

Ideal-Gas Properties of New Refrigerants from Quantum Mechanical Ab Initio Calculations

K. Lucas,¹ U. Delfs,¹ V. Buss,² and M. Speis²

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Theoretical predictions of ideal-gas properties from molecular data such as structure, vibrational frequencies, and the barrier of internal rotation are compared to recent experimental data on heat capacities of new refrigerants. It is demonstrated that the required molecular data can be obtained from quantum-mechanical ab initio calculations with sufficient accuracy to provide heat capacities with an accuracy of $\pm 2\%$. Further improvement of the approach appears feasible. This is of great practical significance, since molecular data obtained from experimental spectra tend to be inaccurate for systems of technical interest with somewhat larger molecules, like the new refrigerants.

KEY WORDS: heat capacity; ideal gas; molecular data; refrigerants; vibrational frequencies.

1. INTRODUCTION

Ideal-gas properties, notably heat capacities, are needed with a good accuracy in many engineering applications. In recent years considerable effort has gone into the production of reliable data for new refrigerants, since the common ones have been identified as having a considerable ozone depletion potential and a contribution to the global greenhouse effect. When the task of providing data for these substances adequate for cycle calculations was considered, it became evident that a considerable experimental effort was required to meet practical needs.

¹ Fachgebiet Thermodynamik, Universität Duisburg, Lotharstr. 1, 47048 Duisburg, Germany.

² Fachgebiet Theoretische Chemie, Universität Duisburg, Lotharstr. 1, 47048 Duisburg, Germany.

It may seem somewhat surprising that providing reliable ideal-gas properties, notably heat capacities, was found to be a problem. Direct measurements of gaseous heat capacities on the basis of calorimetry or speed-of-sound experiments are rather rare and of an uneven quality. Figure 1 serves to illustrate this point for the fluids R 22, R 114, and R 134a. For R 22 measurements over the years differ by up to 6%, while for R 114 the data differ by about 4%. For the new refrigerant R 134a the recent data of Goodwin and Moldover [1], Kohler [2], and Ernst [3] agree to within 1%. For quite a few of the new refrigerants, measurements of gaseous heat capacities are not available at all or are just becoming available by present experimental efforts. The view is frequently taken that statistical thermodynamics provides a convenient route to ideal-gas properties, with an accuracy comparable to that of the best experimental data. While this is certainly correct for small molecules, it is not quite so for somewhat more sophisticated molecules such as the ones addressed in this paper. The molecular properties, notably vibrational frequencies and internal rotation barriers, needed to run the statistical-mechanical machinery

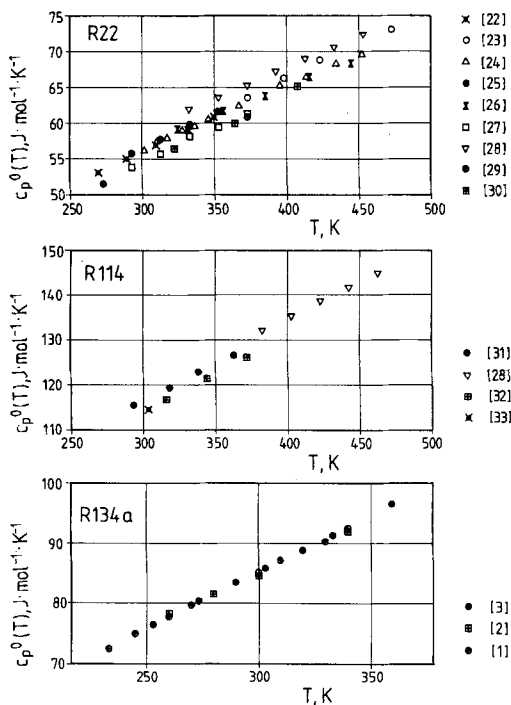


Fig. 1. Experimental heat capacity data at zero pressure.

are easily obtained with good accuracy from spectroscopic measurements only for simple molecules with a few atoms. For the new refrigerants the situation is confusing. Figure 2 illustrates this for the fluids considered in Fig. 1. On the one hand, for the simple molecule R 22 we find a rather satisfactory agreement within 0.5 to 1% between the heat capacities calculated from two sources of frequencies. For R 114, on the other hand, there are differences of 9% between the two sets of frequencies found in the literature. Finally, for R 134a the differences in the calculated ideal gas heat capacities from different sets of frequencies amount to about 2%. Experience generally reveals that ideal-gas heat capacities from different sources for the frequencies which are in good mutual agreement also tend to agree with the most reliable experimental data. If two sets of frequencies lead to different heat capacities, or if only one single set of frequencies is available, there is at present no method to judge the "true" data with any confidence.

In this situation it is helpful to go to the theoretical roots of the statistical-thermodynamics route to the ideal-gas properties, i.e., the internal molecular-force field. We demonstrate in this paper that quantum-

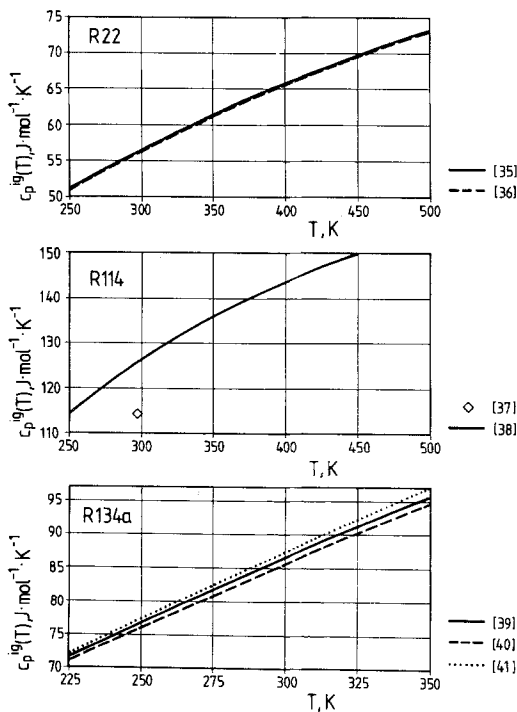


Fig. 2. Ideal-gas heat capacity data.

mechanical ab initio calculations of the intramolecular potential energy yield the required molecular properties for the molecules under consideration with sufficient accuracy to provide safe calculations of ideal-gas properties. The method shows considerable potential of refinement in order to meet the high requirements of accuracy in engineering calculations.

2. STATISTICAL THERMODYNAMICS

The statistical-thermodynamic route to the ideal-gas properties is based on the equation [4]

$$A^{\text{ig}} - U^0 = -kT \ln Q^{\text{ig}} \quad (1)$$

where A^{ig} is the Helmholtz free energy of the ideal gas, U^0 a contribution due to the zero point of energy, k the Boltzmann constant, T the thermodynamic temperature, and Q^{ig} the canonical partition function of the ideal gas, i.e.,

$$Q^{\text{ig}} = \frac{1}{N!} q_{\text{tr}}^N q_{\text{ntr}}^N \quad (2)$$

In the latter equation, N is the number of molecules, q_{tr} the molecular partition function of the translational degrees of freedom, and q_{ntr} the molecular partition function of the nontranslational degrees of freedom. Equation (2) for the canonical partition function of the ideal gas implies corrected Boltzmann statistics as well as the independence of the translational and nontranslational degrees of freedom of the molecules. In the practical calculations of this paper the nontranslational energy of a molecule is synthesized as

$$\varepsilon_{\text{ntr}} = \varepsilon_{\text{r}} + \varepsilon_{\text{v}} + \varepsilon_{\text{ir}} \quad (3)$$

where ε_{r} represents the molecular energy of external rotation, ε_{v} the molecular energy of vibration, and ε_{ir} the molecular energy of internal rotation. Strictly speaking the electronic energy in the Born-Oppenheimer approximation and correction terms such as anharmonic vibration and vibrational-rotational coupling would have to be considered. For the systems and the temperature range considered in this paper, the electronic energy does not contribute and the correction terms are neglected as an approximation. For the ideal-gas heat capacity we thus find the expression

$$c_{\text{p}}^{\text{ig}} = c_{\text{p, tr}}^{\text{ig}} + c_{\text{p, r}}^{\text{ig}} + c_{\text{p, v}}^{\text{ig}} + c_{\text{p, ir}}^{\text{ig}} \quad (4)$$

with

$$c_{p, \text{tr}}^{\text{ig}} = \frac{5}{2} Nk \quad (5)$$

$$c_{p, \text{r}}^{\text{ig}} = \frac{3}{2} Nk \quad (6)$$

$$c_{p, \text{v}}^{\text{ig}} = Nk \sum_{j=1} \frac{(\theta_{v, j}/T)^2 e^{\theta_{v, j}/T}}{(e^{\theta_{v, j}/T} - 1)^2} \quad (7)$$

and $c_{p, \text{ir}}^{\text{ig}}$ being the contribution of hindered internal rotation as computed from a numerical solution of the Schrödinger equation or convenient tabulations [4]. The value for $c_{p, \text{ir}}^{\text{ig}}$ depends on the potential energy of internal rotation which is parametrized in terms of the barrier of internal rotation, i.e., $U_{\text{ir}, \text{max}}$, and the reduced moment of inertia, I_{ir} . In the contribution of vibration $\theta_{v, j} = hv_{0j}/k$ is the characteristic temperature associated with the j th harmonic frequency ν_{0j} and h is Planck's constant.

Evidently, in order to calculate ideal-gas heat capacities from the formulae of statistical thermodynamics, certain molecular properties, i.e., properties of the intramolecular force field, are needed. These are the harmonic frequencies ν_{0j} , the barrier of internal rotation $U_{\text{ir}, \text{max}}$ and the reduced moment of inertia I_{ir} . In standard applications of statistical thermodynamics to the calculation of ideal-gas heat capacities, the frequencies are obtained from compilations based on experimental spectroscopy. For small molecules, rather accurate frequencies can be extracted from such data. For the molecules considered in this paper the resolution of the experimental spectra is complicated and unreliable frequency assignments tend to emerge, as demonstrated in Fig. 2. Values for the barrier of internal rotation can also be found from spectroscopic data but are seldom available with a high accuracy. Frequently they are fitted to experimental values of the heat capacity or entropy, thus depriving the calculations somewhat from their predictive nature. The structure of the molecule, i.e., I_{ir} , is usually known from spectroscopy with sufficient accuracy. Since all these required molecular properties are properties of the intramolecular force field, they can in principle be obtained from quantum-mechanical ab initio calculations.

3. QUANTUM-MECHANICAL CALCULATIONS

According to the basic postulates of quantum mechanics [5] a molecular state is completely described by its wave function Ψ , which is an

eigenfunction of the molecular Hamiltonian \hat{H} in the time-independent Schrödinger equation

$$\hat{H}\Psi = E\Psi \quad (8)$$

\hat{H} contains the quantum-mechanical expressions for the kinetic and potential energy terms of the nuclei and electrons that make up the molecule, and the eigenvalue E is the energy of the state. Ψ , which is a function of the coordinates of all particles, is defined in such a way that $\Psi^*\Psi$ represents the probability density of that particular state.

In quantum theory the concept of an intramolecular force field derives directly from the Born–Oppenheimer approximation [6]. Because the heavy nuclei move much more slowly than the electrons, the nuclear kinetic energy terms are omitted in the so-called electronic Hamiltonian H^{el} , which acts on the electronic wave function Ψ^{el} to yield the energy E^{el} ,

$$H^{\text{el}}\Psi^{\text{el}}(\mathbf{r}, \mathbf{R}) = E^{\text{el}}(\mathbf{R}) \Psi^{\text{el}}(\mathbf{r}, \mathbf{R}) \quad (9)$$

While the electronic wave function depends on the electron coordinates \mathbf{r} as variables (and the nuclear coordinates \mathbf{R} as parameters), the electronic energy is a function of \mathbf{R} only. The variation of E^{el} with the nuclear coordinates gives a potential energy surface, $E(\mathbf{R})$, in which the nuclei are allowed to relax and to find their equilibrium configuration.

The electronic wave function is expressed as a determinantal, i.e., antisymmetrized product of molecular orbitals,

$$\Psi^{\text{el}} = |\psi_1 \cdot \bar{\psi}_1 \cdot \psi_2 \cdot \bar{\psi}_2 \cdot \dots| \quad (10)$$

where the unbarred functions denote occupation by an α -spin electron and the bar signifies β -spin. The pairwise occupation of molecular orbitals with α - and β -spins results in closed-shell states with which we are concerned here only. Finally, the molecular orbitals are expanded in terms of atomic orbitals ϕ , the so-called basis set:

$$\psi_i = \sum_{\mu} c_{\mu i} \phi_{\mu} \quad (11)$$

Variational determination of the expansion coefficients within the Hartree–Fock method leads to the Roothaan–Hall equations [7, 8]:

$$\sum_{\nu=1}^N (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) c_{\nu i} = 0, \quad \mu = 1, 2, \dots, N \quad (12)$$

In these equations $S_{\mu\nu}$ and $F_{\mu\nu}$ are the elements of the overlap and Fock matrix, respectively, calculated in the basis set defined above. The Fock

operator \hat{F} is the sum of one- and two-electron terms, *viz.*, the electron kinetic energy and their attraction due to the field of all nuclei, and the averaged repulsion due to the other electrons, respectively. The ε_i are the molecular orbital energies, and the summation is over all electrons N of the molecule. These equations can be solved only iteratively, since the calculation of the electron repulsion terms depends on the distribution of the electrons in the molecule. Starting with an assumed set of coefficients c the elements of the F matrix are computed and an initial set of ε_i 's is obtained. These are used to calculate a first set of coefficients from which new ε_i 's are derived, and so on. This calculation is repeated until the change of the coefficients from one cycle to the next is negligible and the conditions for the so-called self-consistent field (SCF) are met.

In ab initio theory, only basic natural constants enter the calculation, while in semiempirical methods computationally demanding steps such as calculation of the electron interaction integrals are neglected; other parameters are adjusted empirically to make up for this. Only the results of ab initio calculations are reported here, which are much more time-consuming than semiempirical methods and are restricted presently to calculations involving up to about 1000 basis functions. Geometry optimization and the calculation of (harmonic) frequencies as well as other molecular properties [9] are routinely performed nowadays as part of quantum-mechanical software packages such as the Gaussian 90 routines [10] and CADPAC [11].

There are two factors affecting the accuracy of ab initio calculated properties: one is the size of the basis set, which should be as large as possible but is limited by practical aspects; the other is electron correlation, which is a correction to the independent particle approach inherent in the orbital approximation [Eq. (10)]. Either configuration interaction (CI) or Møller–Plesset perturbation theory to different, e.g., second, order (MP2) is employed to deal with the correlation problem, but both require tremendous computer memory and time.

It is well-known that frequency calculations require a significantly higher accuracy in computation than the calculation of molecular geometries [12]. At the double-zeta level, which represents a rather sophisticated basis set, typical errors of force constants are 10 to 20%, while errors in bond lengths are only of the order of 1%. Scaling of harmonic force constants [13] yields better agreement with experiment, but only at the cost of introducing empirical elements into the calculations.

Taking electron correlation into account improves both calculated geometries and frequencies. At the MP2 level procedures have been developed to obtain analytical energy gradients and force constants to make geometry optimization more efficient [14, 15]. In a systematic study

of correlation effects at the MP2 level on geometries and force constants, it was found [16] that bond distances were off by 0.5 pm and bond angles by 0.2°, provided that an adequate basis set was used. Frequencies were more dependent on basis set size and were calculated with an average error of 2 to 7%.

All optimizations reported in this study were performed at the MP2 level with the standard split-valence 6-31G** and 6-311G** basis sets assuming C_s molecular symmetry. Harmonic frequencies were calculated analytically for the 6-31G** basis with CADPAC and numerically for the 6-311G** basis with Gaussian 90.

4. RESULTS

In order to demonstrate the kind of results that can be obtained from a combination of ab initio calculations and statistical thermodynamics, we have considered two of the new refrigerants, i.e., R 134a and R 152a. We first show the structure of the two molecules as compared to literature values from spectroscopic data presented in Tables I and II and shown in Figs. 3 and 4. It can be seen that the agreement of the ab initio results with the experimental data is generally excellent. In case of deviations the view is taken that the ab initio data are more realistic. In Tables III and IV, we list the harmonic frequencies as obtained from the quantum-mechanical calculations and compare to literature values from spectroscopic data. We observe that the calculated data are, on the average, about 5% too high. This may be due partly to the fact that the experimental frequencies are

Table I. Molecular Structure of R 152a^a

	MP2/6-31G** [42]	MP2/6-311G** [42]	Expt. [20]	Expt. [43]
$r_{C_1C_2}$	1.4978	1.5011	1.540 ^b	1.498
$r_{C_1H_4}$	1.0859	1.0909	1.100 ^b	1.081
$r_{C_1H_7}$	1.0858	1.0907	1.100 ^b	1.081
$r_{C_2H_3}$	1.0894	1.0918	1.100 ^b	1.081
$r_{C_2F_5}$	1.3719	1.3640	1.345 ^b	1.364
$\phi_{C_2C_1H_4}$	108.65	108.83	108.71	111.0
$\phi_{C_2C_1H_7}$	110.02	109.89	108.71	111.0
$\phi_{C_1C_2H_3}$	114.23	114.10	109.82	111.0
$\phi_{C_1C_2F_5}$	109.71	109.92	109.43	110.7
$\phi_{H_7C_1H_8}$	109.37	109.46	110.22 ^b	107.9
$\phi_{F_5C_2F_6}$	107.45	107.46	109.13	107.4

^a Bond distances in Å, angles in deg.

^b Assumed values.

Table II. Molecular Structure of R 134a^a

	MP2/6-31G** [44]	MP2/6-311G** [44]	Expt. [45]	Expt. [46]
$r_{C_1C_2}$	1.5064	1.5104	1.525	1.501
$r_{C_1F_4}$	1.3803	1.3715	1.345	1.389
$r_{C_1H_7}$	1.0871	1.0904	1.090 ^b	1.077
$r_{C_2F_3}$	1.3515	1.3431	1.336	1.334
$r_{C_2F_5}$	1.3442	1.3359	1.336	1.334
$\phi_{C_1C_2F_3}$	109.08	108.88	109.32	110.4
$\phi_{C_1C_2F_5}$	111.54	111.63	111.04	110.4
$\phi_{C_2C_1F_4}$	108.61	109.39	110.40	112.3
$\phi_{C_2C_1H_7}$	108.93	108.58	112.9 ^b	106.1
$\phi_{F_3C_2F_6}$	108.05	108.06	107.79	108.6
$\phi_{H_7C_1H_8}$	110.32	110.72	108.9 ^b	109.4

^a Bond distances in Å, angles in deg.^b Assumed values.Table III. Vibrational Frequencies for R 152a in cm⁻¹

	MP2/6-31G** [42]	MP2/6-311G** [42]	Expt. [18]	Expt. [17]
Symmetry				
a'	3269	3209	3018	3016
	3179	3145	2979	2975
	3157	3104	2963	2959
	1550	1509	1460	1466
	1500	1473	1414	1413
	1443	1413	1372	1362
	1202	1186	1143	1171
	1190	1181	1129	1142
	905	894	868	868
	572	578	571	569
	469	475	470	469
a''	3265	3207	3001	3016
	1551	1510	1460	1457
	1455	1438	1360	1164
	1208	1192	1169	1149
	1000	982	930	942
	387	389	383	383
(Torsion)	267	257	222	222

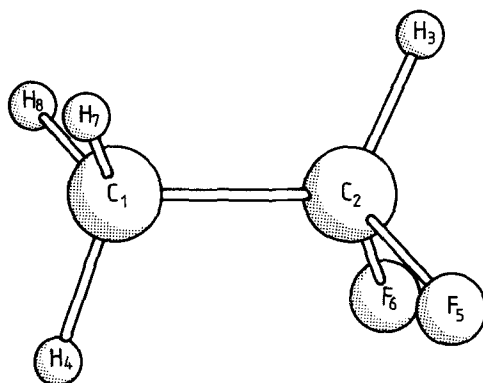


Fig. 3. Atom numbering for R 152a.

not truly harmonic frequencies but, rather, contain anharmonic effects. Corrections of the spectroscopic data to the harmonic values with anharmonic constants would bring the experimental data in even closer agreement with the *ab initio* data. For R 152a, two sets of spectroscopic frequencies are available in the literature. It can be seen that the more recent assignment by Guirgis and Crowder [17] of an additional frequency of 1164 cm^{-1} is not confirmed by the *ab initio* calculations, which rather support the older work of Smith et al. [18]. For R 134a, we note that the set of frequencies given in Ref. 19 is inconsistent with the other sources and leads to large errors in the calculated heat capacities. For R 134a and R 152a the moments of inertia and the barriers of internal rotation are

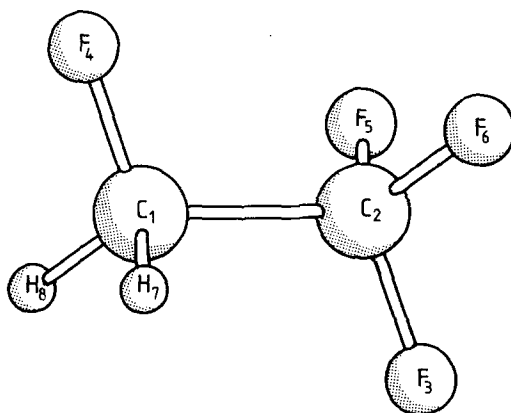


Fig. 4. Atom numbering for R 134a.

Table IV. Vibrational Frequencies for R 134a in cm^{-1}

	MP2/6-31G** [44]	MP2/6-311G** [44]	Expt. [41]	Expt. [19]	Expt. [47]	Expt. [40]
Symmetry						
a'	3176	3141	2984	2984	2986	2984
	1566	1522	1431	1464	1427	1431
	1511	1494	1296	1427	1296	1374
	1361	1347	1096	1298	1186	1296
	1249	1230	1067	1103	1103	1189
	1149	1146	908	972	1070	1096
	867	865	844	843	846	843
	669	677	666	665	666	666
	551	559	550	549	557	550
	414	420	358	408	410	409
	217	223	201	225	222	225
a''	3249	3215	3015	3013	3015	3015
	1366	1351	1374	1182	1463	1296
	1250	1242	1189	665	1296	1189
	1023	1001	972	539	971	972
	531	542	541	352	542	541
	360	360	407	225	358	350
(Torsion)	116	116	124	120	112	120

shown in Tables V and VI. In the ab initio calculations, the barrier of internal rotation was obtained as the difference between eclipsed and staggered conformation. In [20, 21] the experimental value was found from the value of the torsional frequency and the reduced moment of inertia. The agreement between calculated and experimental data is excellent for the

Table V. Moments of Inertia and Barrier of Internal Rotation for R 152a

	MP2/6-31G** [42]	MP2/6-311G** [42]	Expt. [20]	Expt. [43]
I_A ($10^{-40} \text{ g} \cdot \text{cm}^2$)	89.7313	88.5394	88.3795	88.4363
I_B ($10^{-40} \text{ g} \cdot \text{cm}^2$)	92.6254	92.9598	93.6709	93.2384
I_C ($10^{-40} \text{ g} \cdot \text{cm}^2$)	162.5127	161.6595	162.2875	162.6064
$(I_A I_B I_C)$ ($10^{-120} \text{ g}^3 \cdot \text{cm}^6$)	1,350,707	1,330,556	1,343,511	1,340,797
I_{ir} ($10^{-40} \text{ g} \cdot \text{cm}^2$)	4.9620	5.0021	5.1282	4.8908
$U_{\text{ir,max}}$ ($\text{kJ} \cdot \text{mol}^{-1}$)	16.748 ^a	15.883 ^a	14.937 ± 2.427	13.431 ^b

^a Energy difference between eclipsed and staggered conformation.

^b Ref. 21.

Table VI. Moments of Inertia and Barrier of Internal Rotation for R 134a

	MP2/6-31G** [44]	MP2/6-311G** [44]	Expt. [45]	Expt. [46]
I_A (10^{-40} g · cm ²)	158.3929	156.9424	156.6279	154.7731
I_B (10^{-40} g · cm ²)	299.5702	299.0976	299.7755	304.2106
I_C (10^{-40} g · cm ²)	303.2972	303.1248	304.0953	305.7262
$(I_A I_B I_C)$ (10^{-120} g ³ · cm ⁶)	14,391,152	14,229,008	14,278,243	14,394,689
I_{ir} (10^{-40} g · cm ²)	27.1551	26.6415	25.1078	25.1362
$U_{ir,max}$ (kJ · mol ⁻¹)	18.134 ^a	17.136 ^a	13.807 ± 3.347	14.979 ^b ± 0.586

^a Energy difference between eclipsed and staggered conformation.

^b Ref. 48.

moments of inertia and rather satisfactory for the barrier of internal rotation in view of the uncertainty associated with the experimental determination of this quantity.

Finally, in Fig. 5 we show the ideal-gas heat capacity of both molecules as obtained from the combination of statistical thermodynamics with quantum mechanical ab initio results as compared to experimental data.

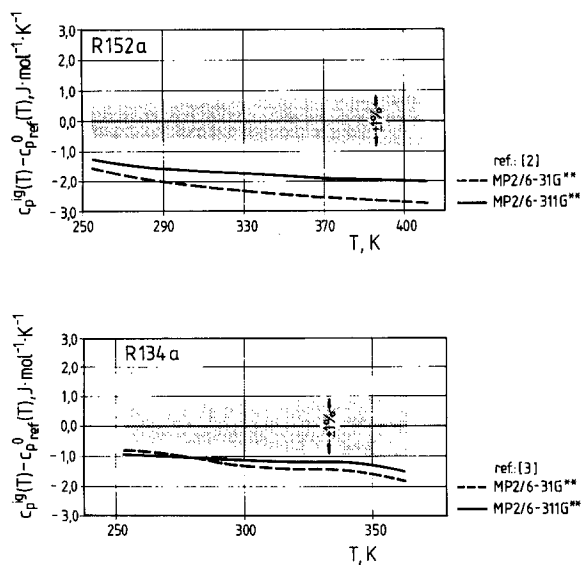


Fig. 5. Comparison of calculated and experimental heat capacity data.

For both gases the experimental data [2, 3] are about 2% higher than the calculated values. The results for both substances thus confirm that the combination of statistical thermodynamics with quantum-mechanical ab initio calculations is a rather fruitful route to ideal gas properties. The frequencies obtained are truly harmonic frequencies with unquestionable assignments. They can serve to discover obvious errors in the evaluations of spectra by earlier authors. Their accuracy, while not better than about 2% at this time, suffice to provide ideal-gas heat capacities with a great reliability. There is still a potential for higher accuracy in the final results. It is possible to extract anharmonicity and other correction effects from the quantum mechanically determined force field. These contributions should effectively make the final heat capacities somewhat larger, and this will bring the calculated values in even closer agreement with experimental data.

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