frac{1}{2}\right) + \omega_2(v_2 + 1) + x_{11}\left(v_1 + \frac{1}{2}\right)^2 + (x_{12} + x_{21})\left(v_1 + \frac{1}{2}\right)(v_2 + 1) \\ &+ x_{22}(v_2 + 1)^2 + x_{l_2 l_2} l_2^2 + J(J + 1)B_v - \kappa^2(B_v - C_v) - J^2(J + 1)^2 D_J \\ &- J(J + 1)\kappa^2 D_{J\kappa} - \kappa^4 D_\kappa \mp 2C_e \zeta_2 l_2 \kappa \end{aligned} \tag{B18}$$

where the quantum numbers v_1, v_2, l_2, κ, and J take on the values

$$\left.\begin{aligned} v_1 &= 0, 1, 2, 3, \ldots \\ v_2 &= 0, 1, 2, 3, \ldots \\ l_2 &= v_2, v_2 - 2, v_2 - 4, \ldots, 1, \text{ or } 0 \\ \kappa &= 0, 1, 2, 3, \ldots \\ J &= \kappa, \kappa + 1, \kappa + 2, \ldots \end{aligned}\right\} \tag{B19}$$

and the other quantities are constants. The E_o/hc term in equation (B18) was not evaluated by Nielsen and is probably very small. Consequently, it is neglected. The last term in equation (B18) accounts for the Coriolis splitting of the degenerate vibrational levels. Since the effect of Coriolis splitting on the partition function should be very small (ref. 30), the last term is neglected.

Expressions for the spectroscopic constants in equation (B18) with the exception of ζ_2 must all be found. From the section Harmonic Oscillator Approximation,

$$\omega_1 = \frac{\lambda_1^{1/2}}{2\pi c} \tag{B20}$$

$$\omega_2 = \frac{\lambda_2^{1/2}}{2\pi c} \tag{B21}$$

By using equation (B13) and Nielsen's relations (ref. 27), the remaining spectroscopic constants are

$$x_{11} = \frac{h}{32\pi^4 \omega_1^2 c^3}\left(3k_{1111} - \frac{15k_{111}^2}{8\pi^2 c^2 \omega_1^2}\right) \tag{B22}$$

$$x_{12} + x_{21} = \frac{h}{32\pi^4 \omega_1 \omega_2 c^3}\left[2k_{1122} - \frac{3k_{111}k_{122}}{2\pi^2 c^2 \omega_1^2} - \frac{k_{122}^2}{\pi^2 c^2\left(4\omega_2^2 - \omega_1^2\right)}\right] \tag{B23}$$

$$x_{22} = \frac{h}{32\pi^4 \omega_2^2 c^3}\left\{3k_{2222} - \frac{k_{122}^2}{4\pi^2 c^2}\left[\frac{1}{\omega_1^2} - \frac{1}{2\left(4\omega_2^2 - \omega_1^2\right)}\right]\right\} \tag{B24}$$

$$x_{l_2 l_2} = \frac{-h}{32\pi^4 \omega_2^2 c^3}\left[k_{2222} + \frac{k_{122}^2}{8\pi^2 c^2\left(4\omega_2^2 - \omega_1^2\right)} - \frac{4\pi^2 c^2 \omega_2^2}{I_{zz}^{(e)}}\right] \tag{B25}$$

$$B_v = B_e - \alpha_0 - \left(v_1 + \frac{1}{2}\right)\alpha_1 - (v_2 + 1)\,\alpha_2 \tag{B26}$$

$$C_v = C_e - \gamma_0 - \left(v_1 + \frac{1}{2}\right)\gamma_1 - (v_2 + 1)\,\gamma_2 \tag{B27}$$

$$D_J = B_e^3\left(\frac{2}{\omega_1^2} + \frac{2}{\omega_2^2}\right) \tag{B28}$$

$$D_{J\kappa} = -B_e^3\left(\frac{2}{\omega_1^2} + \frac{4}{\omega_2^2}\right) \tag{B29}$$

$$D_\kappa = B_e^3\left(\frac{1}{2\omega_1^2} + \frac{2}{\omega_2^2}\right) \tag{B30}$$

where, according to Nielsen (ref. 29), α_0 and γ_0 are small and may be neglected and

$$B_e = \frac{h}{8\pi^2 I_{xx}^{(e)} c} \tag{B31}$$

$$\alpha_1 = -\frac{3B_e h}{8\pi^2 c I_{xx}^{(e)} \omega_1}\left\{1 + \frac{\left[I_{zz}^{(e)}\right]^{1/2} k_{111}}{2\pi^2 c^2 \omega_1^2}\right\} \tag{B32}$$

$$\alpha_2 = -\frac{B_e h}{16\pi^2 c I_{xx}^{(e)} \omega_2}\left\{6 + \frac{\left[I_{zz}^{(e)}\right]^{1/2} k_{122}}{\pi^2 c^2 \omega_1^2}\right\} \tag{B33}$$

$$C_e = \frac{h}{8\pi^2 I_{zz}^{(e)} c} = \frac{B_e}{2} \tag{B34}$$

$$\gamma_1 = -\frac{3B_e h}{8\pi^2 c I_{zz}^{(e)} \omega_1}\left\{1 + \frac{\left[I_{zz}^{(e)}\right]^{1/2} k_{111}}{2\pi^2 c^2 \omega_1^2}\right\} \tag{B35}$$

$$\gamma_2 = -\frac{B_e h k_{122}}{16\pi^4 c^3 \left[I_{zz}^{(e)}\right]^{1/2} \omega_1^2 \omega_2} \tag{B36}$$

For calculating the partition function, the rotational-stretching constant ρ is required in Woolley's approximation (ref. 12) rather than the constants D_J, $D_{J\kappa}$, and D_κ. These four quantities are related by the following equation (ref. 31):

$$\rho = \frac{k}{hc}\left[\frac{3(D_J + D_{J\kappa} + D_\kappa)}{4C_e^2} + \frac{2D_J}{B_e^2} + \frac{2D_J + D_{J\kappa}}{2C_e B_e}\right] \tag{B37}$$

Equations (B28) to (B30), (B34), and (B37) result in

$$\rho = \frac{kB_e}{hc}\left(\frac{15}{2\omega_1^2} + \frac{4}{\omega_2^2}\right) \tag{B38}$$

The spectroscopic constants were evaluated from equations (B9), (B16), (B17), (B20) to (B25), (B31) to (B36), and (B38) and are

$$\left.\begin{aligned} \omega_1 &= 3476\ \mathrm{cm}^{-1} & C_e &= 21.52\ \mathrm{cm}^{-1} \\ \omega_2 &= 3601\ \mathrm{cm}^{-1} & \alpha_1 &= 1.1848\ \mathrm{cm}^{-1} \\ x_{11} &= -70.40\ \mathrm{cm}^{-1} & \alpha_2 &= 0.1303\ \mathrm{cm}^{-1} \\ x_{12} + x_{21} &= -180.43\ \mathrm{cm}^{-1} & \gamma_1 &= 0.5924\ \mathrm{cm}^{-1} \\ x_{22} &= -76.11\ \mathrm{cm}^{-1} & \gamma_2 &= 0.8372\ \mathrm{cm}^{-1} \\ x_{l_2 l_2} &= 23.83\ \mathrm{cm}^{-1} & \rho &= 2.780\times10^{-5}\ {}^{\circ}\mathrm{K}^{-1} \\ B_e &= 43.05\ \mathrm{cm}^{-1} \end{aligned}\right\} \tag{B39}$$

Values for ω_1 and ω_2 obtained by other investigators from calculated potential energies are given in table I. The agreement is not good, but the values (eq. (B39)) used in this report are probably the most reliable. It is probable that not one of the constants in equation (B39) is accurate to the number of significant digits given, because the H_3^+ potential energy (ref. 5) was not evaluated for a sufficient number of isosceles or equilateral triangle configurations nor for any scalene triangle configurations.

Since the ground electronic state of H_3^+ is a $^1A_1$ state, it has an electronic degeneracy g_e of 1.

The energy D_o required to dissociate H_3^+ in its rotationless ground vibrational state into two ground state H atoms and a proton (all infinitely separated) is obtained by subtracting the zero-point energy from the absolute value of V_e and is 72 707 centimeters^{-1}.

From equations (B18) and (B39) the nondegenerate fundamental frequency ω_1' is 3155 centimeters^{-1} and the doubly degenerate fundamental frequency ω_2' is 3306 centimeters^{-1}. This completes the calculation of the spectroscopic constants and dissociation energy of H_3^+.

APPENDIX C

HIGH-TEMPERATURE APPROXIMATION FOR THE PARTITION FUNCTION OF H_3^+

At temperatures of the order of 10 000° K and higher, the usual approximations (ref. 12) for the partition functions of polyatomic molecules and molecular ions do not, in general, give accurate results, nor does equation (B18) have sufficient terms to accurately predict all the energy levels of H_3^+ that contribute significantly to the internal partition function. Instead, in this appendix the partition function of H_3^+ is calculated classically, and corrections for the quantization of vibration are then applied. Due to necessary assumptions, the treatment is quite approximate.

Analysis

The determination of the internal partition function of H_3^+ starts with equation (11-131) of Davidson (ref. 32). Davidson makes no distinction between bound states of a molecule and states in which the atoms have too much energy relative to one another to be bound. Hence, the partition function for all these three-atom states collectively is

$$q''_{ct} = \frac{1}{h^9} \int_W \int_W \int_W \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\mathcal{H}/kT}\, d^3\vec{p}_1\, d^3\vec{p}_2\, d^3\vec{p}_3\, d^3\vec{r}_1\, d^3\vec{r}_2\, d^3\vec{r}_3 \tag{C1}$$

where q''_{ct} is the classical partition function including translation of the atoms, the $\vec{r}$ vectors all have an origin fixed in space, W is the volume of the container, and the number subscripts 1, 2, and 3 refer to the three atoms, respectively. The Hamiltonian $\mathcal{H}$ is given by

$$\mathcal{H} = \sum_{j=1}^{3} \frac{\vec{p}_j \cdot \vec{p}_j}{2m} + V\left(\vec{r}_1, \vec{r}_2, \vec{r}_3\right) \tag{C2}$$

If equation (C2) is substituted into equation (C1), the momentum integrals can be evaluated with the result

$$q''_{ct} = \left(\frac{2\pi mkT}{h^2}\right)^{9/2} Z'' \tag{C3}$$

where Z'' is the configuration integral given by

$$Z'' = \int_W \int_W \int_W e^{-V/kT}\, d^3\vec{r}_1\, d^3\vec{r}_2\, d^3\vec{r}_3 \tag{C4}$$

Let r_{12} be the distance between atoms 1 and 2, r_{13} the distance between atoms 1 and 3, and r_{23} the distance between atoms 2 and 3 (fig. 5). The crude assumption is made that V is the sum of three two-atom potential energies, irrespective of where the two electrons are; that is,

$$V = U_{12}(r_{12}) + U_{13}(r_{13}) + U_{23}(r_{23}) \tag{C5}$$

Hill (ref. 26) has shown that $\exp(-U_{12}/kT)$ may be expressed as

$$e^{-U_{12}/kT} = e^{-U_{12}^{*}/kT} + e^{-U_{12}^{\ddagger}/kT} \tag{C6}$$

and similarly for U_{13} and U_{23}. Here U_{ij}^{*} is the effective potential energy between unbound atoms i and j and is given by

$$U_{ij}^{*}(r_{ij}) = \begin{cases} U_{ij}(r_{ij}) & U_{ij}(r_{ij}) > 0 \\ U_{ij}(r_{ij}) - kT \ln\left[1 - F(r_{ij})\right] & U_{ij}(r_{ij}) \leq 0 \end{cases} \tag{C7}$$

where the function $F(r_{ij})$ has been defined by Hill (ref. 26). The quantity $U_{ij}^{\ddagger}$ is the effective potential energy between bound atoms i and j and is given by

$$U_{ij}^{\ddagger}(r_{ij}) = \begin{cases} \infty & U_{ij}(r_{ij}) > 0 \\ U_{ij}(r_{ij}) - kT \ln F(r_{ij}) & U_{ij}(r_{ij}) \leq 0 \end{cases} \tag{C8}$$

Combining equations (C4) to (C6) results in

$$
\begin{aligned}
Z'' = \int_W \int_W \int_W \Big[& e^{-(U^*_{12}+U^*_{13}+U^*_{23})/kT} + e^{-(U^*_{12}+U^\ddagger_{13}+U^*_{23})/kT} \\
& + e^{-(U^\ddagger_{12}+U^*_{13}+U^*_{23})/kT} + e^{-(U^*_{12}+U^*_{13}+U^\ddagger_{23})/kT} + e^{-(U^\ddagger_{12}+U^\ddagger_{13}+U^*_{23})/kT} \\
& + e^{-(U^*_{12}+U^\ddagger_{13}+U^\ddagger_{23})/kT} + e^{-(U^\ddagger_{12}+U^*_{13}+U^\ddagger_{23})/kT} + e^{-(U^\ddagger_{12}+U^\ddagger_{13}+U^\ddagger_{23})/kT} \Big] \\
& d^3\vec{r}_1 \, d^3\vec{r}_2 \, d^3\vec{r}_3
\end{aligned}
\tag{C9}
$$

The first four terms in equation (C9) correspond to states in which at least one atom is not bound to any other atom and hence should be discarded. Integrals involving the next three terms are equal because of symmetry. Therefore, the appropriate configuration integral Z' for H_3^+ is the sum of the last four terms in equation (C9) or

$$
Z' = \int_W \int_W \int_W \left[3e^{-(U^*_{12}+U^\ddagger_{13}+U^\ddagger_{23})/kT} + e^{-(U^\ddagger_{12}+U^\ddagger_{13}+U^\ddagger_{23})/kT} \right] d^3\vec{r}_1 \, d^3\vec{r}_2 \, d^3\vec{r}_3
\tag{C10}
$$

To evaluate equation (C10), it is necessary to express $d^3\vec{r}_1 \, d^3\vec{r}_2 \, d^3\vec{r}_3$ in terms of r_{12}, r_{13}, and r_{23}. The coordinate system for this transformation is shown in figure 5. Proton 2 is the origin for polar coordinates r_{12}, θ_1, φ_1 of proton 1. An extension of r_{12} serves as the z' axis for polar coordinates r_{13}, θ_2, φ_2 of proton 3 with proton 1 as the origin. Obviously,

$$
\left| d^3\vec{r}_1 \, d^3\vec{r}_2 \, d^3\vec{r}_3 \right| = \left| d^3\vec{r}_2 \, r_{12}^2 \, dr_{12} \sin\theta_1 \, d\theta_1 \, d\varphi_1 \, r_{13}^2 dr_{13} \sin\theta_2 \, d\theta_2 \, d\varphi_2 \right|
\tag{C11}
$$

The integrand in equation (C10) is independent of $\vec{r}_2$, φ_1, θ_1, and φ_2, so these six integrations can be carried out immediately. Integration over $\vec{r}_2$ gives the volume W. Equation (C11) becomes

$$
\int_{\varphi_2} \int_{\varphi_1} \int_{\theta_1} \int_W \left| d^3\vec{r}_2 \, r_{12}^2 \, dr_{12} \sin\theta_1 \, d\theta_1 \, d\varphi_1 \, r_{13}^2 dr_{13} \sin\theta_2 \, d\theta_2 \, d\varphi_2 \right|
$$

$$
= \left| 8\pi^2 W r_{12} \, dr_{12} \, r_{13} \, dr_{13} \, r_{23} \, dr_{23} \right|
\tag{C12}
$$

Combining equations (C10), (C11), and (C12) gives

$$Z' = 8\pi^2 W(3I_1 + I_2) \tag{C13}$$

where

$$I_1 \equiv \int_0^\infty r_{12} e^{-U_{12}^\ddagger/kT} \int_0^\infty r_{13} e^{-U_{13}^\ddagger/kT} \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} r_{23} e^{-U_{23}^\ddagger/kT} \, dr_{23} \, dr_{13} \, dr_{12} \tag{C14}$$

and

$$I_2 \equiv \int_0^\infty r_{12} e^{-U_{12}^\ddagger/kT} \int_0^\infty r_{13} e^{-U_{13}^\ddagger/kT} \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} r_{23} e^{-U_{23}^\ddagger/kT} \, dr_{23} \, dr_{13} \, dr_{12} \tag{C15}$$

The corresponding classical partition function including translation is

$$q'_{ct} = \left(\frac{2\pi mkT}{h^2}\right)^{9/2} Z' \tag{C16}$$

(Compare with eq. (C3)).

Equation (C16) was derived classically, so it requires two corrections: (1) it must be multiplied by the electronic degeneracy g_e and (2) it must be divided by the symmetry number σ. To obtain the internal partition function q'_c, the resulting expression must be divided by the translational partition function of the H_3^+ ion; that is,

$$q'_c = \frac{8\pi^2 g_e}{3^{3/2}\sigma} \left(\frac{2\pi mkT}{h^2}\right)^3 (3I_1 + I_2) \tag{C17}$$

The usual internal partition function q_c has the energy of the rotationless ground vibrational state as reference energy. Since q'_c has infinitely separated $H + H + H^+$ as the reference energy,

$$q_c = q'_c e^{-hcD_o/kT} \tag{C18}$$

where D_o is multiplied by hc because D_o is given in centimeters^{-1} in appendix B.

At low temperatures, equation (C18) is not accurate because the vibrations are quantized. As Davidson (ref. 32) has pointed out, this can be corrected for the l^{th} normal vibration by multiplying the classical partition function by the ratio $\mathcal{R}_l$ of the quantum-mechanical harmonic-oscillator partition function to the classical harmonic-oscillator partition function.

$$\mathcal{R}_l = \frac{u_l e^{-u_l/2}}{1 - e^{-u_l}} \tag{C19}$$

where

$$u_l \equiv \frac{hc\omega'_l}{kT} \tag{C20}$$

At high temperature, $\mathcal{R}_l$ approaches 1.

The final internal partition function $q_{H_3^+}$ is then given by

$$\begin{aligned} q_{H_3^+} &= q_c \mathcal{R}_1 \mathcal{R}_2^2 \\ &= \frac{8\pi^2 g_e}{3^{3/2}\sigma}\left(\frac{2\pi mkT}{h^2}\right)^3 (3I_1 + I_2)e^{-hcD_o/kT} \mathcal{R}_1\mathcal{R}_2^2 \end{aligned} \tag{C21}$$

where $\mathcal{R}_2$ is squared because ω'_2 belongs to a doubly degenerate vibration.

Description of Digital Computer Program

Equation (C21) was evaluated by means of a FORTRAN IV program for the Lewis IBM 7094 digital computer.

The two-atom potential energy $U(r_{ij})$ was obtained by taking one-third of Conroy's $V(r_{ij})$ for the equilateral triangular configuration (after adding 1.00 Hartree

(2.19475×10^{5} cm^{-1}) to Conroy's values, of course). These V's are given on the line labeled Q in figure 2 and were read with an optical comparitor on large graphs similar to figure 2 of this report and to figure 8 of reference 5. These large graphs were very kindly furnished by Conroy. Thus $U(r_{ij})$ was obtained for internuclear distances from 0.4768×10^{-8} to 1.9473×10^{-8} centimeter.

For larger and smaller internuclear distances, it was necessary to extrapolate $U(r_{ij})$. For internuclear distances less than 0.4768×10^{-8} centimeter, a Morse potential (ref. 33) passing through the points $U(0.4768\times10^{-8})$ and $U(0.4937\times10^{-8})$ and with the same potential well depth as $U(r_{ij})$ obtained from Conroy's data was used. For internuclear distances greater than 1.9473×10^{-8} centimeter, another Morse potential passing through the points $U(1.8748\times10^{-8})$ and $U(1.9473\times10^{-8})$ and with the same potential well depth as $U(r_{ij})$ obtained from Conroy's data was used.

The triple integrals I_1 and I_2 were evaluated by numerical methods in the program. The values of $q_{H_3^+}$ calculated by the program were mathematically accurate to within 0.03 percent.

APPENDIX D

COMPUTER PROGRAM FOR WKB ROTATIONAL ENERGIES OF DIATOMIC MOLECULES AND MOLECULAR IONS

No complete table of vibration-rotation energies or term values of any diatomic molecule or molecular ion is available directly from an analysis of observed molecular bands. Such a complete table is necessary to calculate an accurate internal partition function for a diatomic molecule or molecular ion at high temperatures. Vibration-rotation energies may be calculated from theory if the potential energy U(r) of the molecule is known. For H_2^+ the potential energy and vibrational energies are known from quantum theory (refs. 15 and 23). For many diatomic molecules, the most reliable potential energy curve that is obtainable is one calculated by the Rydberg-Klein-Rees (RKR) method (refs. 34, 35, and 36) which involves application of the WKB approximation (refs. 37 and 38) to observed molecular bands, the calculation of vibrational energies being an intermediate step.

Since the vibration-rotation energy may be regarded as the sum of vibrational and rotational energies, a complete table of rotational energies (or term values) is generally the only missing data for calculating accurate internal partition functions. The program in this appendix calculates either a complete table of vibration-rotation term values or a complete table of rotational term values if a potential energy table is given as input.

In the past, vibration-rotation energies of diatomic molecules have been calculated by at least three methods. Davidson (ref. 39) and Cooley (ref. 40) found a few energy eigenvalues of the appropriate second-order differential equation by supplying initial estimates of the vibration-rotation energy eigenvalues and iterating. Woolley, Scott, and Brickwedde (ref. 20) used the WKB connection formula to find noninteger values of the vibrational quantum number for given vibration-rotation term values and total angular momentum.

For H_2^+ three very sophisticated methods (refs. 15, 22, and 24) have been used to compute a few vibration-rotation energy eigenvalues to higher accuracy than for any diatomic molecule.

For calculating partition functions, extremely accurate vibration-rotation energies are not required. Since in most cases the available potential energies are based on the RKR and WKB approximations, it is consistent to use the WKB connection formula to compute vibration-rotation energies. In this appendix the WKB connection formula is used to calculate vibration-rotation energy eigenvalues for any diatomic molecular ion or diatomic molecule to which the assumptions and restrictions listed in the next section apply. The described program has the unique advantages that it is unnecessary to know beforehand if a state exists and that no initial estimates of vibration-rotation energies (or term values) are needed as input.

Assumptions and Restrictions

The assumptions and restrictions utilized inthe program are listed herein for convenience; they are as follows:

(1) Only $^1\Sigma$ electronic states and electronic states obeying Hund's coupling cases (a) and (b) (ref. 33) are considered. (The ground state of H_2^+ is a $^2\Sigma$ state and obeys Hund's case (b)).

(2) The extensions of the Born-Oppenheimer approximation (refs. 41 and 42) are assumed to be applicable.

(3) The potential energy U(r) possesses only one well, as shown in figure 6, but it may have a hump (not shown).

(4) The electronic state has no more than 100 vibrational energy eigenvalues (or term values) for its ground rotational state.

Analysis

In this section Hund's coupling cases (a) and (b) are treated. When the total electron spin S and the component of orbital angular momentum along the internuclear axis Λ are zero, both coupling cases reduce to the case for $^1\Sigma$ states. The effective potentials for use with the WKB connection formula are given.

Hund's coupling case (a). - In Hund's coupling case (a) the electronic motion including spin is coupled very strongly to the internuclear axis. From the relations given by Van Vleck (ref. 41) and Kronig (ref. 42) it can be shown that the differential equation for the radial wave function P(r) is approximately

$$\left\{B \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) - W_a'(r) - B\left[J(J + 1) - 2\Lambda^2 - 2\Sigma\Omega + S(S + 1) + \frac{4\pi^2\langle \vec{L} \cdot \vec{L}\rangle}{h^2}\right] + E_F\right\} P(r) = 0 \qquad \text{(D1)}$$

where $\langle\ \rangle$ indicates a time average over the electronic coordinates.

The vibrational wave function ψ is defined by

$$\psi \equiv r\ P(r) \tag{D2}$$

Combining equations (D1) and (D2) gives

$$\frac{\partial^2\psi}{\partial r^2} + \frac{8\pi^2\mu}{h^2}\left\{E_F - W_a'(r) - \frac{h^2}{8\pi^2\mu r^2}\left[J(J+1) - 2\Lambda^2 - 2\Sigma\Omega + S(S+1) + \frac{4\pi^2\langle\vec{L}\cdot\vec{L}\rangle}{h^2}\right]\right\}\psi = 0 \tag{D3}$$

The WKB connection formula (ref. 38) for equation (D3) is

$$2(2\mu hc)^{1/2}\int_{r_{min}}^{r_{max}}\left\{\mathscr{F}(v,J) - U_a'(r) - \frac{h}{8\pi^2\mu r^2 c}\left[J(J+1) - 2\Lambda^2 - 2\Sigma\Omega + S(S+1) + \frac{4\pi^2\langle\vec{L}\cdot\vec{L}\rangle}{h^2}\right]\right\}^{1/2} dr = \left(v + \frac{1}{2}\right)h \qquad v = 0,\ 1,\ 2,\ \ldots \tag{D4}$$

where $\mathscr{F}$ is the vibration-rotation term value

$$\mathscr{F}(v,J) \equiv \frac{E_F}{hc} \tag{D5}$$

and

$$U_a'(r) \equiv \frac{W_a'(r)}{hc} \tag{D6}$$

and v is the vibrational quantum number. Equation (D4) can also be written

$$2(2\mu hc)^{1/2}\int_{r_{min}}^{r_{max}}\left[\mathscr{F}(v,J) - U_a''(r,J)\right]^{1/2} dr = \left(v + \frac{1}{2}\right)h \qquad v = 0,\ 1,\ 2,\ \ldots \tag{D7}$$

where U_a'' is an effective potential given by

$$U_a''(r, J) \equiv U_a(r) + \frac{hJ(J + 1)}{8\pi^2 \mu r^2 c} \tag{D8}$$

and

$$U_a(r) \equiv U_a'(r) + \frac{h}{8\pi^2 \mu r^2 c}\left[-2\Lambda^2 - 2\Sigma\Omega + S(S + 1) + \frac{4\pi^2\langle\vec{L} \cdot \vec{L}\rangle}{h^2}\right] \tag{D9}$$

The potential $U_a(r)$ is the quantity obtained by applying the RKR approximation to a molecular state obeying Hund's case (a).

Hund's coupling case (b). - In Hund's coupling case (b) only the electronic orbital motion is coupled very strongly to the internuclear axis. From the relations given by Kronig (ref. 42) and Mathews and Walker (ref. 38) it can be shown by a derivation similar to that for Hund's case (a) that the WKB connection formula is approximately

$$2(2\mu hc)^{1/2} \int_{r_{min}}^{r_{max}} \left[\mathscr{F}(v, K) - U_b''(r, K)\right]^{1/2} dr = \left(v + \frac{1}{2}\right)h \qquad v = 0,\ 1,\ 2,\ .\ .\ . \tag{D10}$$

where

$$U_b''(r, K) \equiv U_b(r) + \frac{hK(K + 1)}{8\pi^2 \mu r^2 c} \tag{D11}$$

$$U_b(r) \equiv U_b'(r) + \frac{h}{8\pi^2 \mu r^2 c}\left(-2\Lambda^2 + \frac{4\pi^2\langle\vec{L} \cdot \vec{L}\rangle}{h^2}\right) \tag{D12}$$

The potential $U_b(r)$ is the quantity obtained by applying the RKR approximation to a molecular state obeying Hund's case (b).

$^1\Sigma$ electronic states. - The WKB connection formula for $^1\Sigma$ states may be obtained from equations (D7) to (D9) or (D10) to (D12) and is as follows:

$$2(2\mu hc)^{1/2} \int_{r_{min}}^{r_{max}} \left[\mathscr{F}(v, J) - U''_\sigma(r, J)\right]^{1/2} dr = \left(v + \frac{1}{2}\right)h \qquad v = 0,\ 1,\ 2,\ \ldots \tag{D13}$$

where

$$U''_\sigma(r, J) \equiv U_\sigma(r) + \frac{hJ(J + 1)}{8\pi^2 \mu r^2 c} \tag{D14}$$

and

$$U_\sigma(r) \equiv U'_\sigma(r) + \frac{\langle \vec{L} \cdot \vec{L} \rangle}{2\mu r^2 ch} \tag{D15}$$

The potential $U_\sigma(r)$ is the quantity obtained by applying the RKR approximation to a $^1\Sigma$ state.

Generalized variables and rotation quantum number. - Inspection of equations (D7), (D8), (D10), (D11), (D13), and (D14) shows that the WKB connection formulas and the expressions for the effective potentials all have the same form, so that one computer program can be used for Hund's case (a) or (b) or for $^1\Sigma$ states provided the following correspondences (reading across) are kept in mind:

Hund's coupling case (a)	Hund's coupling case (b)	$^1\Sigma$ electronic states	Generalized variable or quantum number	FORTRAN variable
U''_a	U''_b	U''_σ	U''	UPP
U_a	U_b	U_σ	U	U
J	K	J	j	AJ

In the remainder of this appendix, the generalized variables U'' and U and the generalized rotation quantum number j are used instead of the corresponding quantities for particular coupling cases.

Typical U and U'' are shown in figure 6. In figure 6 and in the program, the reference for energy is arbitrarily shifted to be $U(r_e)$. If U'' does not possess a well, there are no bound states. Even if U'' does possess a small well, there will not be any bound state unless the left-hand side of equation (D7), (D10), or (D13) (as appropriate) equals or exceeds $h/2$ when $\mathcal{F} = U''(r_{04})$ (see fig. 6).

The rotational term values f are found from

$$f(v, j) + \mathcal{F}(v, j) - \mathcal{F}(v, 0) \tag{D16}$$

Program Procedure

The program used to calculate $\mathcal{F}$ or f was programmed in FORTRAN IV, IBM Version 13, for an IBM 7094 digital computer with the Lewis monitor system. Basically, the program interpolates a small table of $U(r)$ given as input and obtains a large, equispaced table of $U(r)$. For each value of j provided as input, the program computes a large, equispaced table of $U''(r)$, determines if $U''(r)$ possesses a well, and, if U'' does, finds all $\mathcal{F}(v, j)$ by iteration of the generalized version of equations (D7), (D10), and (D13). These procedures are explained in detail in this section.

Interpolation of $U(r)$. - A set of points $U(r)$ provided as input are represented by circles in figure 6. (In an actual problem many more points would normally be provided as input). The same interpolation formula is not used for all values of r. Instead, r is divided into regions 1, 2, 3, and 4 as shown in figure 6. In regions 1 and 4, the four-point interpolation formula of Lagrange is used. In region 2, a third-degree polynominal in r with zero slope at r_e is chosen to pass through $U(r_e)$ and the two points to the left of r_e and is then used for interpolation. In region 3, a third-degree polynominal in r with zero slope at r_e is chosen to pass through $U(r_e)$ and the two points to the right of r_e and is then used for interpolation.

Interpolation of the points $U(r)$ provided as input produces a large table of $U(r)$ equispaced in r. The number of entries NMESH in this table is an input quantity. The first entry is the input point with smallest r, and the last entry is the input point with largest r.

Procedure for each j value. - For each value of j provided as input, all solutions $\mathcal{F}$ (if there are any) are obtained and $\mathcal{F}$ or f is printed out before going on to the next value of j.

Calculation and examination of $U''(r)$: The first step in this solution is to compute a value of $U''(r)$ for each $U(r)$ in the equispaced table by means of the generalized version of equations (D8), (D11), and (D14). All curves $U''(r)$ (fig. 6) possess two inflection points r_{01} and r_{02}. By iterating on the second derivative of $U''(r)$, the inflection point r_{01} (fig. 6) is found. Examination of the first derivative of $U''(r_{01})$

then reveals whether or not $U''(r)$ has a well. If the first derivative is positive, there is a well; otherwise there is not.

If there is a well, iterations on the first derivative of $U''(r)$ provide r_{03} and r_{04} (fig. 6). Setting $\mathscr{F}$ equal to $U''(r_{04})$ (see fig. 6) in the generalized version of equations (D7), (D10), and (D13) gives the maximum value of v, which is generally a noninteger and is designated v_{max}. If v_{max} is negative, there are no eigenvalues $\mathscr{F}$. If v_{max} is 0, there is only one $\mathscr{F}$ (i.e., $\mathscr{F} = U''(r_{04})$). If v_{max} is positive, there are truncate $(v_{max}) + 1$ eigenvalues $\mathscr{F}$, where truncate ( ) means to drop any fraction in the argument.

Table construction and search, and iteration: For v_{max} that is positive, a table search and one or two successive iteration procedures are used to find each eigenvalue $\mathscr{F}$ because the use of one iteration procedure alone is frequently inefficient or diverges in some case. Construction of the table, searching of the table, and iterating are explained in the following paragraphs.

For use in the table searches, a table of $v(\mathscr{F})$ is constructed from the generalized version of equations (D7), (D10), and (D13) for equispaced $\mathscr{F}$ possessing values from $U''(r_{03})$ to $U''(r_{04})$. The quantities $r_{min}(\mathscr{F})$ and $r_{max}(\mathscr{F})$ are also included in the table for use in the subsequent iterations. Although this table is adequate for table searches, v deviates substantially from being a linear function of $\mathscr{F}$, so v and $\mathscr{F}$ are not appropriate variables for iteration. To overcome this, a Morse potential $U_t(r)$ (ref. 33) is fit to each $U''(r)$ so that the dissociation asymptote of the Morse potential has the value $U''(r_{04})$. The vibrational term values $\mathscr{F}_t(v)$ of the Morse potential are used to obtain $\mathscr{F}_t(\mathscr{F})$. This is, in general, almost a linear relation, so $\mathscr{F}_t$ and $\mathscr{F}$ are appropriate variables for iteration, $\mathscr{F}_t$ being given. The table for use in table searches therefore includes the five variables v, $\mathscr{F}$, r_{min}, r_{max}, and $\mathscr{F}_t$. It should be emphasized that the use of $\mathscr{F}_t$ is merely a mathematical device to make iterations converge more rapidly and in no way affects the accuracy of the resulting eigenvalues $\mathscr{F}$.

To find each eigenvalue $\mathscr{F}$ corresponding to an integer v, the table is searched to find the interval in the table wherein v falls. The value of $\mathscr{F}_t$ corresponding to the desired integer v is calculated and linear interpolation is used M times (M is an input FORTRAN quantity) to get successively better values of $\mathscr{F}$. After M linear interpolations, iteration is performed by using linear interpolation or linear extrapolation based on the last two points calculated. If the new value of $\mathscr{F}$ so obtained falls outside the limits established in the table search, the new value of $\mathscr{F}$ is discarded, and five more linear interpolations are performed before attempting iteration by linear interpolation or linear extrapolation based on the last two points. Either iteration procedure is halted when the absolute value of the estimated error in $\mathscr{F}$ is less than the input FORTRAN quantity TOL (the allowable error).

Output options: After all eigenvalues $\mathscr{F}(v, j)$ have been found for a given value of j, the input FORTRAN quantities GV are subtracted from them. If all GV are zero, the output FORTRAN quantities FV will be the vibration-rotation term values $\mathscr{F}(v, j)$. If the GV are assigned the values $\mathscr{F}(v, 0)$ determined from a previous run of the program, then according to equation (D16) the output quantities FV will be the rotational term values $f(v, j)$.

After writing (and, if specified, punching) the results for a given value of j, the processes are repeated for the next value of j.

Organization of program and description of subprograms: A block diagram of the program and its subprograms is given in figure 7. SIMPS1 is shown as a subprogram although at Lewis it is a built-in library function. Listings of the program and subprograms are given at the end of this appendix.

The calls of the subprograms and the operations performed by them are as follows:

The function LBINT has the call BINT(X, Y, Z, N) and performs four-point interpolation by the method of Lagrange. X and Y are the independent and dependent variables, respectively, in a table of N entries. Z is the argument (value of X desired). BINT is the interpolated value of Y.

The function LDER has the call DER(R) and is the first derivative of UPP with respect to internuclear distance R.

The subroutine LDIFU has the call DIFU(RLOW, RHIGH, ROOT, $ STATEMENT NO.) and finds the zero of UPP-FAA (FAA is a vibration-rotation term value in COMMON) which has R between RLOW and RHIGH. The value of R corresponding to the zero is ROOT.

The function LEN has the call EN(R). EN is the value of the squareroot inside the integral in the generalized version of equations (D7), (D10), and (D13).

The subroutine LROOT has the call FIND(UUU1, UUU2, G, DELR, ROOT, $ STATEMENT NO.) and finds the zero of some specified function G(R) for R between UUU1 and UUU2 by interval halving and linear interpolation. DELR is the spacing of the R table and is needed because G(R) is always derived from a table and is not continuous. The value of R corresponding to the zero is ROOT.

The function LSECD has the call SECD(R) and is the second derivative of UPP with respect to R.

The function LUP has the call UP(R). UP is the value of UPP at R obtained by linear interpolation of the equispaced UPP table.

The subroutine LVVV has the call VVV(F, RMINH, RMINL, RMAXH, RMAXL, V, RMIN, RMAX, $ STATEMENT NO.) and finds the vibrational quantum number V and corresponding near turning point RMIN and far turning point RMAX if the vibration-rotation term value F is given. It uses the generalized version of equations (D7), (D10), and (D13). RMINL and RMINH are the values of R between which the search for RMIN is made. RMAXL and RMAXH are the values of R between which the search for RMAX is made.

The function SIMPS1 has the call SIMPS1(RMIN, RMAX, EN, L) and finds the integral of the function EN(R) between the limits R = RMIN and R = RMAX by a modified Simpson's rule. If an accuracy of 1 part in 10^6 cannot be achieved, 1 is added to L to flag the result. SIMPS1 is the value of the integral. This function was developed by T. E. Fessler and W. F. Ford of Lewis Research Center.

Accuracy

When TOL is set at its usual value of 0.25 centimeter^{-1}, the accuracy of the computed $\mathscr{F}(v,j)$ or $f(v,j)$ is believed to be limited by the extended Born-Oppenheimer approximation, the WKB approximation, or insufficient points $U(r)$ provided as input rather than being limited by inaccuracies in the program itself. For example, rotational term values for H_2^+ (table V) computed by the program agreed within 0.9 centimeter^{-1} with rotational term values calculated from Wind's results (ref. 15). For the $X^1\Sigma_g^+$ state of H_2 the rotational term values agreed to within 7 centimeters^{-1} with rotational term values calculated from wave numbers of lines measured by Herzberg and Howe (ref. 43).

In general, slightly better accuracy is obtained if the program is used to compute $f(v,j)$ rather than $\mathscr{F}(v,j)$. If it is then desired to find $\mathscr{F}(v,j)$ by adding $f(v,j)$ and $\mathscr{F}(v,0)$, values of $\mathscr{F}(v,0)$ should be obtained from the same source as the potential $U(r)$.

Input

Table VI shows the input variables required as they are to be punched on the data cards. The simplified sample problem given is H_2^+ with only 30 potential energy points specified in addition to RE. The input FORTRAN variables are as follows:

NL	Number of members in UL and RL arrays; maximum of 100.
UL	Potential energy U for internuclear distances less than RE, measured from bottom of potential well (first value must be greater than dissociation energy), cm^{-1}.
RL	Internuclear distance r in monotonically increasing order; the RL array has a one-to-one correspondence with the UL array, Å (1 Å = 10^{-8} cm).
NR	Number of members in UR and RR arrays; maximum of 440.
UR	Potential energy U for internuclear distances greater than RE, measured from bottom of potential well, cm^{-1}.

RR	Internuclear distance r in monotonically increasing order; the RR array has a one-to-one correspondence with the UR array (a suggested value for the last RR is 25), Å (1 Å = 10^{-8} cm).
NJ	Number of members of AJ and NSTOP arrays; maximum of 45.
AJ	Generalized rotational quantum number j.
NSTOP	Number of mesh point where searches for zeros of first and second derivatives of effective potential with respect to internuclear distance are to stop; must be less than or equal to NMESH. The NSTOP array has a one-to-one correspondence with the AJ array. The purpose of this array of constants is to prevent searches at very large internuclear distances where the effective potential may be nearly constant, and consequently the four-point interpolation may cause erroneous values of the first and second derivatives of effective potential with respect to internuclear distance. If there is no reason to suspect such errors or if there is no basis for estimating NSTOP, it should be set equal to NMESH. A value of NSTOP corresponding to AJ = 0 must always be set equal to NMESH if the potential possesses no hump.
NV	Number of members of GV array; maximum of 100.
GV	Vibrational term values measured from bottom of potential well, in monotonically increasing order. If the number of vibrational term values is unknown or if it is desired to have FV of output be vibration-rotation term values, put in 100 zeros and set NV = 100. If it is desired to have FV of output be rotational term values, put in values of GV equal to FV from a previous AJ = 0 run which had all GV values equal to zero, cm^{-1}.
RE	Equilibrium internuclear distance, r_e, Å (1 Å = 10^{-8} cm).
RM	Reduced mass of the two atoms of the diatomic molecule or molecular ion, including masses of electrons, μ, g.
TOL	Allowable absolute value of estimated error in FV of output (a suggested value is 0.25 cm^{-1}), cm^{-1}.
NZ	Number of mesh points to be included in each increment in coarse search for negative second derivative of effective potential with respect to internuclear distance (a suggested value is the nearest integer to NMESH/50). If no negative second derivative is found in the coarse search, a fine search is always made.
NMESH	Number of potential energy and effective potential mesh points; maximum 5000 (a suggested value is 5000).

N	Maximum number of iterations to find FV of output (a suggested value is 10).
NRITE	A value of 1 will cause NMESH values of internuclear distance RRR, potential energy U, and effective potential UPP to be printed out. Zero will cause this output to be omitted.
NPUNCH	A value of 1 will cause output to be punched on cards in addition to being printed. Zero will cause the output shown in table VII to be printed only.
M	Number of interpolations in iteration on FV before switching to interpolation or extrapolation based on the last two values (a suggested value is 5).
NAME	Diatomic molecule and electronic state; this will appear on the printed output and on any cards punched out.

Output

The output for the sample problem is given in table VII. Each section of the output has been numbered to correspond to the following descriptions:

(1) The first output of the program is a listing of the input data.

(2) Output for AJ = 1, 30, and 41, respectively. There were 18, 7, and 1 rotational term values (eigenvalues) FV, respectively. The variables and their units are given in the next paragraph.

(3) Output for AJ = 43. The effective potential had a well but no eigenvalue FV.

(4) Output for AJ = 44. The effective potential did not have a well, so there were no eigenvalues FV. The slope of the effective potential at the inflection point r_{01} (fig. 6) was negative.

(5) Appearance of output that should be obtained if the slope of the effective potential at the inflection point r_{01} (fig. 6) was zero (this has never occurred).

In the output with descriptions (2) to (5), the 14 unlabeled numbers that extend in a row to the far right are the flags M and L(1) to L(13), respectively. The flags L(1) to L(13) are described in the following paragraph.

The variables unique to output are as follows:

VV	Vibrational quantum number, v.
FV	Eigenvalue, cm^{-1}. If all GV's are zero, FV is the vibrational-rotation term value $\mathcal{F}$. If the GV's are the vibrational term values, FV is the rotational term value f.
ERROR	Estimated error in FV, cm^{-1}.

The quantities VV, FV, and ERROR occur in triads along a row, each triad corresponding to an eigenvalue.

V(1)	Value of v_{max}.
F(1)	Effective potential $U''(r_{04})$ measured from bottom of potential well (see fig. 6), cm^{-1}.
V(100)	Value of v for bottom of effective potential well (always has value -0.5).
F(100)	Effective potential $U''(r_{03})$ measured from bottom of potential well (see fig. 6), cm^{-1}.
AJ	Generalized rotation quantum number j.
R4	Internuclear distance r_{04} (see fig. 6), Å (1 Å = 10^{-8} cm).
RRR(NSTOP)	Internuclear distance r at which searches for zeros of first and second derivatives of effective potential with respect to internuclear distance stop, Å (1 Å = 10^{-8} cm). For a valid solution R4 < RRR(NSTOP) unless (1) NSTOP = NMESH, (2) AJ is so small that there is little difference between U and UPP, and (3) UL has no hump.
L(1)	= 1 if search for negative second derivative of effective potential with respect to internuclear distance is unsuccessful. Normally, = 0.
L(2)	= 1 if search for inflection point r_{01} (fig. 6) is unsuccessful. Normally, = 0.
L(3)	= 1 if slope of effective potential at inflection point r_{01} (fig. 6) is negative. Normally, = 0.
L(4)	= 1 if search for r_{03} (fig. 6) is unsuccessful. Normally, = 0.
L(5)	= 1 if slope of effective potential at RRR(NSTOP) is positive or 0. This is satisfactory if (1) NSTOP = NMESH, (2) AJ is so small that there is little difference between U and UPP, and (3) UL has no hump. Normally, = 0.
L(6)	= 1 if search for r_{04} (fig. 6) is unsuccessful. Normally, = 0.
L(7)	= 1 if search for r_{min} for $\mathscr{F}(v_{max}, j)$ (see fig. 6) is unsuccessful. Normally, = 0.
L(8)	= 1 if there are more than 100 eigenvalues FV for a given AJ, thereby exceeding the capacity of the program. Normally, = 0.
L(9)	= 1 if search for r_{min} for $\mathscr{F} \neq \mathscr{F}(v_{max}, j)$ is unsuccessful. Normally, = 0.

L(10) = 1 if search for r_{max} is unsuccessful. Normally, = 0.

L(11) Positive if subprogram SIMPS1 is unable to integrate the generalized version of equation (D13) for $\mathcal{F}(v_{max}, j)$ to an accuracy of 1 part in 10^6 or better. Normally, = 0.

L(12) Positive if subprogram SIMPS1 is unable to integrate the generalized version of equation (D13) for $\mathcal{F} \neq \mathcal{F}(v_{max}, j)$ to an accuracy of 1 part in 10^6 or better. Normally, = 0.

L(13) = 1 if iteration to find FV does not converge in N iterations. Normally, = 0.

When NPUNCH = 1, values of VV, AJ, FV, and NAME will be punched on cards, in that order.

Running Characteristics

The time for the computer to execute solutions for 348 rotational term values with a tolerance of 0.25 centimeter^{-1} was 7 minutes. A case has not been found that required more than six iterations to converge to this accuracy.

If the program runs improperly for no apparent reason, set NRITE = 1 and check the UPP array for spurious bumps, which may result from inaccurate or too small UR or UL arrays.

Listing of Program

```
$IBFTC MAIN
C PROGRAM FOR WKB ROTATIONAL ENERGIES OF DIATOMIC MOLECULES AND
C MOLECULAR IONS
C
      EXTERNAL SECD,DER,EN
      DIMENSION RRR(5000),L(13),UL(100),RL(100),UR(440
     1),RR(440),AJ(45),GV(100),F(100),V(100),FV(100),VV(100),NSTOP(45)
     2,RMIN(100),RMAX(100),FFT(100),FFFT(100),ERROR(100)
      COMMON/BLOCK1/UPP,RRR,RATIO/BLOCK2/RM/BLOCK3/DELR,NMESH/BLOCK4/
     1FAA/BLOCK5/L
      DOUBLE PRECISION U(5000),UPP(5000),BINT
      EQUIVALENCE (U(1),UPP(1))
   42 READ(5,100)NL,(UL(I),I=1,NL)
      WRITE(6,101)NL,(UL(I),I=1,NL)
      READ(5,102)(RL(IA),IA=1,NL)
      WRITE(6,103)(RL(IA),IA=1,NL)
      READ(5,100)NR,(UR(IB),IB=1,NR)
      WRITE(6,105)NR,(UR(IB),IB=1,NR)
      READ(5,102)(RR(IC),IC=1,NR)
      WRITE(6,107)(RR(IC),IC=1,NR)
      READ(5,100)NJ,(AJ(ID),ID=1,NJ)
      WRITE(6,104)NJ,(AJ(ID),ID=1,NJ)
      READ(5,106)(NSTOP(IAA),IAA=1,NJ)
      WRITE(6,108)(NSTOP(IAA),IAA=1,NJ)
      READ(5,100)NV,(GV(IE),IE=1,NV)
      WRITE(6,109)NV,(GV(IE),IE=1,NV)
      READ(5,110)RE,RM,TOL,NZ,NMESH,N,NRITE,NPUNCH,M,NAME
      WRITE(6,111)RE,RM,TOL,NZ,NMESH,N,NRITE,NPUNCH,M,NAME
C END OF INPUT
C CONSTRUCT INTERNUCLEAR DISTANCE RRR ARRAY
      DELR=(RR(NR)-RL(1))/FLOAT(NMESH-1)
      RATIO=1./DELR
      RRR(1)=RL(1)
      DO 1 IG=2,NMESH
    1 RRR(IG)=RRR(IG-1)+DELR
C PRINT OUT RRR ARRAY
      IF(NRITE)44,44,43
   43 WRITE(6,121)
      KB= 1
  303 IF(KB-NMESH+8) 300,300,301
  300 KC= KB+7
      GO TO 302
  301 KC= NMESH
  302 WRITE(6,124)KB,(RRR(I),I=KB,KC)
      IF(KC-NMESH) 304,44,44
  304 KB= KB+8
```

```
      GO TO 303
   44 U(1)=UL(1)
C INTERPOLATE POTENTIAL UL IN REGION 1
      NLAS1=INT(1.+(RL(NL)-RRR(1))/DELR)
      DO 2 IH=2,NLAS1
    2 U(IH)=BINT(RL,UL,RRR(IH),NL)
C INTERPOLATE UL IN REGION 2
      NLAS2=INT(1.+(RE-RRR(1))/DELR)
      NFIR2=NLAS1+1
      DENOM=(RL(NL-1)-RE)**2*(RL(NL)-RE)**3-(RL(NL)-RE)**2*(RL(NL-1)-RE)
     1**3
      A=(UL(NL-1)*(RL(NL)-RE)**3-UL(NL)*(RL(NL-1)-RE)**3)/DENOM
      B=(UL(NL)*(RL(NL-1)-RE)**2-UL(NL-1)*(RL(NL)-RE)**2)/DENOM
      DO 3 II=NFIR2,NLAS2
    3 U(II)=(RRR(II)-RE)**2*(A+B*(RRR(II)-RE))
C INTERPOLATE POTENTIAL UR IN REGION 3
      NFIR3=NLAS2+1
      NLAS3=INT(1.+(RR(1)-RRR(1))/DELR)
      DENOM=(RR(1)-RE)**2*(RR(2)-RE)**3-(RR(2)-RE)**2*(RR(1)-RE)**3
      A=(UR(1)*(RR(2)-RE)**3-UR(2)*(RR(1)-RE)**3)/DENOM
      B=(UR(2)*(RR(1)-RE)**2-UR(1)*(RR(2)-RE)**2)/DENOM
      DO 4 IJ=NFIR3,NLAS3
    4 U(IJ)=(RRR(IJ)-RE)**2*(A+B*(RRR(IJ)-RE))
C INTERPOLATE UR IN REGION 4
      NFIR4=NLAS3+1
      DO 5 IK=NFIR4,NMESH
    5 U(IK)=BINT(RR,UR,RRR(IK),NR)
      DEBUG NLAS1,NFIR2,NLAS2,NFIR3,NLAS3,NFIR4
C PRINT OUT POTENTIAL U ARRAY
      IF(NRITE)46,46,45
   45 WRITE(6,122)
      KB= 1
  305 IF(KB-NMESH+8) 306,306,307
  306 KC= KB+7
      GO TO 308
  307 KC= NMESH
  308 WRITE(6,125)KB,(U(I),I=KB,KC)
      IF(KC-NMESH) 309,46,46
  309 KB= KB+8
      GO TO 305
   46 REWIND 3
      WRITE(3)(U(I),I=1,NMESH)
      BACKSPACE 3
C ENTER GENERALIZED-ROTATION-QUANTUM-NUMBER AJ LOOP
      DO 6 JI=1,NJ
      NSTP=NSTOP(JI)
      DO 7 IL=1,13
    7 L(IL)=0
C CONSTRUCT EFFECTIVE POTENTIAL UPP ARRAY
      ANUM=2.799E-23*AJ(JI)*(AJ(JI)+1.)/RM
      READ(3)(U(I),I=1,NMESH)
      BACKSPACE 3
      DO 8 IM=1,NMESH
    8 UPP(IM)=U(IM)+ANUM/RRR(IM)**2
      DEBUG AJ(JI),ANUM
C PRINT OUT UPP ARRAY
```

```
      IF(NRITE)48,48,47
   47 WRITE(6,123)
      KB= 1
  310 IF(KB-NMESH+8) 311,311,312
  311 KC= KB+7
      GO TO 313
  312 KC= NMESH
  313 WRITE(6,125)KB,(UPP(I),I=KB,KC)
      IF(KC-NMESH) 314,48,48
  314 KB= KB+8
      GO TO 310
C FIND INTERNUCLEAR DISTANCE RN WHERE SECOND DERIVATIVE OF UPP WITH
C RESPECT TO INTERNUCLEAR DISTANCE IS NEGATIVE
   48 TEMS=1.E+38
      DO 9 IN=NFIR3,NSTP,NZ
      TEM=SECD(RRR(IN))
      IF(TEM)49,50,50
   49 RN=RRR(IN)
      GO TO 13
   50 IF(TEM-TEMS)51,9,9
   51 TEMS=TEM
      KTEM=IN
    9 CONTINUE
      KT1=KTEM-NZ+1
      KT2=KTEM+NZ-1
      DO 10 IO=KT1,KT2
      TEM=SECD(RRR(IO))
      IF(TEM)52,10,10
   10 CONTINUE
      L(1)=1
      GO TO 11
   52 RN=RRR(IO)
C FIND INFLECTION POINT R1
   13 CALL FIND(RE,RN,SECD,DELR,R1,$12)
      DEBUG R1,RN
C FIND SLOPE OF UPP AT INFLECTION POINT R1
      SLOPE=DER(R1)
      DEBUG SLOPE
      V(100)=-.5
C TEST IF UPP HAS A WELL BY EXAMINING SIGN OF SLOPE
      IF(SLOPE)14,15,61
   61 IF(AJ(JI))62,62,16
   62 R3=RE
      GO TO 63
   12 L(2)=1
      GO TO 11
   14 L(3)=1
      R4=0.
      GO TO 11
   15 V(1)=-.5
      R4=0.
      F(100)=UP(R1)
      F(1)=F(100)
      GO TO 41
C FIND INTERNUCLEAR DISTANCE R3 CORRESPONDING TO BOTTOM OF UPP WELL
   16 CALL FIND(RE,R1,DER,DELR,R3,$17)
```

```
   63 F(100)=UP(R3)
C FIND INTERNUCLEAR DISTANCE R4 CORRESPONDING TO TOP OF HUMP OF UPP
      SLOP=DER(RRR(NSTP))
      DEBUG R3,F(100),SLOP
      IF(SLOP)19,18,18
   17 L(4)=1
      GO TO 11
   18 L(5)=1
      R4=RRR(NSTP)
      GO TO 53
   19 CALL FIND(R1,RRR(NSTP),DER,DELR,R4,$20)
   53 F(1)=UP(R4)
      DEBUG R4,F(1)
      FAA=F(1)
C FIND NEAR TURNING POINT RMIN(1) FOR TERM VALUE EQUAL TO UPP AT R4
      CALL DIFU(RRR(1),R3,RMIN(1),$21)
      RMAX(1)=R4
C FIND VIBRATION NUMBER V FOR TERM VALUE EQUAL TO UPP AT R4
      V(1)=SQRT(3.620E+21*RM)*SIMPS1(RMIN(1),RMAX(1),EN,L(11))-.5
      DEBUG V(1),RMIN(1)
      IF(V(1)-99.999)40,40,22
   20 L(6)=1
      GO TO 11
   21 L(7)=1
      GO TO 11
   22 L(8)=1
      GO TO 11
C TEST IF THERE ARE ANY EIGENVALUES (NONE IF V(1) IS NEGATIVE)
   40 IF(V(1))41,23,23
   41 WRITE(6,116)V(1),F(1),V(100),F(100)
      GO TO 11
C CONSTRUCT TABLE OF TERM VALUES F, VIBRATION NUMBERS V, NEAR TURNING
C POINTS RMIN, AND FAR TURNING POINTS RMAX
   23 NN=INT(V(1))
      IF(NN-10)25,26,26
   25 NN=10
   26 DELF=(F(1)-F(100))/FLOAT(NN)
      IQ=NN+1
      DO 27 IP=2,IQ
   27 F(IP)=F(IP-1)-DELF
      DEBUG(F(IR),IR=1,IQ)
      V(IQ)=-.5
      RMIN(IQ)=R3
      RMAX(IQ)=R3
      DO 28 NM=2,NN
      CALL VVV(F(NM),R3,RMIN(NM-1),RMAX(NM-1),R3,V(NM),RMIN(NM),
     1RMAX(NM),$11)
      DEBUG F(NM),V(NM),RMIN(NM),RMAX(NM)
   28 CONTINUE
C FIT MORSE POTENTIAL
      DISE=F(1)-F(100)
      FAA=F(100)+DISE*.5
      CALL DIFU(R3,R4,R5,$21)
      OMEG=1.301E-11*SQRT(DISE/RM)/(R5-R3)
      OMEGX=(OMEG*(V(1)+.5)-DISE)/(V(1)+.5)**2
      DEBUG DISE,FAA,R5,OMEG,OMEGX
```

```
C ADD MORSE TERM VALUE FFT TO TABLE
      DO 700 NQ=1,IQ
  700 FFT(NQ)=(V(NQ)+.5)*(OMEG-OMEGX*(V(NQ)+.5))
      DEBUG (FFT(I),I=1,IQ)
C CONSTRUCT TABLE OF DESIRED VALUES OF VIBRATION QUANTUM NUMBER VV AND
C MORSE TERM VALUE FFFT
   32 VV(1)=0.
      FFFT(1)=OMEG*.5-OMEGX*.25
      IQ=INT(V(1))+1
      IF(IQ-1)70,70,85
   85 DO 35 NS=2,IQ
      VV(NS)=VV(NS-1)+1.
   35 FFFT(NS)=(VV(NS)+.5)*(OMEG-OMEGX*(VV(NS)+.5))
      DEBUG(VV(I),I=1,IQ)
      DEBUG(FFFT(I),I=1,IQ)
C ENTER LOOP THAT SOLVES FOR ALL EIGENVALUES FV FOR GIVEN UPP
   70 DO 97 IZ=1,IQ
      NRR=0
C SEARCH F, V, FFT TABLE
      K=2
   71 IF(V(K)-VV(IZ))73,72,72
   72 K=K+1
      GO TO 71
   73 FFT1=FFT(K)
      FFT2=FFT(K-1)
      F1=F(K)
      F2=F(K-1)
      FFTNEW=FFT1
      FNEW=F1
C ENTER ITERATION LOOP FOR EIGENVALUES FV
  701 FOLD=FNEW
      FNEW=F1+(F2-F1)*(FFFT(IZ)-FFT1)/(FFT2-FFT1)
   77 NRR=NRR+1
      IF(NRR-N)79,79,78
   78 L(13)=1
      GO TO 97
   79 CALL VVV(FNEW,RMIN(K),RMIN(K-1),RMAX(K-1),RMAX(K),V3,RMMIN,
     1RMMAX,$11)
      FFTOLD=FFTNEW
      FFTNEW=(V3+.5)*(OMEG-OMEGX*(V3+.5))
      SLOPP=(FOLD-FNEW)/(FFTOLD-FFTNEW)
      ERROR(IZ)=(FFTNEW-FFFT(IZ))*SLOPP
      DEBUG FNEW,FFFT(IZ),FFTNEW,SLOPP,ERROR(IZ),FFT1,FFT2,F1,F2,M
      IF(ABS(ERROR(IZ))-TOL)702,702,74
  702 FV(IZ)=FNEW-GV(IZ)
      GO TO 97
   74 IF(NRR-M)80,703,703
   80 IF(ERROR(IZ))81,81,82
   81 FFT1=FFTNEW
      F1=FNEW
      GO TO 701
   82 FFT2=FFTNEW
      F2=FNEW
      GO TO 701
  703 FOLD=FNEW
      FNEW=FOLD+SLOPP*(FFFT(IZ)-FFTNEW)
```

```
      IF(FNEW-F(K))704,705,705
  705 IF(FNEW-F(K-1))77,77,704
  704 M=M+5
      FNEW=FOLD
      GO TO 80
   97 CONTINUE
C PRINT OUT AND PUNCH ANSWERS
      WRITE(6,117)(VV(I),FV(I),ERROR(I),I=1,IQ)
      IF(NPUNCH)201,41,201
  201 DO 200 NA=1,IQ
  200 PUNCH 120,VV(NA),AJ(JI),FV(NA),NAME
      GO TO 41
   11 WRITE(6,118)AJ(JI),R4,RRR(NSTP),M,(L(I),I=1,13)
    6 CONTINUE
      GO TO 42
  100 FORMAT(I10,7F10.0/(8F10.0))
  101 FORMAT(1H1,3H NL,I3,3H UL,1P9E13.6/(1X,9E13.6))
  102 FORMAT(8F10.0)
  103 FORMAT(1H0,3H RL,1P9E13.6/(1X,9E13.6))
  104 FORMAT(1H0,3H NJ,I3,3H AJ,1P9E13.6/(1X,9E13.6))
  105 FORMAT(1H0,3H NR,I3,3H UR,1P9E13.6/(1X,9E13.6))
  106 FORMAT(16I5)
  107 FORMAT(1H0,3H RR,1P9E13.6/(1X,9E13.6))
  108 FORMAT(1H0,6H NSTOP,24I5/1X,21I5)
  109 FORMAT(1H0,3H NV,I3,3H GV,1P9E13.6/(1X,9E13.6))
  110 FORMAT(3E13.6,6I5,A6)
  111 FORMAT(1H0,3H RE,1PE13.6,3H RM,E13.6,4H TOL,E13.6,3H NZ,I5,6H NMES
     1H,I5,2H N,I5,6H NRITE,I5,7H NPUNCH,I5,2H M,I5,2X,A6//)
  116 FORMAT(1H0,5H V(1),F9.5,5H F(1),F10.2,9X,7H V(100),F9.5,7H F(100),
     1F10.2)
  117 FORMAT(1H0,3(3H VV,F4.0,3H FV,F10.2,6H ERROR,F9.2,5X)/(1X,3(3H VV,
     1F4.0,3H FV,F10.2,6H ERROR,F9.2,5X)))
  118 FORMAT(1H0,3H AJ,F10.5,3H R4,1PE14.7,11H RRR(NSTOP),E14.7,14I5//)
  120 FORMAT(F4.0,2X,F10.5,2X,F10.2,2X,A6)
  121 FORMAT(1H0,4H RRR)
  122 FORMAT(1H0,2H U)
  123 FORMAT(1H0,4H UPP)
  124 FORMAT(1H ,I4,1P8E14.7)
  125 FORMAT(1H ,I4,1P8D14.7)
      END
```

```
$IBFTC LBINT
C SUBPROGRAM FOR 4 POINT INTERPOLATION
C
      DOUBLE PRECISION FUNCTION BINT(X,Y,Z,N)
      DIMENSION X(440),Y(440)
      DOUBLE PRECISION Q1,Q2,Q3,Q4,Q12,Q34,P21,P32,P42,P31,P41,P43
      M1=1
      M2=N
    5 IF(M2-M1-1)7,7,6
    6 MTEM=M1+INT(.5*(FLOAT(M2-M1)+.0001))
      IF(Z-X(MTEM))8,1,9
    8 M2=MTEM
      GO TO 5
    9 M1=MTEM
      GO TO 5
    1 BINT=Y(MTEM)
      RETURN
    7 IF(M1-1)2,2,3
    2 I=2
      GO TO 4
    3 IF(M2-N)11,10,10
   10 I=N-2
      GO TO 4
   11 I=M1
    4 Q1=Z-X(I-1)
      Q2=Z-X(I)
      Q3=Z-X(I+1)
      Q4=Z-X(I+2)
      Q12=Q1*Q2
      Q34=Q3*Q4
      P21=X(I)-X(I-1)
      P32=X(I+1)-X(I)
      P42=X(I+2)-X(I)
      P31=X(I+1)-X(I-1)
      P41=X(I+2)-X(I-1)
      P43=X(I+2)-X(I+1)
      BINT=Q34*(Q1*Y(I)/(P32*P42)-Q2*Y(I-1)/(P31*P41))/P21+Q12*(Q3*Y(I+2
     1)/(P41*P42)-Q4*Y(I+1)/(P31*P32))/P43
      RETURN
      END
```

```
$IBFTC LDER

C SUBPROGRAM FOR FIRST DERIVATIVE OF UPP
C
      FUNCTION DER(R)
      COMMON /BLOCK1/UPP,RRR,RATIO/BLOCK3/DELR,NMESH
      DIMENSION RRR(5000)
      DOUBLE PRECISION UPP(5000)
      FLOM=1.+(R-RRR(1))*RATIO
      I=INT(FLOM)
      IF(I-NMESH)1,2,2
    2 DER=(UPP(NMESH)-UPP(NMESH-1))/DELR
      RETURN
    1 DER=(UPP(I+1)-UPP(I))/DELR
      RETURN
      END
```

```
$IBFTC LDIFU

C SUBPROGRAM TO FIND ROOT OF UPP-FAA
C
      SUBROUTINE DIFU(RLOW,RHIGH,ROOT,*)
      COMMON/BLOCK4/FAA/BLOCK1/UPP,RRR,RATIO/BLOCK3/DELR,NMESH
      DIMENSION RRR(5000),NU(2),F(2)
      DOUBLE PRECISION UPP(5000)
      NU(1)=INT(1.+(RLOW-RRR(1))*RATIO)
      NU(2)=INT(1.+(RHIGH-RRR(1))*RATIO)+1
      IF(NU(2)-NMESH)21,21,20
   20 NU(2)=NMESH
   21 DO 100 I=1,2
      NV=NU(I)
  100 F(I)=UPP(NV)-FAA
    3 IF(F(1))4,22,5
    4 IF(F(2))13,14,23
   13 RETURN 1
   14 N1=NU(2)
   15 ROOT=RRR(N1)
      RETURN
   22 N1=NU(1)
      GO TO 15
    5 IF(F(2))18,14,13
   18 NTEM1=NU(1)
      TEM2=F(1)
      NU(1)=NU(2)
      F(1)=F(2)
      NU(2)=NTEM1
      F(2)=TEM2
   23 NV=INT((FLOAT(NU(1)+NU(2))+.0001)/2.)
      FUNC=UPP(NV)-FAA
    9 IF(FUNC)10,16,11
   10 NU(1)=NV
      F(1)=FUNC
      GO TO 24
   16 ROOT=RRR(NV)
      RETURN
   11 NU(2)=NV
      F(2)=FUNC
   24 IF(IABS(NU(1)-NU(2))-1)25,25,23
   25 N1=NU(1)
      N2=NU(2)
      ROOT=(RRR(N1)*F(2)-RRR(N2)*F(1))/(F(2)-F(1))
      RETURN
      END
```

```
$IBFTC LEN

C SUBPROGRAM FOR SIMPS1 INTEGRAND
C
      FUNCTION EN(R)
      COMMON/BLOCK4/F
      RR=R
      A=F-UP(RR)
      IF(A)1,1,2
    1 EN=0.
      RETURN
    2 EN=SQRT(A)
      RETURN
      END
```

```
$IBFTC LROOT

C SUBPROGRAM TO FIND ROOT OF G(R)
C
      SUBROUTINE FIND(UUU1,UUU2,G,DELR,ROOT,*)
      DIMENSION U(2),F(2)
      U(1)=UUU1
      U(2)=UUU2
      JMAX=1+INT(ALOG((U(2)-U(1))/DELR)/.6931)
      I=0
    1 I=I+1
      V=U(I)
  100 FUNC=G(V)
      IF(2-I)9,2,2
    2 F(I)=FUNC
      IF(2-I)3,3,1
    3 I=I+1
      IF(F(1))4,15,5
    4 IF(F(2))13,14,7
   13 RETURN 1
   15 ROOT=U(1)
      RETURN
   14 ROOT=U(2)
      RETURN
    5 IF(F(2))18,14,13
   18 TEM1=U(1)
      TEM2=F(1)
      U(1)=U(2)
      F(1)=F(2)
      U(2)=TEM1
      F(2)=TEM2
    7 J=0
    8 J=J+1
      V=(U(1)+U(2))/2.
      GO TO 100
    9 IF(FUNC)10,16,11
   10 U(1)=V
      F(1)=FUNC
      GO TO 12
   11 U(2)=V
      F(2)=FUNC
   12 IF(JMAX-J)17,17,8
   16 ROOT=V
      RETURN
   17 ROOT=(U(1)*F(2)-U(2)*F(1))/(F(2)-F(1))
      RETURN
      END
```

```
$IBFTC LSECD

C SUBPROGRAM FOR SECOND DERIVATIVE OF UPP
C
      FUNCTION SECD(R)
      COMMON /BLOCK1/UPP,RRR,RATIO/BLOCK3/DELR,NMESH
      DIMENSION RRR(5000)
      DOUBLE PRECISION UPP(5000)
      FLOM=1.+(R-RRR(1))*RATIO
      I=INT(FLOM)
      IF(I-1)1,1,2
    1 SECD=(UPP(3)-2.*UPP(2)+UPP(1))/DELR**2
      RETURN
    2 IF(I-NMESH)4,3,3
    3 SECD=(UPP(NMESH)-2.*UPP(NMESH-1)+UPP(NMESH-2))/DELR**2
      RETURN
    4 SECD=(UPP(I+1)-2.*UPP(I)+UPP(I-1))/DELR**2
      RETURN
      END
```

```
$IBFTC LUP

C SUBPROGRAM TO LINEARLY INTERPOLATE UPP
C
      FUNCTION UP(R)
      COMMON /BLOCK1/UPP,RRR,RATIO
      DIMENSION RRR(5000)
      DOUBLE PRECISION UPP(5000)
      FLOM=1.+(R-RRR(1))*RATIO
      I=INT(FLOM)
      UP=UPP(I)+(UPP(I+1)-UPP(I))*(FLOM-FLOAT(I))
      RETURN
      END
```

```
$IBFTC LVVV

C SUBPROGRAM TO FIND VIBRATION NUMBER (OR QUANTUM NUMBER) FOR GIVEN TERM
C VALUE F
C
      SUBROUTINE VVV(F,RMINH,RMINL,RMAXH,RMAXL,V,RMIN,RMAX,*)
      COMMON/BLOCK4/FAA/BLOCK2/RM/BLOCK5/L
      DIMENSION L(13)
      EXTERNAL EN
      FAA=F
      CALL DIFU(RMINL,RMINH,RMIN,$29)
      CALL DIFU(RMAXL,RMAXH,RMAX,$30)
      V=SQRT(3.620E+21*RM)*SIMPS1(RMIN,RMAX,EN,L(12))-.5
      RETURN
   29 L(9)=1
      RETURN 1
   30 L(10)=1
      RETURN 1
      END
```

REFERENCES

1. Vardya, M. S.: Pressure Dissociation and the Hydrogen Molecular Ion. Rep. No. 45, Joint Inst. for Lab. Astrophysics, Aug. 25, 1965.
2. Slater, John C.: Electronic Structure of Molecules. Vol. 1 of Quantum Theory of Molecules and Solids. McGraw-Hill Book Co., Inc., 1963.
3. Hirschfelder, Joseph O.: The Energy of the Triatomic Hydrogen Molecule and Ion, V. J. Chem. Phys., vol. 6, no. 12, Dec. 1938, pp. 795-806.
4. Christoffersen, Ralph E.: Configuration-Interaction Study of the Ground State of the H_3^+ Molecule. J. Chem. Phys., vol. 41, no. 4, Aug. 15, 1964, pp. 960-971.
5. Conroy, Harold: Molecular Schrödinger Equation. IV. Results for One- and Two-Electron Systems. J. Chem. Phys., vol. 41, no. 5, Sept. 1, 1964, pp. 1341-1351.
6. Hoyland, James R.: Two-Center Wavefunctions for ABH_n Systems. Illustrative Calculations on H_3^+ and H_3. J. Chem. Phys., vol. 41, no. 5, Sept. 1, 1964, pp. 1370-1376.
7. Pearson, A. G.; Poshusta, R. D.; and Browne, J. C.: Some Potential-Energy Surfaces on H_3^+ Computed with Generalized Gaussian Orbitals. J. Chem. Phys., vol. 44, no. 5, Mar. 1, 1966, pp. 1815-1818.
8. Ellison, Frank O.; Huff, Norman T.; and Patel, Jashbhai C.: A Method of Diatomics in Molecules. II. H_3 and H_3^+. J. Am. Chem. Soc., vol. 85, no. 22, Nov. 20, 1963, pp. 3544-3547.
9. Stevenson, D. P.; and Schissler, D. O.: Reactions of Gaseous Molecule Ions with Gaseous Molecules. IV. Experimental Method and Results. J. Chem. Phys., vol. 29, no. 2, Aug. 1958, pp. 282-294.
10. Conroy, Harold; and Bruner, Buddy L.: Energy Surface for the Linear H_3 System. J. Chem. Phys., vol. 42, no. 11, June 1, 1965, pp. 4047-4048.
11. Farkas, Adalbert; and Farkas, Ladislas: Experiments on Heavy Hydrogen. V-The Elementary Reactions of Light and Heavy Hydrogen. The Thermal Conversion of Ortho-Deuterium and the Interaction of Hydrogen and Deuterium. Proc. Roy. Soc., Ser. A, vol. 152, no. 875, Oct. 15, 1935, pp. 124-151.
12. McBride, Bonnie J.; and Gordon, Sanford: FORTRAN IV Program for Calculation of Thermodynamic Data. NASA TN D-4097, 1967.
13. Herzberg, Gerhard: Infrared and Raman Spectra of Polyatomic Molecules. Vol. II of Molecular Spectra and Molecular Structure. D. Van Nostrand Co., Inc., 1945.

14. Anon.: New Values for the Physical Constants. Natl. Bur. Std. Tech. News Bull., vol. 47, no. 10, Oct. 1963, pp. 175-177.

15. Wind, H.: Vibrational States of the Hydrogen Molecular Ion. J. Chem. Phys., vol. 43, no. 9, Nov. 1, 1965, pp. 2956-2958.

16. Herzberg, G.; and Monfils, A.: The Dissociation Energies of the H_2, HD, and D_2 Molecules. J. Molec. Spectry., vol. 5, no. 6, Dec. 1960, pp. 482-498.

17. Spindler, Robert J., Jr.: Optical Functions for Molecular Hydrogen. Rep. No. AVSSD-0287-66-RR (NASA CR-72107), Avco Corp., Sept. 30, 1966.

18. Namioka, T.: Absorption Spectra of H_2 in the Vacuum-Ultraviolet Region. I. The Lyman and the Werner Bands. J. Chem. Phys., vol. 40, no. 11, June 1, 1964, pp. 3154-3165.

19. Moore, Charlotte E.: Atomic Energy Levels as Derived from the Analyses of Optical Spectra. Vol. 1, Circ. No. 467, Natl. Bur. Std., June 15, 1949.

20. Woolley, Harold W.; Scott, Russell B.; and Brickwedde, F. G.: Compilation of Thermal Properties of Hydrogen in Its Various Isotopic and Ortho- Para Modifications. J. Res. Natl. Bur. Std., vol. 41, no. 5, Nov. 1948, pp. 379-475.

21. Teller, Eduard: Über das Wasserstoffmolekülion. Z. Physik, vol. 61, no. 7-8, Apr. 15, 1930, pp. 458-480.

22. Cohen, Stanley; Hiskes, John R.; and Riddell, Robert J., Jr.: Vibrational States of the Hydrogen Molecular Ion. Phys. Rev., vol. 119, no. 3, Aug. 1, 1960, pp. 1025-1027.

23. Wind, H.: Electron Energy for H_2^+ in the Ground State. J. Chem. Phys., vol. 42, no. 7, Apr. 1, 1965, pp. 2371-2373.

24. Hunter, G.; and Pritchard, H. O.: Born-Oppenheimer Separation for Three-Particle Systems. III. Applications. J. Chem. Phys., vol. 46, no. 6, Mar. 15, 1967, pp. 2153-2158.

25. Wilson, E. Bright, Jr.; Decius, J. C.; and Cross, Paul C.: Molecular Vibrations; The Theory of Infrared and Raman Vibrational Spectra. McGraw-Hill Book Co., Inc., 1955.

26. Hill, Terrell L.: Molecular Clusters in Imperfect Gases. J. Chem. Phys., vol. 23, no. 4, Apr. 1955, pp. 617-622.

27. Nielsen, Harald H.: The Vibration-Rotation Energies of Polyatomic Molecules. Phys. Rev., vol. 60, no. 11, Dec. 1, 1941, pp. 794-810.

28. Christoffersen, Ralph E.; Hagstrom, Stanley; and Prosser, Franklin: H_3^+ Molecule Ion. Its Structure and Energy. J. Chem. Phys., vol. 40, no. 1, Jan. 1, 1964, pp. 236-237.

29. Nielsen, Harald H.: Errata: The Vibration-Rotation Energies of Polyatomic Molecules. Phys. Rev., vol. 61, no. 7-8, Apr. 1-15, 1942, p. 540.

30. Wilson, E. Bright, Jr.: Partition Functions for Partly Classical Systems. J. Chem. Phys., vol. 7, no. 10, Oct. 1939, pp. 948-950.

31. Woolley, Harold William: The Calculation of Thermodynamic Functions for Asymmetric Rotator Molecules and Other Polyatomic Molecules. Ph. D. Thesis, University of Michigan, 1955.

32. Davidson, Norman R.: Statistical Mechanics. McGraw-Hill Book Co., Inc., 1962.

33. Herzberg, Gerhard: Spectra of Diatomic Molecules. Vol. 1 of Molecular Spectra and Molecular Structure. Second ed., D. Van Nostrand Co., Inc., 1950.

34. Rees, A. L. G.: The Calculation of Potential-Energy Curves from Band-Spectroscopic Data. Proc. Phys. Soc., vol. 59, pt. 6, Nov. 1, 1947, pp. 998-1008.

35. Vanderslice, J. T.; Mason, E. A.; Maisch, W. G.; and Lippincott, E. R.: Ground State of Hydrogen by the Rydberg-Klein-Rees Method. J. Molec. Spectry., vol. 3, no. 1, Feb. 1959, pp. 17-29.

36. Singh, N. L.; and Jain, D. C.: The Rydberg-Klein-Rees Method of Constructing the True Potential Energy Curves of Diatomic Molecules. Proc. Phys. Soc., vol. 79, pt. 2, Feb. 1962, pp. 274-278.

37. Kramers, H. A.: Wellenmechanik und halbzahlige Quantisierung. Z. Physik, vol. 39, Nov. 16, 1926, pp. 828-840.

38. Mathews, Jon; and Walker, R. L.: Mathematical Methods of Physics. W. A. Benjamin, Inc., 1964, p. 37.

39. Davidson, Ernest R.: Comparison of Theoretical Calculations on Diatomic Molecules with Experiment. J. Chem. Phys., vol. 34, no. 4, Apr. 1961, pp. 1240-1242.

40. Cooley, James W.: Some Computational Methods for the Study of Diatomic Molecules. Rep. No. NYO-9490, New York University, May 1, 1961.

41. Van Vleck, J. H.: On σ-Type Doubling and Electron Spin in the Spectra of Diatomic Molecules. Phys. Rev., vol. 33, no. 4, Apr. 1929, pp. 467-506.

42. Kronig, R. de L.: Band Spectra and Molecular Structure. The MacMillan Co., 1930.

43. Herzberg, G.; and Howe, L. L.: The Lyman Bands of Molecular Hydrogen. Can. J. Phys., vol. 37, no. 5, May 1959, pp. 636-659.

44. Huff, Norman T.; and Ellison, Frank O.: On the Theoretical Calculation of Vibrational Frequencies and Intensities of Polyatomic Molecules; H_3^+, H_2D^+, HD_2^+, and D_3^+. J. Chem. Phys., vol. 42, no. 1, Jan. 1, 1965, pp. 364-370.

45. Richardson, Owen Willans: Molecular Hydrogen and Its Spectrum. Yale University Press, 1934.

46. Beutler, H.; and Jünger, H.-O.: Über das Absorptionsspektrum des Wasserstoffs. III. Die Autoionisierung im Term $3p\pi\ {}^1\Pi_u$ des H_2 und ihre Auswahlgesetze. Bestimmung der Ionisierungsenergie des H_2. Z. Physik, vol. 100, Apr. 17, 1936, pp. 80-94.

47. Kerwin, L.; Marmet, P.; and Clarke, E. M.: Recent Work with the Electrostatic Electron Selector. Advances in Mass Spectrometry. Vol. 2. R. M. Elliott, ed., MacMillan Co., 1963, pp. 522-526.

48. Frost, D. C.; McDowell, C. A.; and Vroom, D. A.: Photoelectron Spectroscopy with a Spherical Analyzer. The Vibrational Energy Levels of H_2^+. Phys. Rev. Letters, vol. 15, no. 15, Oct. 11, 1965, pp. 612-614.

TABLE I. - COMPARISON OF CONSTANTS FOR THE EQUILATERAL TRIANGLE CONFIGURATION OF H_3^+ OBTAINED IN VARIOUS CALCULATIONS

Investigators	Equilibrium internuclear distance, r_e, cm	Equilibrium potential energy, V_e/hc, cm^{-1}	Zero-order vibrational constant, cm^{-1}		Reference
			ω_1	ω_2	
Hirschfelder	9.47×10^{-9}	-6.439×10^{4}	1550	1100	3
Ellison, Huff, and Patel	9.31	-7.832	3454	2326	8, 44
Christoffersen	8.771	-7.3006	3354	2790	4
Conroy	8.89	-7.835	(a)	(a)	5
Hoyland	8.89	-5.983	(a)	(a)	6
Pearson, Poshusta, and Browne	8.78	-6.990	3610	4440	7
This report[b]	8.816	-7.786	3476	3601	----

[a] Not given.

[b] Using least-squares fit to Conroy's potential energy (ref. 5).

TABLE II. - PARTITION FUNCTIONS OF H_3^+ AND H_2^+

Temperature, T, °K	Partition function of H_3^+, $q_{H_3^+}$	Partition function of H_2^+, $q_{H_2^+}$
298.15	4.8065	7.5178
300	4.8506	7.5627
400	7.4266	1.0001×10^1
500	1.0359×10^1	1.2472
600	1.3623	1.4998
700	1.7220×10^1	1.7606×10^1
800	2.1167	2.0319
900	2.5503	2.3159
1000	3.0275	2.6143
1100	3.5544	2.9285
1200	4.1372×10^1	3.2597×10^1
1300	4.7830	3.6088
1400	5.4991	3.9768
1500	6.2936	4.3643
1600	7.1746	4.7721
1700	8.1509×10^1	5.2010×10^1
1800	9.2319	5.6516
1900	1.0427×10^2	6.1245
2000	1.1748	6.6205
2200	1.4809	7.6846
2400	1.8511×10^2	8.8495×10^1
2600	2.2965	1.0121×10^2
2800	2.8294	1.1507
3000	3.4637	1.3014
3200	4.2149	1.4648
3400	5.1005×10^2	1.6417×10^2
3600	6.1401	1.8327
3800	7.3555	2.0385
4000	8.7712	2.2595
4300	1.1331×10^3	2.6207
4600	1.4509×10^3	3.0184×10^2
4900	1.8428	3.4530
5200	2.3235	3.9247
5600	3.1320	4.6104
6000	4.1768	5.3590
6 500	5.9064×10^3	6.3778×10^2
7 000	8.2440	7.4813
7 500	1.1374×10^4	8.6603
8 000	1.5520	9.9048
8 500	2.0951	1.1205×10^3
9 000	2.7988×10^4	1.2552×10^3
9 500	3.7011	1.3937
10 000	4.8460	1.5351
11 000	8.0735	1.8238
12 000	1.2969×10^5	2.1165
13 000	2.0129×10^5	2.4092×10^3
14 000	3.0243	2.6991
15 000	4.4063	2.9839
16 000	6.2364	3.2623
17 000	8.5881	3.5332
18 000	1.1525×10^6	3.7959×10^3
19 000	1.5091	4.0501
20 000	1.9310	4.2955
22 000	2.9635	4.7604
24 000	4.2018	5.1916
26 000	5.5432×10^6	5.5908×10^3
28 000	6.8387	5.9605
30 000	8.2173	6.3031
32 000	9.6610	6.6208
34 000	1.1154×10^7	6.9160
36 000	1.2682×10^7	7.1906×10^3
38 000	1.4233	7.4465
40 000	1.5797	7.6855
43 000	1.8147	8.0154
46 000	2.0485	8.3149
49 000	2.2790×10^7	8.5879×10^3
52 000	2.5052	8.8376
56 000	2.7985	9.1390

TABLE III. - THERMODYNAMIC PROPERTIES OF H_3^+

T, ^oK	$\frac{C_p}{R}$	$\frac{H_T - H_0}{RT}$	$\frac{S_T^o}{R}$	$-\frac{G_T^o - H_0}{RT}$	$\frac{H_T}{RT}$	$-\frac{G_T^o}{RT}$
298.15	4.0176	3.9745	17.7831	13.8086	441.1777	-423.3946
300	4.0177	3.9748	17.8080	13.8332	438.4819	-420.6739
400	4.0264	3.9865	18.9648	14.9783	329.8668	-310.9020
500	4.0517	3.9965	19.8655	15.8689	264.7008	-244.8353
600	4.1113	4.0101	20.6088	16.5987	221.2637	-200.6548
700	4.2132	4.0314	21.2497	17.2184	190.2487	-168.9990
800	4.3535	4.0625	21.8211	17.7586	167.0027	-145.1816
900	4.5216	4.1040	22.3433	18.2394	148.9397	-126.5963
1000	4.7057	4.1548	22.8292	18.6743	134.5070	-111.6778
1100	4.8959	4.2136	23.2866	19.0730	122.7155	-99.4289
1200	5.0849	4.2783	23.7207	19.4424	112.9051	-89.1844
1300	5.2680	4.3474	24.1350	19.7875	104.6183	-80.4833
1400	5.4424	4.4195	24.5318	20.1123	97.5281	-72.9963
1500	5.6067	4.4932	24.9130	20.4198	91.3946	-66.4817
1600	5.7606	4.5677	25.2798	20.7121	86.0378	-60.7580
1700	5.9042	4.6421	25.6334	20.9913	81.3198	-55.6864
1800	6.0380	4.7160	25.9747	21.2587	77.1338	-51.1591
1900	6.1626	4.7889	26.3045	21.5156	73.3953	-47.0907
2000	6.2789	4.8605	26.6236	21.7631	70.0366	-43.4130
2100	6.3875	4.9307	26.9326	22.0020	67.0031	-40.0705
2200	6.4894	4.9992	27.2322	22.2329	64.2502	-37.0180
2300	6.5852	5.0661	27.5228	22.4566	61.7410	-34.2182
2400	6.6755	5.1313	27.8050	22.6736	59.4447	-31.6398
2500	6.7611	5.1948	28.0792	22.8844	57.3357	-29.2565
2600	6.8423	5.2566	28.3460	23.0893	55.3921	-27.0461
2700	6.9198	5.3168	28.6057	23.2889	53.5954	-24.9897
2800	6.9939	5.3754	28.8587	23.4833	51.9297	-23.0710
2900	7.0650	5.4324	29.1054	23.6729	50.3814	-21.2761
3000	7.1336	5.4880	29.3460	23.8580	48.9387	-19.5927
3100	7.1999	5.5422	29.5810	24.0389	47.5912	-18.0102
3200	7.2642	5.5950	29.8106	24.2157	46.3300	-16.5194
3300	7.3267	5.6465	30.0351	24.3886	45.1472	-15.1120
3400	7.3877	5.6968	30.2548	24.5579	44.0357	-13.7809
3500	7.4474	5.7460	30.4698	24.7238	42.9895	-12.5197
3600	7.5060	5.7941	30.6804	24.8863	42.0030	-11.3226
3700	7.5636	5.8411	30.8868	25.0457	41.0714	-10.1846
3800	7.6203	5.8872	31.0893	25.2021	40.1904	-9.1011
3900	7.6764	5.9324	31.2880	25.3556	39.3560	-8.0680
4000	7.7318	5.9767	31.4830	25.5064	38.5647	-7.0817
4100	7.7868	6.0201	31.6746	25.6545	37.8133	-6.1387
4200	7.8415	6.0628	31.8629	25.8001	37.0991	-5.2361
4300	7.8958	6.1048	32.0481	25.9432	36.4193	-4.3712
4400	7.9499	6.1462	32.2302	26.0840	35.7716	-3.5414
4500	8.0039	6.1868	32.4095	26.2226	35.1540	-2.7445
4600	8.0579	6.2269	32.5860	26.3590	34.5644	-1.9784
4700	8.1118	6.2665	32.7599	26.4934	34.0010	-1.2411
4800	8.1658	6.3055	32.9312	26.6257	33.4622	-0.5310
4900	8.2200	6.3440	33.1001	26.7561	32.9465	0.1537
5000	8.2742	6.3821	33.2667	26.8847	32.4525	0.8143

TABLE III. - Concluded. THERMODYNAMIC PROPERTIES OF H_3^+

T, °K	$\frac{C_p}{R}$	$\frac{H_T - H_0}{RT}$	$\frac{S_T^o}{R}$	$\frac{G_T^o - H_0}{RT}$	$\frac{H_T}{RT}$	$-\frac{G_T^o}{RT}$
5100	8.3287	6.4197	33.4311	27.0114	31.9789	1.4522
5200	8.3835	6.4569	33.5934	27.1365	31.5246	2.0687
5300	8.4385	6.4938	33.7536	27.2598	31.0885	2.6651
5400	8.4938	6.5303	33.9119	27.3815	30.6696	3.2422
5500	8.5495	6.5665	34.0682	27.5017	30.2669	3.8013
5600	8.6056	6.6024	34.2228	27.6203	29.8796	4.3432
5700	8.6621	6.6381	34.3756	27.7375	29.5069	4.8687
5800	8.7191	6.6735	34.5267	27.8533	29.1480	5.3788
5900	8.7765	6.7086	34.6763	27.9676	28.8022	5.8741
6000	8.8344	6.7436	34.8243	28.0807	28.4689	6.3553
6100	8.8929	6.7783	34.9708	28.1924	28.1475	6.8232
6200	8.9518	6.8129	35.1158	28.3029	27.8374	7.2784
6300	9.0114	6.8473	35.2595	28.4122	27.5381	7.7214
6400	9.0715	6.8816	35.4019	28.5203	27.2491	8.1528
6500	9.1323	6.9158	35.5431	28.6273	26.9699	8.5731
6600	9.1936	6.9498	35.6829	28.7331	26.7001	8.9828
6700	9.2556	6.9838	35.8217	28.8379	26.4393	9.3824
6800	9.3183	7.0176	35.9592	28.9416	26.1871	9.7722
6900	9.3816	7.0514	36.0957	29.0443	25.9430	10.1527
7000	9.4456	7.0852	36.2312	29.1460	25.7069	10.5243
7100	9.4601	7.1185	36.3653	29.2467	25.4780	10.8873
7200	9.4733	7.1511	36.4977	29.3465	25.2556	11.2421
7300	9.4849	7.1830	36.6284	29.4454	25.0395	11.5889
7400	9.4948	7.2142	36.7575	29.5433	24.8294	11.9282
7500	9.5030	7.2447	36.8851	29.6404	24.6250	12.2601
7600	9.5096	7.2744	37.0110	29.7365	24.4260	12.5849
7700	9.5146	7.3035	37.1353	29.8318	24.2323	12.9030
7800	9.5180	7.3319	37.2581	29.9262	24.0437	13.2144
7900	9.5198	7.3596	37.3794	30.0198	23.8598	13.5195
8000	9.5201	7.3866	37.4991	30.1126	23.6806	13.8185
8100	9.5189	7.4129	37.6174	30.2045	23.5057	14.1116
8200	9.5162	7.4386	37.7342	30.2956	23.3352	14.3990
8300	9.5120	7.4636	37.8495	30.3859	23.1686	14.6808
8400	9.5064	7.4879	37.9634	30.4754	23.0060	14.9573
8500	9.4993	7.5116	38.0758	30.5642	22.8472	15.2287
8600	9.4908	7.5347	38.1869	30.6522	22.6919	15.4950
8700	9.4809	7.5571	38.2966	30.7394	22.5401	15.7564
8800	9.4697	7.5789	38.4048	30.8259	22.3917	16.0132
8900	9.4571	7.6001	38.5118	30.9117	22.2464	16.2654
9000	9.4432	7.6207	38.6174	30.9967	22.1042	16.5131
9100	9.4280	7.6406	38.7216	31.0810	21.9650	16.7566
9200	9.4114	7.6599	38.8246	31.1646	21.8286	16.9959
9300	9.3937	7.6787	38.9262	31.2476	21.6950	17.2312
9400	9.3746	7.6968	39.0266	31.3298	21.5641	17.4625
9500	9.3544	7.7144	39.1257	31.4113	21.4357	17.6900
9600	9.3329	7.7313	39.2235	31.4922	21.3097	17.9138
9700	9.3102	7.7477	39.3201	31.5724	21.1861	18.1340
9800	9.2864	7.7636	39.4155	31.6519	21.0648	18.3507
9900	9.2614	7.7788	39.5097	31.7308	20.9457	18.5640
10000	9.2352	7.7935	39.6026	31.8091	20.8287	18.7739

TABLE IV. - COMPARISON OF CONSTANTS FOR THE GROUND ELECTRONIC STATE OF H_2^+ OBTAINED FROM THEORY AND EXPERIMENT

Investigators	Method	Equilibrium internuclear distance, r_e, cm	Dissociation energy, D_o, cm^{-1}	Fundamental vibrational frequency, ω', cm^{-1}	Reference
Cohen, Hiskes, and Riddell	Theory	(a)	21343.71	2190.96	22
Wind	Theory	1.057×10^{-8}	21379.36	2191.34	15, 23
Hunter and Pritchard	Theory	1.061	21379.22	2191.23	24
Richardson	Experiment[b]	1.057	(c)	2173.	45
Beutler and Jünger, Herzberg and Monfils, and Namioka	Experiment[d]	(a)	21363.	(a)	46 16 18
Kerwin, Marmet, and Clarke	Experiment[e]	(a)	(a)	2194.	47
Frost, McDowell, and Vroom	Experiment[f]	(a)	(a)	2178.	48

[a] Not given.

[b] Extrapolations from H_2 bands.

[c] No experimental value.

[d] Obtained from dissociation and ionization energies of H_2.

[e] Obtained from monoenergetic electron collision experiment.

[f] Obtained by photoelectron spectroscopy.

TABLE V. - COMPLETE TABLE OF ROTATIONAL TERM VALUES OF GROUND ELECTRONIC STATE OF H_2^+

Total angular momentum quantum number, K	Vibrational quantum number, v									
	0	1	2	3	4	5	6	7	8	9
	Rotational term value, f, cm^{-1}									
0	-0.	-0.	-0.	0.	0.	-0.	0.	-0.	-0.	0.
1	58.26	55.19	52.21	49.36	46.56	43.84	41.10	38.45	35.79	33.13
2	174.18	165.11	156.26	147.73	139.51	131.01	123.09	115.01	107.02	98.95
3	347.14	328.91	311.25	294.20	277.61	260.98	244.99	228.96	213.05	197.02
4	575.62	545.29	515.97	487.63	459.96	432.55	405.88	379.31	352.88	326.27
5	858.04	812.59	768.80	726.53	685.04	644.28	604.38	564.81	525.36	485.68
6	1191.99	1128.80	1067.83	1008.93	951.15	894.49	838.91	783.74	728.74	673.40
7	1575.00	1491.61	1410.87	1332.52	1256.23	1181.25	1107.52	1034.34	961.32	887.91
8	2005.08	1898.47	1795.45	1695.72	1598.02	1502.42	1408.17	1314.65	1221.24	1127.15
9	2478.71	2346.58	2218.91	2095.01	1974.19	1855.50	1738.48	1622.31	1506.19	1389.34
10	2992.87	2833.21	2678.57	2528.60	2382.13	2238.21	2096.29	1955.26	1814.18	1671.78
11	3545.07	3355.23	3171.58	2993.38	2819.15	2647.94	2478.90	2310.81	2142.67	1972.92
12	4131.31	3909.69	3695.04	3486.52	3282.60	3082.04	2883.97	2686.87	2489.32	2289.81
13	4749.06	4493.25	4245.87	4005.26	3769.73	3537.95	3308.99	3080.56	2851.82	2619.99
14	5394.80	5103.40	4821.22	4546.76	4277.70	4012.95	3750.92	3489.67	3227.28	2961.42
15	6065.55	5736.82	5418.24	5108.23	4804.05	4504.53	4208.01	3911.79	3613.84	3311.13
16	6758.13	6390.63	6034.20	5686.73	5346.04	5010.09	4676.84	4343.74	4008.29	3666.66
17	7469.61	7061.87	6666.09	6280.13	5901.04	5527.05	5155.59	4783.69	4408.36	4025.39
18	8197.14	7747.86	7311.21	6885.21	6466.65	6052.98	5641.53	5229.08	4811.49	4384.58
19	8937.96	8445.72	7967.31	7500.04	7040.26	6585.40	6132.26	5676.96	5215.31	4741.35
20	9689.47	9153.28	8631.77	8121.77	7619.57	7121.95	6625.32	6125.26	5616.62	5092.62
21	10448.80	9867.93	9302.22	8748.36	8202.41	7660.38	7118.57	6571.27	6012.95	5434.81
22	11214.11	10587.39	9976.39	9377.44	8786.05	8198.13	7608.88	7012.35	6400.93	5764.36
23	11982.93	11309.45	10652.09	10006.83	9368.73	8733.10	8094.45	7445.72	6777.61	6075.87
24	12753.12	12031.99	11327.24	10634.44	9948.28	9263.00	8572.50	7868.30	7138.29	6362.34
25	13522.70	12753.00	11999.80	11258.42	10522.05	9785.28	9040.28	8276.75	7478.30	6610.26
26	14289.72	13470.59	12667.86	11876.02	11088.34	10297.63	9494.78	8666.33	7789.16	
27	15052.35	14182.92	13329.47	12485.95	11644.71	10797.32	9932.47	9032.08	8054.29	
28	15809.09	14888.16	13982.77	13085.89	12188.77	11281.33	10348.72	9364.56		
29	16557.66	15584.59	14625.88	13673.70	12717.98	11746.15	10737.97	9640.79		
30	17297.25	16270.72	15256.87	14247.14	13229.34	12187.14	11089.39			
31	18025.43	16944.20	15873.75	14803.69	13719.23	12597.55				
32	18741.38	17603.89	16474.41	15340.41	14182.90	12964.77				
33	19443.30	18247.75	17056.51	15853.73	14612.85					
34	20129.59	18873.78	17616.98	16338.61	14993.43					
35	20798.63	19479.77	18152.43	16786.77						
36	21448.63	20062.99	18657.86	17178.21						
37	22077.51	20620.03	19124.20							
38	22682.94	21145.94								
39	23261.79	21631.45								
40	23809.66									
41	24319.10									

Total angular momentum quantum number, K	Vibrational quantum number, v									
	10	11	12	13	14	15	16	17	18	19
	Rotational term value, f, cm^{-1}									
0	0.	-0.	0.	-0.	0.	0.	0.	0.	-0.	0.
1	30.44	27.70	24.84	21.93	18.84	15.54	11.92	7.90	3.42	0.63
2	91.06	82.68	74.32	65.48	56.24	46.27	35.42	23.28	9.50	
3	181.10	164.62	147.69	130.06	111.53	91.59	69.81	45.37	17.71	
4	299.71	272.33	244.14	214.77	183.67	150.53	114.05	72.90	25.67	
5	445.69	404.70	362.48	318.46	271.78	221.58	166.74	104.15		
6	617.54	560.32	501.26	439.66	374.15	303.68	226.12	136.67		
7	813.62	737.50	658.87	576.70	489.36	394.71	289.95	166.48		
8	1031.95	934.43	833.41	727.72	615.00	492.44	355.45			
9	1270.75	1149.06	1022.89	890.46	748.99	594.54	418.72			
10	1527.62	1379.09	1225.09	1062.86	888.81	697.17	474.36			
11	1800.31	1622.58	1437.66	1242.14	1031.56	797.23				
12	2086.50	1876.79	1658.01	1425.91	1173.91	889.08				
13	2383.67	2139.26	1883.20	1610.65	1311.80	961.38				
14	2689.31	2407.35	2110.86	1792.98	1439.82					
15	3000.78	2678.22	2337.25	1968.69	1548.68					
16	3315.39	2948.77	2559.13	2132.20						
17	3630.21	3215.73	2771.66	2274.33						
18	3942.16	3475.33	2969.24							
19	4247.94	3723.01	3142.26							
20	4543.56	3952.84								
21	4824.31	4154.04								
22	5083.64									
23	5310.09									

TABLE VI. - INPUT FORM WITH DATA FOR SAMPLE PROBLEM FOR COMPUTER PROGRAM FOR WKB ROTATIONAL ENERGIES OF DIATOMIC MOLECULES AND MOLECULAR IONS

[Top row contains card column numbers.]

1 10	11 20	21 30	31 40	41 50	51 60	61 70	71 80
NL	UL ARRAY →						
15	46608.72	39310.12	33107.52	27823.25	23313.34	19460.11	16166.64
13352.53	8904.35	5695.57	3423.70	1866.97	860.12	278.37	26.27

1 10	11 20	21 30	31 40	41 50	51 60	61 70	71 80
RL ARRAY →							
.47625	.50271	.52917	.55563	.58208	.60854	.63500	.66146
.71438	.76729	.82021	.87313	.92604	.97896	1.03188	

1 10	11 20	21 30	31 40	41 50	51 60	61 70	71 80
NR	UR ARRAY →						
15	30.24	394.04	1334.71	2934.51	4753.17	8100.62	13818.30
17689.41	19994.73	21249.66	21891.94	22208.96	22363.11	22438.30	22475.68

1 10	11 20	21 30	31 40	41 50	51 60	61 70	71 80
RR ARRAY →							
1.08479	1.16417	1.27000	1.40229	1.53458	1.77271	2.24896	2.72521
3.20146	3.67771	4.15396	4.63021	5.10646	5.58271	6.05896	

1 10	11 20	21 30	31 40	41 50	51 60	61 70
NJ	AJ ARRAY →					
5	1.	30.	41.	43.	44.	

1 5	6 10	11 15	16 20	21 25	26 30
NSTOP ARRAY →					
1143	1143	1143	1143	1143	

1 10	11 20	21 30	31 40	41 50	51 60	61 70	71 80
NV	GV ARRAY →						
18	1145.08	3336.71	5400.56	7340.29	9161.62	10861.50	12450.33
13932.54	15299.56	16554.96	17700.85	18733.55	19650.84	20450.59	21128.60
21679.25	22095.95	22371.29					

1 13	14 26	27 39	40 44	45 49	50 54	55 59	60 64	65 69	70 75
RE	RM	TOL	NZ	NMESH	N	NRITE	NPUNCH	M	NAME
1.05685	.8364900E-24	.25	100	1143	10	0	0	5	H2+ X

TABLE VII. - OUTPUT FOR SAMPLE PROBLEM FOR COMPUTER PROGRAM FOR WKB ROTATIONAL ENERGIES OF DIATOMIC MOLECULES AND MOLECULAR IONS

```
Descrip-
tion[a]

    NL 15 UL 4.660872E 04 3.931012E 04 3.310752E 04 2.782325E 04 2.331334E 04 1.946011E 04 1.616664E 04 1.335253E 04 8.904350E 03
    5.695570E 03 3.423700E 03 1.866970E 03 8.601200E 02 2.783700E 02 2.627000E 01

    RL 4.762500E-01 5.027100E-01 5.291700E-01 5.556300E-01 5.820800E-01 6.085400E-01 6.350000E-01 6.614600E-01 7.143800E-01
    7.672900E-01 8.202100E-01 8.731300E-01 9.260400E-01 9.789600E-01 1.031880E 00

    NR 15 UR 3.024000E 01 3.940400E 02 1.334710E 03 2.934510E 03 4.753170E 03 8.100620E 03 1.381830E 04 1.768941E 04 1.999473E 04
    2.124966E 04 2.189194E 04 2.220896E 04 2.236311E 04 2.243830E 04 2.247568E 04

 1  RR 1.084790E 00 1.164170E 00 1.270000E 00 1.402290E 00 1.534580E 00 1.772710E 00 2.248960E 00 2.725210E 00 3.201460E 00
    3.677710E 00 4.153960E 00 4.630210E 00 5.106460E 00 5.582710E 00 6.058960E 00

    NJ  5 AJ 1.000000E 00 3.000000E 01 4.100000E 01 4.300000E 01 4.400000E 01

    NSTOP 1143 1143 1143 1143 1143

    NV 18 GV 1.145080E 03 3.336710E 03 5.400560E 03 7.340290E 03 9.161620E 03 1.086150E 04 1.245033E 04 1.393254E 04 1.529956E 04
    1.655496E 04 1.770085E 04 1.873355E 04 1.965084E 04 2.045059E 04 2.112860E 04 2.167925E 04 2.209595E 04 2.237129E 04

    RE 1.056850E 00 RM 8.364900E-25 TOL 2.500000E-01 NZ  100 NMESH 1143 N   10 NRITE    0 NPUNCH    0 M    5  H2+ X


    VV  0. FV     58.02 ERROR    -0.24      VV  1. FV     55.17 ERROR    -0.00      VV  2. FV     52.18 ERROR    -0.25
    VV  3. FV     49.38 ERROR    -0.08      VV  4. FV     46.25 ERROR    -0.22      VV  5. FV     43.73 ERROR    -0.01
    VV  6. FV     41.12 ERROR     0.        VV  7. FV     38.50 ERROR    -0.00      VV  8. FV     35.79 ERROR     0.00
    VV  9. FV     33.05 ERROR    -0.17      VV 10. FV     30.50 ERROR    -0.00      VV 11. FV     27.79 ERROR    -0.01
    VV 12. FV     24.65 ERROR    -0.00      VV 13. FV     21.98 ERROR    -0.10      VV 14. FV     18.77 ERROR     0.00
    VV 15. FV     15.57 ERROR    -0.05      VV 16. FV     11.94 ERROR    -0.08      VV 17. FV      7.94 ERROR    -0.17

    V(1) 17.65541 F(1)  22477.50           V(100) -0.50000 F(100)     60.08

    AJ    1.00000 R4 6.0589564E 00 RRR(NSTOP) 6.0589564E 00    5    0    0    0    0    1    0    0    0    0    0    0    0    0


 2  VV  0. FV  17287.65 ERROR    -0.00      VV  1. FV  16257.42 ERROR     0.19      VV  2. FV  15248.52 ERROR     0.01
    VV  3. FV  14241.00 ERROR     0.01      VV  4. FV  13227.36 ERROR     0.01      VV  5. FV  12192.86 ERROR     0.01
    VV  6. FV  11100.11 ERROR    -0.03      VV

    V(1)  6.48732 F(1)  23699.72           V(100) -0.50000 F(100)  17808.08

    AJ  30.00000 R4 4.2616532E 00 RRR(NSTOP) 6.0589564E 00    5    0    0    0    0    0    0    0    0    0    0    0    0    0


    VV  0. FV  24308.23 ERROR     0.01      VV

    V(1)  0.44822 F(1)  25618.54           V(100) -0.50000 F(100)  25208.24

    AJ  41.00000 R4 3.2549785E 00 RRR(NSTOP) 6.0589564E 00    5    0    0    0    0    0    0    0    0    0    0    0    0    0

    V(1) -0.42914 F(1)  26218.21           V(100) -0.50000 F(100)  26198.25
 3
    AJ  43.00000 R4 2.8684221E 00 RRR(NSTOP) 6.0589564E 00    5    0    0    0    0    0    0    0    0    0    0    0    0    0

 4  AJ  44.00000 R4 0.                 RRR(NSTOP) 6.0589564E 00    5    0    0    1    0    0    0    0    0    0    0    0    0    0

    V(1) -0.50000 F(1)  26300.12           V(100) -0.50000 F(100)  26300.12
 5
    AJ  43.00000 R4 0.                 RRR(NSTOP) 6.0589564E 00    5    0    0    0    0    0    0    0    0    0    0    0    0    0
                                                                                                REC=  00000 FIL=
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[a] See p. 43.

TABLE VIII. - THERMODYNAMIC PROPERTIES OF H_2^+

T, °K	$\frac{C_p}{R}$	$\frac{H_T - H_0}{RT}$	$\frac{S_T^o}{R}$	$-\frac{G_T^o - H_0}{RT}$	$\frac{H_T}{RT}$	$-\frac{G_T^o}{RT}$
298.15	3.5224	3.4623	17.1098	13.6475	606.3907	-589.2810
300	3.5227	3.4626	17.1316	13.6690	602.6731	-585.5415
400	3.5509	3.4806	18.1482	14.6676	452.8884	-434.7402
500	3.6100	3.5000	18.9463	15.4463	363.0263	-344.0800
600	3.6947	3.5251	19.6117	16.0865	303.1304	-283.5187
700	3.7922	3.5562	20.1885	16.6322	260.3607	-240.1723
800	3.8918	3.5920	20.7013	17.1094	228.2959	-207.5945
900	3.9874	3.6307	21.1653	17.5347	203.3675	-182.2022
1000	4.0760	3.6708	21.5901	17.9193	183.4340	-161.8439
1100	4.1568	3.7114	21.9824	18.2710	167.1324	-145.1500
1200	4.2301	3.7516	22.3473	18.5957	153.5542	-131.2069
1300	4.2967	3.7910	22.6886	18.8975	142.0704	-119.3818
1400	4.3576	3.8294	23.0093	19.1799	132.2316	-109.2223
1500	4.4136	3.8665	23.3118	19.4454	123.7086	-100.3967
1600	4.4658	3.9023	23.5984	19.6961	116.2543	-92.6559
1700	4.5149	3.9369	23.8706	19.9337	109.6799	-85.8093
1800	4.5615	3.9703	24.1300	20.1597	103.8387	-79.7088
1900	4.6065	4.0026	24.3778	20.3752	98.6148	-74.2370
2000	4.6502	4.0339	24.6152	20.5813	93.9155	-69.3003
2100	4.6931	4.0643	24.8431	20.7788	89.6658	-64.8226
2200	4.7355	4.0938	25.0624	20.9686	85.8044	-60.7419
2300	4.7775	4.1227	25.2739	21.1512	82.2805	-57.0067
2400	4.8193	4.1508	25.4781	21.3273	79.0521	-53.5740
2500	4.8607	4.1784	25.6757	21.4973	76.0836	-50.4080
2600	4.9017	4.2054	25.8671	21.6617	73.3451	-47.4780
2700	4.9419	4.2319	26.0528	21.8209	70.8109	-44.7580
2800	4.9811	4.2580	26.2333	21.9753	68.4591	-42.2258
2900	5.0189	4.2836	26.4087	22.1251	66.2709	-39.8621
3000	5.0548	4.3087	26.5795	22.2708	64.2298	-37.6503
3100	5.0885	4.3333	26.7458	22.4125	62.3214	-35.5756
3200	5.1194	4.3574	26.9079	22.5504	60.5334	-33.6255
3300	5.1473	4.3809	27.0658	22.6849	58.8546	-31.7888
3400	5.1718	4.4038	27.2199	22.8160	57.2754	-30.0555
3500	5.1925	4.4261	27.3701	22.9440	55.7870	-28.4169
3600	5.2093	4.4476	27.5166	23.0690	54.3818	-26.8652
3700	5.2218	4.4684	27.6595	23.1911	53.0530	-25.3935
3800	5.2301	4.4883	27.7989	23.3106	51.7944	-23.9955
3900	5.2341	4.5074	27.9348	23.4274	50.6005	-22.6657
4000	5.2336	4.5256	28.0673	23.5417	49.4664	-21.3990
4100	5.2290	4.5428	28.1965	23.6537	48.3875	-20.1910
4200	5.2201	4.5590	28.3224	23.7634	47.3598	-19.0374
4300	5.2072	4.5743	28.4451	23.8708	46.3797	-17.9346
4400	5.1905	4.5885	28.5646	23.9762	45.4437	-16.8791
4500	5.1702	4.6016	28.6811	24.0794	44.5490	-15.8679
4600	5.1465	4.6138	28.7944	24.1807	43.6927	-14.8983
4700	5.1198	4.6248	28.9048	24.2800	42.8723	-13.9674
4800	5.0901	4.6348	29.0123	24.3775	42.0855	-13.0731
4900	5.0579	4.6438	29.1170	24.4732	41.3301	-12.2132
5000	5.0235	4.6517	29.2188	24.5671	40.6043	-11.3856

TABLE VIII. - Concluded. THERMODYNAMIC PROPERTIES OF H_2^+

T, ^oK	$\frac{C_p}{R}$	$\frac{H_T - H_0}{RT}$	$\frac{S^o_T}{R}$	$\frac{G^o_T - H_0}{RT}$	$\frac{H_T}{RT}$	$-\frac{G^o_T}{RT}$
5100	4.9870	4.6587	29.3179	24.6593	39.9063	-10.5884
5200	4.9487	4.6646	29.4144	24.7498	39.2344	-9.8201
5300	4.9089	4.6696	29.5083	24.8387	38.5872	-9.0789
5400	4.8679	4.6736	29.5996	24.9260	37.9631	-8.3635
5500	4.8258	4.6768	29.6886	25.0118	37.3610	-7.6724
5600	4.7829	4.6791	29.7752	25.0961	36.7796	-7.0045
5700	4.7394	4.6805	29.8594	25.1789	36.2179	-6.3585
5800	4.6954	4.6812	29.9415	25.2603	35.6748	-5.7333
5900	4.6511	4.6810	30.0214	25.3403	35.1493	-5.1280
6000	4.6068	4.6802	30.0992	25.4190	34.6407	-4.5415
6100	4.5624	4.6786	30.1749	25.4964	34.1480	-3.9730
6200	4.5182	4.6764	30.2488	25.5724	33.6704	-3.4216
6300	4.4742	4.6735	30.3207	25.6472	33.2073	-2.8866
6400	4.4306	4.6700	30.3908	25.7208	32.7580	-2.3672
6500	4.3874	4.6660	30.4592	25.7932	32.3219	-1.8627
6600	4.3447	4.6615	30.5258	25.8644	31.8983	-1.3725
6700	4.3026	4.6564	30.5909	25.9344	31.4868	-0.8959
6800	4.2611	4.6509	30.6543	26.0034	31.0867	-0.4324
6900	4.2204	4.6450	30.7162	26.0712	30.6976	0.0186
7000	4.1803	4.6386	30.7766	26.1380	30.3191	0.4576
7100	4.1410	4.6319	30.8357	26.2038	29.9506	0.8850
7200	4.1024	4.6248	30.8933	26.2685	29.5919	1.3014
7300	4.0647	4.6174	30.9496	26.3322	29.2425	1.7072
7400	4.0278	4.6097	31.0047	26.3950	28.9020	2.1027
7500	3.9917	4.6017	31.0585	26.4568	28.5701	2.4884
7600	3.9564	4.5934	31.1111	26.5177	28.2465	2.8647
7700	3.9220	4.5849	31.1626	26.5777	27.9308	3.2319
7800	3.8883	4.5762	31.2130	26.6368	27.6228	3.5903
7900	3.8556	4.5673	31.2624	26.6951	27.3221	3.9402
8000	3.8236	4.5582	31.3107	26.7525	27.0286	4.2821
8100	3.7925	4.5489	31.3580	26.8090	26.7419	4.6161
8200	3.7621	4.5395	31.4043	26.8648	26.4618	4.9425
8300	3.7326	4.5300	31.4497	26.9198	26.1882	5.2616
8400	3.7038	4.5203	31.4943	26.9740	25.9207	5.5736
8500	3.6758	4.5105	31.5379	27.0274	25.6591	5.8788
8600	3.6486	4.5007	31.5808	27.0801	25.4034	6.1774
8700	3.6221	4.4907	31.6228	27.1321	25.1531	6.4696
8800	3.5963	4.4807	31.6640	27.1833	24.9083	6.7557
8900	3.5712	4.4706	31.7045	27.2339	24.6687	7.0358
9000	3.5469	4.4605	31.7443	27.2838	24.4342	7.3101
9100	3.5231	4.4503	31.7834	27.3330	24.2045	7.5788
9200	3.5001	4.4401	31.8217	27.3816	23.9796	7.8421
9300	3.4777	4.4299	31.8594	27.4296	23.7593	8.1002
9400	3.4559	4.4196	31.8965	27.4769	23.5434	8.3531
9500	3.4347	4.4094	31.9330	27.5236	23.3318	8.6012
9600	3.4141	4.3991	31.9688	27.5697	23.1245	8.8444
9700	3.3940	4.3889	32.0041	27.6152	22.9211	9.0830
9800	3.3746	4.3786	32.0388	27.6602	22.7218	9.3170
9900	3.3556	4.3684	32.0730	27.7046	22.5263	9.5467
10000	3.3372	4.3582	32.1066	27.7485	22.3345	9.7722

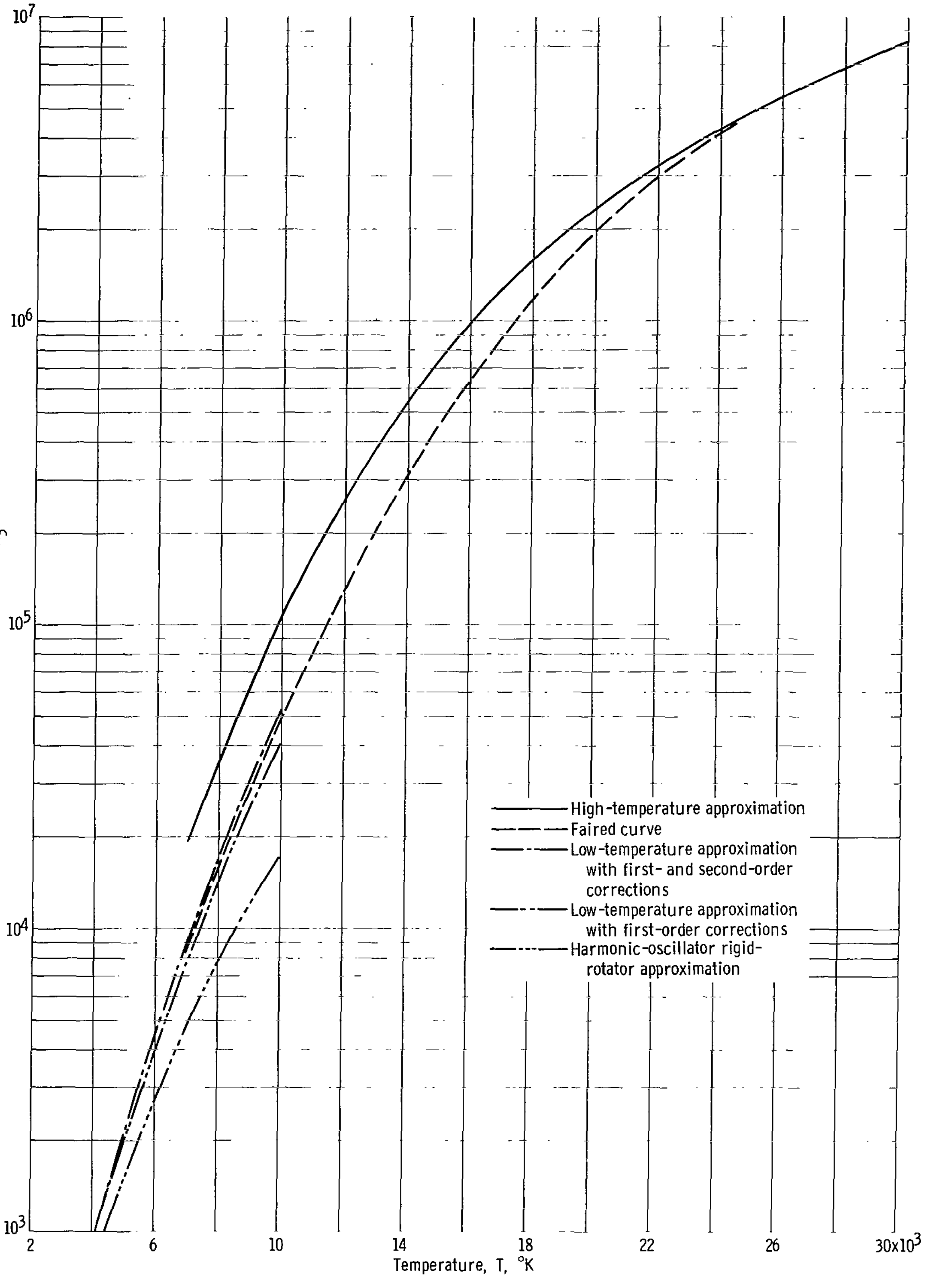

Figure 1. - Fairing together of low- and high-temperature approximations for partition function of H_3^+.

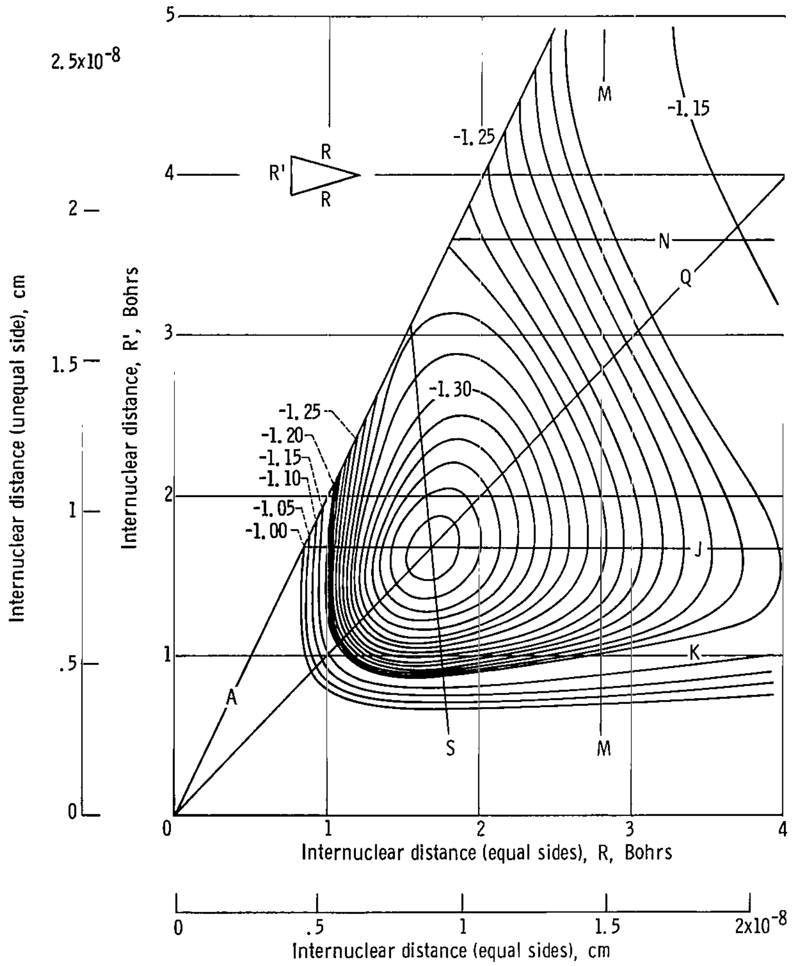

Figure 2. - Potential energy of H_3^+ for isosceles and equilateral triangle configurations (reproduced from fig. 13 of ref. 5). Inner ordinate gives internuclear distance R' in Bohrs (1 Bohr = 5.29167x10^{-9} cm) shown in the sketch. Inner abscissa corresponds to two equal internuclear distances R (in Bohrs) also shown in sketch. Additional ordinate and abscissa scales in centimeters have been added. Potential energies were computed along lines A, J, K, M, N, Q, and S. Contours are lines of constant potential energy in Hartrees (1 Hartree = 219 475 cm^{-1}) and were faired in. To be consistent with figure 4 and rest of this report, 1.00 Hartree must be added to all potential energies in this figure.

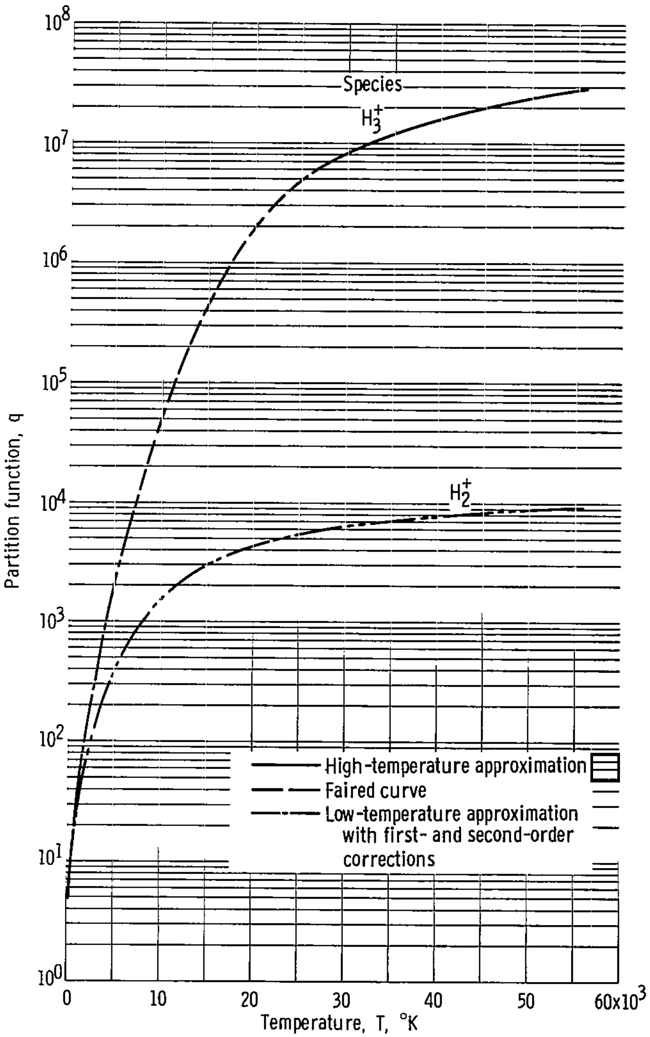

Figure 3. - Partition functions of H_3^+ and H_2^+.

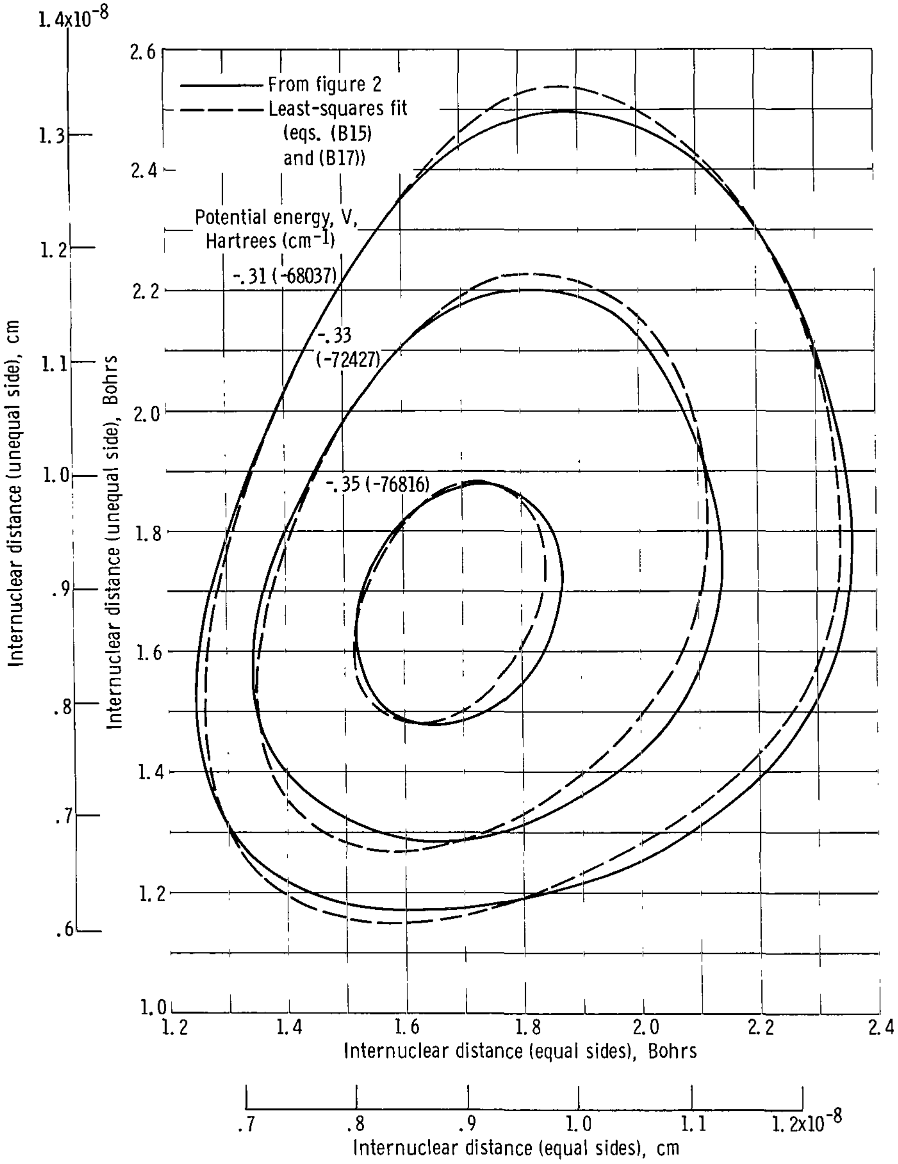

Figure 4. - Enlarged view of bottom of H_3^+ potential well in figure 2, showing accuracy of least-squares fit.

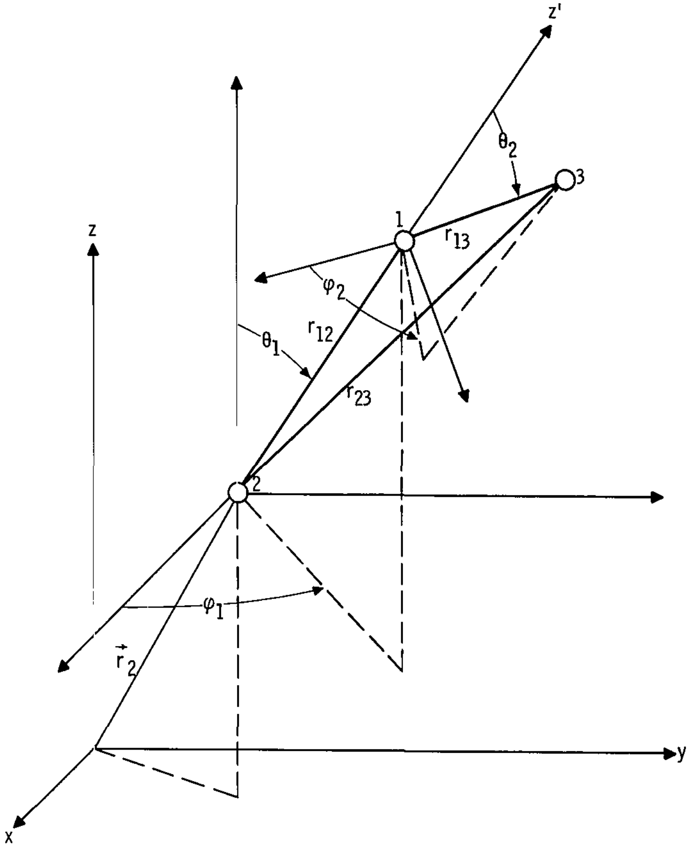

Figure 5. - Coordinate system for high-temperature approximation for partition function of H_3^+. Axes x, y, and z are fixed in space. Three protons are represented by circles.

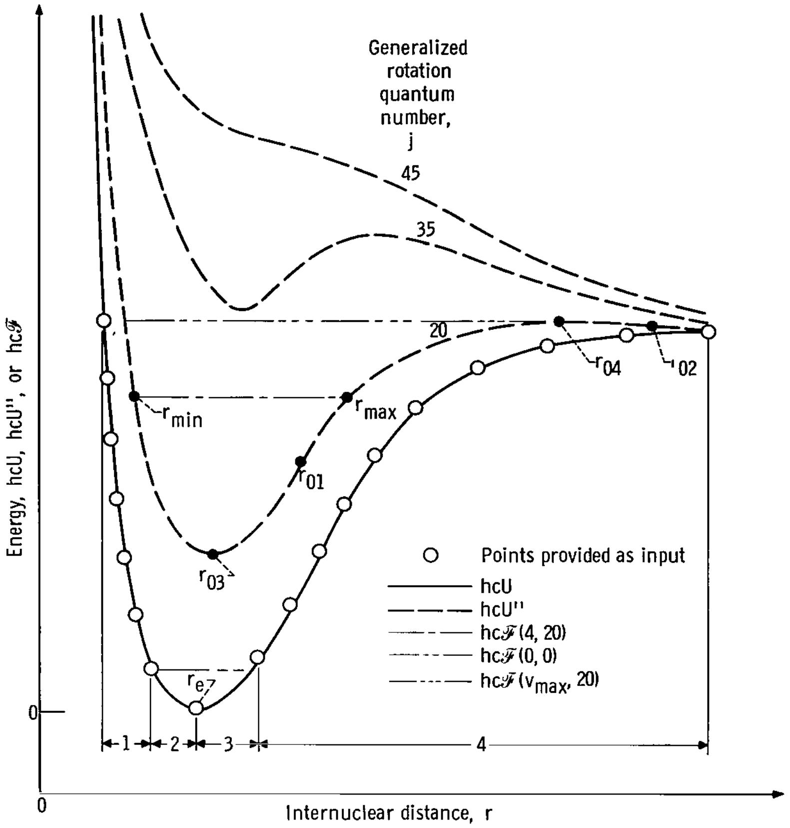

Figure 6. - Typical potential energy hcU and effective potential energy hcU'' for diatomic molecule or diatomic molecular ion (not to scale). For j = 0, hcU and hcU'' coincide. Vibration-rotation energy eigenvalues $hc\mathscr{F}(4, 20)$ and $hc\mathscr{F}(0, 0)$ are also shown, as well as $hc\mathscr{F}(v_{max}, 20)$, which is not an eigenvalue. Four interpolation regions 1, 2, 3, and 4 are indicated just above abscissa.

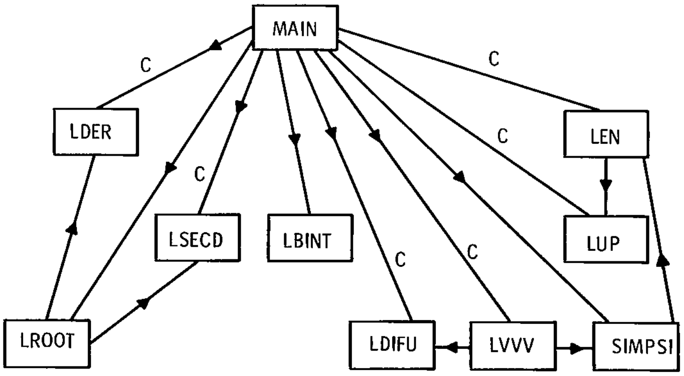

Figure 7. - Block diagram of program and subprograms for WKB rotational energies of diatomic molecules and molecular ions. Direction of call is indicated by arrowhead. Common storage is indicated by letter C.

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