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Equilibrium Vibrational Properties of Ground State Nitrogen up to 35,000 K

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The Rydberg–Klein–Reese (RKR) potential is extended beyond observed vibrational levels by an inverse sixth power attraction along with a short range repulsion that preserves the slope and approximates the second derivative of the potential at the observational limit. Vibrational energies are obtained to the dissociation limit by digitizing the action integral. For the ground state nitrogen molecule, this results in 64 vibrational states, compared with 58 levels provided by the JANAF series approximation and 68 levels by the Morse approximation. The vibrational energy and specific heat of ground state nitrogen based on this extended RKR potential are calculated to 35,000 K. Variations between models are due primarily to differences in the number of levels rather than to different anharmonicity of upper levels.

Introduction

IN the subsonic flight era, fluid properties of the atmosphere were adequately accounted for by ignoring vibrations in the gas and using constant specific heats. As aeronautical science moved on to low Mach number supersonic flight, the excitation of vibrational energy had to be accounted for. The harmonic oscillator model then adequately accounted for variation in internal energy and specific heat up to a few thousand degrees Kelvin. With the advent of space flight, temperatures on the order of 15,000 K were encountered in flow about re-entry vehicles like Gemini and Apollo. Then vibrational eigenvalues up to about 4 eV or so were required to evaluate vibrational energy and specific heat accurately. Fortunately spectroscopists have measured vibrational levels of N_2 and O_2 accurately to this level, and sixth degree power series were found to fit these measurements very well.[1] Currently aerospace science contemplates space vehicles returning to Earth from deep space missions, such as the exploration of Mars. Then transient temperatures up to about 35,000 K are encountered in portions of the flow about such vehicles, and vibrational eigenvalues beyond those measured, all the way to the dissociation limit, become important. Since there is no guarantee that a power series fit to the lower levels will extrapolate accurately beyond these levels, this paper investigates the vibrational properties of N_2 that can be deduced from reasonable extension of the RKR intermolecular potential that has been determined from spectroscopic data.

For temperatures up to the characteristic vibrational temperature $\theta = \hbar w/k$ (3395 K for N_2 and 2274 K for O_2), the vibrational energy and specific heat of diatomics are provided rather well by the harmonic oscillator model. At much higher temperatures than θ, the model predicts that the vibrational partition function Q_v approaches T/θ as a limit, whereas the dimensionless energy $(E_v - E_0)/RT$ and the specific heat C_v/R both approach unity. Deviations from this simple model occur for two reasons: anharmonic effects increase the number of vibrational levels in a given energy range, and truncation of states at the dissociation energy limits the vibrational levels to a finite number, rather than the infinite number allowed in the harmonic oscillator model. It is well known that these effects cause energy and specific heat to be larger than harmonic oscillator values at temperatures larger than θ. However, it seems not always recognized that when T/θ is much greater than unity, the dimensionless vibrational energy and specific heat do not approach a constant limit but go through a maximum and then tail off toward zero.

The nitrogen molecule, which is the major component in Earth's atmosphere, will be used to illustrate typical deviations from harmonic oscillator behavior. Truncation at a finite number of energy levels and anharmonic effects will be considered. The Morse potential, the JANAF series, and the Rydberg–Klein–Reese (RKR) potential will be used to show sensitivity to the accuracy of the potential function.

Effect of a Finite Number of Vibrational Levels

The vibrational partition function Q_v, energy E_v, and specific heat C_v are defined exactly once the vibrational energies ϵ_v above the ground state are given:

$$Q_v = \sum_{v=0}^{v_{\max}} e^{-\epsilon_v/kT} \tag{1}$$

$$\frac{E_v - E_0}{RT} = \frac{1}{Q_v}\sum_{v=0}^{v_{\max}} \frac{\epsilon_v}{kT} e^{-\epsilon_v/kT} \tag{2}$$

$$\frac{C_v}{R} = \frac{1}{R}\frac{\mathrm{d}E_v}{\mathrm{d}T} = \frac{1}{Q_v}\sum_{v=0}^{v_{\max}}\left(\frac{\epsilon}{kT}\right)^2 e^{-\epsilon_v/kT} - \left(\frac{E_v - E_0}{RT}\right)^2 \tag{3}$$

where E_0 is the vibrational energy of a mol of vibrators at zero temperature, $N\hbar w/2$.

The qualitative effect that a finite number of vibrational levels will have on limiting properties of any oscillator is clear. As temperature approaches infinity, all levels become equally populated, the partition function Q_v is simply the total number of levels, the energy E_v becomes a constant, and the specific heat C_v vanishes. For example, consider a harmonic oscillator truncated at the dissociation energy D. The partition function, the energy, and the specific heat then become

$$Q_v = \sum_{v=0}^{D/k\theta} e^{-v\theta/T} = \frac{1 - e^{-D/kT}}{1 - e^{-\theta/T}} \xrightarrow[\theta \ll T \ll \frac{D}{k}]{} \frac{T}{\theta}(1 - e^{-D/kT}) \tag{4}$$

$$\frac{E_v - E_0}{RT} = T\frac{\mathrm{d}\,\ln Q}{\mathrm{d}T} = \frac{\theta/T}{e^{\theta/T} - 1} - \frac{D/kT}{e^{D/kT} - 1} \xrightarrow[\theta \ll T \ll \frac{D}{k}]{} \left(1 - \frac{D}{kT}e^{-D/kT}\right) \tag{5}$$

$$\frac{C_v}{R} = \frac{1}{R}\frac{\mathrm{d}E_v}{\mathrm{d}T} = \left(\frac{\theta/T}{e^{\theta/T} - 1}\right)^2 e^{\theta/T} - \left(\frac{D/kT}{e^{D/kT} - 1}\right)^2 e^{D/kT} \xrightarrow[\theta \ll T \ll \frac{D}{k}]{} \left(1 - \frac{\theta}{T}\right) - \left(\frac{D/2kT}{\sinh D/2kT}\right)^2 \tag{6}$$

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At infinite temperature the partition function is just the number of vibrational levels $D/k\theta$, the dimensionless energy vanishes as $D/2kT$, and the specific heat vanishes as D/kT.

Although $T \gg D/k$ is far beyond the range of interest for space vehicle re-entry, the vanishing limits show that dimensionless energy and specific heat must go through maxima. This is a general result for any oscillator system with a finite number of levels. For precise results, potential functions that accurately account for anharmonic effects are required of course.

Anharmonic Effects

Vibrational energies for the $X^1\Sigma_g^+$ state of N_2 have been measured experimentally up to the 27th level. The JANAF Thermochemical Tables[1] fit these levels precisely with a sixth power Dunham series. For the rotationless $j = 0$ state, this series is

$$\begin{aligned} E_v &= 2358.583Y - 14.33594Y^2 - 3.76775 \cdot 10^{-3}Y^3 \\ &\quad + 2.753652 \cdot 10^{-4}Y^4 - 2.701198 \cdot 10^{-5}Y^5 \\ &\quad + 1.749062 \cdot 10^{-7}Y^6 \end{aligned} \tag{7}$$

where $Y = (v + \frac{1}{2})$. The series has been empirically adjusted to converge at the measured dissociation limit[2] and provides a total of 58 vibrational levels when $j = 0$. The vibrational partition function, the energy, and the specific heat can all be determined from these vibrational energy levels, as given by Eqs. (1–3). The extrapolation to levels above the 27th is uncertain and the total number of levels is in doubt, but these uncertainties do not affect the results up to 6000 K, which is the limit of tabulations in the JANAF Thermochemical Table. In fact, levels above the 27th do not contribute very much at temperatures up to 15,000 K, which is sufficient for most plasma properties required in analyzing the Apollo re-entry mission. However, when re-entry from deep space is considered, temperatures up to 35,000 K or so exist transiently in flow behind the strong shock waves produced. Then the number of vibrational levels and their spacing in upper levels do affect the energy and specific heat functions.

The JANAF series that gives vibrational eigenvalues does not translate directly to a potential function; the latter is needed, for example, in calculation of collision cross sections that determine transport coefficients for mass, momentum, and energy. Accurate attractive potentials are based on observed vibrational and rotational levels from which points on the potential function are deduced by the RKR method.[3,4] Repulsive potentials need to be determined either by computational quantum chemistry methods, which are now quite accurate,[5] or from molecular beam type measurements.[6]

The RKR points on the potential function for the N_2 $X^1\Sigma_g^+$ state are listed by Loftus and Krupenie[7] up to the 21st vibrational level. At this point, the variation in the potential function at long range is similar to an inverse sixth power of the internuclear distance r, which is in accord with the long-range attraction between neutral molecules produced by induced-dipole effects.[8] Therefore a reasonable extrapolation of the RKR potential is provided by fitting an inverse sixth power attraction along with a short-range repulsion to the RKR potential at the 21st level. The remaining vibrational levels can then be calculated by choosing the vibrational energies E_v to give an action integral, which equals the vibrational eigenvalue

$$\frac{2}{\hbar}\int_{r_{\min}}^{r_{\max}} p\,\mathrm{d}r = \frac{2}{\hbar}\int_{r_{\min}}^{r_{\max}} \{2\mu[E_v - U(r)]\}^{\frac{1}{2}}\,\mathrm{d}r = v + \frac{1}{2} \tag{8}$$

where $U(r)$ is the potential, μ the reduced mass of the two N atoms, and v an integer. The action integral was evaluated numerically using a Morse-like analytic fit between adjacent points of the RKR potential

$$U(r) = D\left[1 - e^{-a(r-r_e)}\right]^2 \tag{9}$$

where the constants a and r_e are chosen to fit the points r_n and r_{n+1} with vibrational energies E_n and E_{n+1},

$$\begin{aligned} a &= \frac{1}{r_{n+1} - r_n} \ln\left(\frac{1 - (E_n/D)^{\frac{1}{2}}}{1 - (E_{n+1}/D)^{\frac{1}{2}}}\right) \\ r_e &= r_n + (1/a) \ln\left[1 - (E_n/D)^{\frac{1}{2}}\right] \end{aligned} \tag{10}$$

The repulsive inner branch of the potential above the 21st level is assumed to be the continuation of the Morse function that fits the 20th and 21st levels. This part of the potential is so steep that it does not affect the integral of Eq. (8) very much in any case. The attractive branch of the potential above the 21st level is continued with a two-term power series that matches the slope and approximates the second derivative of the RKR potential at the 21st level,

$$U/D(r > r_{21}) = 1 - B(r_{21}/r)^6 + C(r_{21}/r)^{16} \tag{11}$$

where the coefficients B and C are

$$B = 1.6\left(1 - \frac{E_{21}}{D}\right) - 0.1\left(\frac{r_{21}}{D}\right)\left(\frac{\mathrm{d}E}{\mathrm{d}r}\right)_{21} = 0.51585 \tag{11a}$$

$$C = 0.6\left(1 - \frac{E_{21}}{D}\right) - 0.1\left(\frac{r_{21}}{D}\right)\left(\frac{\mathrm{d}E}{\mathrm{d}r}\right)_{21} = 0.06677 \tag{11b}$$

These coefficients provide the vibrational energy at the 21st level $U_{21}/D = 0.55092$ and the derivative $(\mathrm{d}U/\mathrm{d}r)_{21}/D = 1.30/\text{Å}$. A derivative mismatch does not change the vibrational levels more than a couple percent or so. However, if the potential is used for calculation of collision trajectories, a discontinuity in derivative results in a noticeable bump in trajectory direction. The second derivative is of much less importance, but choice of the very short range repulsive term inversely proportional to the 16th power of r gives a second derivative $(\mathrm{d}^2U/\mathrm{d}r^2)_{21}/D = -1.44/\text{Å}^2$, which is more or less in accord with the RKR potential at this point.

The computer iterates on the choice of level E_v until the action integral gives an integral vibrational quantum number v. Above the 21st, the levels are slightly more closely spaced than suggested by the JANAF series of Eq. (7), leading to a total of 64 levels at the dissociation limit rather than 58. This produces slightly larger values of energy and specific heat at high temperatures than given by the JANAF series. The first 21 vibrational levels were essentially the same as tabulated by Loftus and Krupenie.[7] These RKR levels along with the higher vibrational levels found by the present method are listed in Table 1.

Table 1 Vibrational energy levels for $X^1\Sigma_g^+$ state of N_2

v	E_v, cm^{-1}	v	E_v, cm^{-1}	v	E_v, cm^{-1}
0	1,175.5	22	45,701	44	72,857
1	3,505.2	23	47,345	45	73,597
2	5,806.5	24	48,950	46	74,292
3	8,079.2	25	50,518	47	74,940
4	10,323.3	26	52,050	48	75,543
5	12,538.8	27	53,546	49	76,100
6	14,725.4	28	55,006	50	76,613
7	16,883.1	29	56,429	51	77,082
8	19,011.8	30	57,814	52	77,507
9	21,111.5	31	59,160	53	77,891
10	23,182.0	32	60,468	54	78,234
11	25,223.3	33	61,737	55	78,538
12	27,235.3	34	62,964	56	78,804
13	29,218.0	35	64,150	57	79,035
14	31,171.2	36	65,294	58	79,232
15	33,094.9	37	66,395	59	79,396
16	34,989.0	38	67,453	60	79,532
17	36,853.5	39	68,466	61	79,641
18	38,688.3	40	69,435	62	79,726
19	40,493.4	41	70,360	63	79,789
20	42,268.6	42	71,238	64	79,834
21	44,014.1	43	72,070		

For some engineering purposes it is convenient to use a relatively simple analytic expression that captures the important functional behavior of the exact potential. The Morse function is surprisingly good in this respect, even though it gives a slightly fatter potential well than realistic and 68 levels at the dissociation limit. For the Morse function, r_e in Eq. (9) is just the equilibrium interatomic distance, and the constant a is related to the measured vibrational frequency ω in the ground vibrational state:

$$\begin{aligned} r_e &= 1.094\ \text{Å} \\ a &= (\mu\omega/2D)^{\frac{1}{2}} = 2.6905\ \text{Å}^{-1} \end{aligned} \tag{12}$$

The next section compares the vibrational partition functions, energies, and specific heats obtained with these different potential functions.

Comparison of Results

Figure 1 shows the vibrational partition function obtained for the ground state N_2 molecule with the RKR potential, the JANAF series, the Morse potential, and the harmonic oscillator. The RKR potential probably provides the best estimate for the total number of vibrational levels and for vibrational properties at very high temperature. The JANAF series gives a slightly smaller partition function because it provides fewer levels; the deviation caused by differences in anharmonicity is small. For example, if the RKR potential is truncated at the 58th level, the difference with the JANAF series result is almost eliminated. The Morse function provides a total of 68 vibrational levels and gives slightly too large a partition function. Even at 35,000 K the differences are not great; the JANAF partition function is only 2.5% low, whereas the Morse value is 4.6% high. The harmonic oscillator partition function is much too low because anharmonic effects are ignored.

Figure 2 shows the dimensionless vibrational energy for the different potentials. Since this parameter involves only the logarithmic derivative of the partition function, the results are not highly sensitive to small differences in anharmonicity and again differences depend primarily on the number of vibrational levels available. At

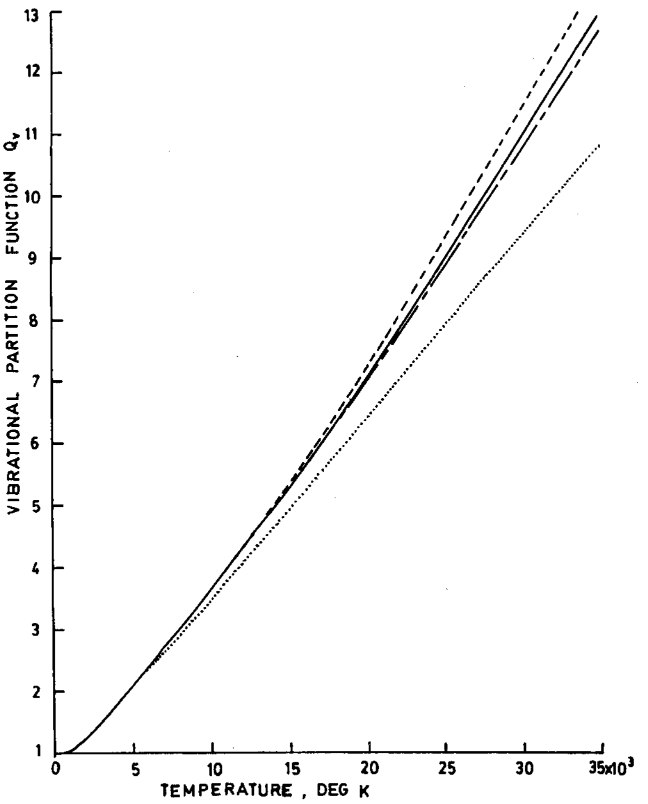

Fig. 1 Vibrational partition function of N_2, Q_v: ——, RKR potential; — - —, JANAF series; - - - -, Morse potential; and ······, harmonic oscillator.

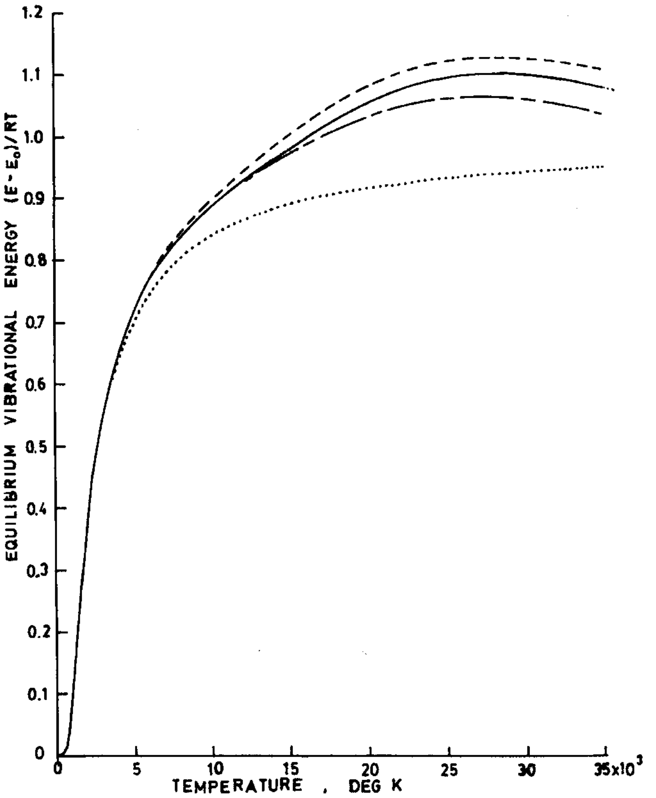

Fig. 2 Equilibrium vibrational energy of N_2, $(E-E_0)/RT$: ——, RKR potential; — - —, JANAF series; - - - -, Morse potential; and ······, harmonic oscillator.

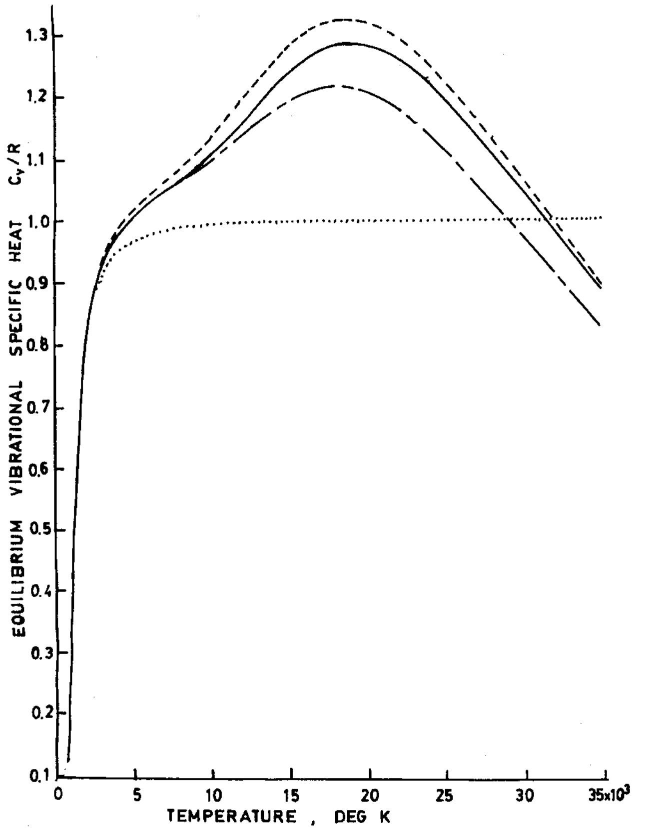

Fig. 3 Equilibrium specific heat of N_2, C_v/R: ——, RKR potential; — - —, JANAF series; - - - -, Morse potential; and ······, harmonic oscillator.

35,000 K the JANAF result is 3.3% low, whereas the Morse result is 3.1% high compared to the RKR result. The maximum in the dimensionless energy occurs near 30,000 K and at much high temperatures will decrease far below the harmonic oscillator limit of unity.

Figure 3 shows the equilibrium specific heat for the different potential models. A pronounced maximum in the specific heat occurs around 20,000 K, where the JANAF result is 4.3% lower and the Morse result is 4.5% higher than given by the RKR potential. At 35,000 K the specific heat is on its way to vanishing and dips well below the harmonic oscillator limit.

Vibration Rotation Coupling

When rotations are present, the diatomic molecule is stretched and vibrational levels are depressed, while the total internal energy of the molecule includes rotational energy as well as vibrational. With the Dunham series this is handled by fitting the series to both rotational and vibrational levels. The JANAF tables express the total internal energy $E(v, j)$ for vibrational and rotational quantum numbers v and j, respectively,

$$
\begin{gathered}
E(v, j) = E_v + Bj(j+1) - Dj^2(j+1)^2 \\
B = 1.998197\,Y - 3.283 \cdot 10^{-5}\,Y^2\,\mathrm{cm}^{-1} \qquad (13) \\
D = 5.74 \cdot 10^{-6}\,\mathrm{cm}^{-1}
\end{gathered}
$$

where E_v is obtained from Eq. (7). Although this type of correction could be added to the RKR vibrational levels of Table 1 to account for rotational effects, it is not necessary to resort to the approximation inherent in extrapolation of a power series beyond observed levels. Once the $j = 0$ potential is known accurately, an exact correction to the potential for finite rotational quantum number j is

$$
U(v, j) = U(v, 0) + \frac{j(j+1)\hbar^2}{2\mu r^2} \qquad (14)
$$

and precise eigenvalues for state v, j can be calculated by finding integer values for the action integral, Eq. (8), just as was done for the rotationless state.

Concluding Remarks

At temperatures where differences due to anharmonicity and the number of vibrational states become apparent, the plasma around space vehicles is not likely to be in equilibrium because of the low atmospheric density where these very high speed vehicles decelerate. The computational fluid dynamics (CFD) codes used to analyze such flow are not based on equilibrium chemistry, as they were for much of the Apollo re-entry problem, but are concerned with rate processes in the plasma. However, the equilibrium energy function is useful in evaluating the relaxation toward equilibrium in the flow, since expressions for the relaxation rate[9,10] are proportional to the difference between the equilibrium energy and the local energy that exists at the same kinetic temperature. For this purpose, the RKR energy levels listed in Table 1 should provide the best estimate for equilibrium vibrational energy.

Although high vibrational levels are somewhat uncertain, whether given by extending an empirical series that has been fit to measured lower levels or by continuation of the RKR potential with a function having the correct asymptotic behavior, these levels do not strongly influence the action integral since the major contribution to the integral at high quantum numbers still comes from the lower levels. Actually the two models are reasonably supportive. At the 27th level, the highest level measured, the JANAF vibrational level is only 0.4% higher than found by the present method, and out to the dissociation limit the JANAF levels are generally no more than 1.5% higher. The different results given by the two models are primarily due to the different number of total levels taken to reach the dissociation limit, not to the small differences in vibrational energy eigenvalues.

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