The dissociation energy of \( N_3 \)

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Unlike the substantial amount of information available on the azide anion \( \text{N}_3^- \), studies on the \( \text{N}_3 \) radical are relatively limited. Recently, a Fourier transform IR study yielded a very precise \( r_0 = 1.1815 \pm 0.0005 \) Å for the \( \text{X}\,^2\text{II}_g \) ground state, as well as a \( \sigma_u \) fundamental of 1644.6784 cm\(^{-1}\). Unpublished \textit{ab initio} calculations by Adamowicz\(^\text{2}^{\text{3}}\) yielded \( r_e = 1.181 \) Å at the CCSD/6-311G* level, and 1.186 Å at the MP4/6-311G* level. Matrix IR spectra were published by Tian \textit{et al.}\(^\text{4}^{\text{5}}\) who found the \( \sigma_u \) fundamental at 1657.5 cm\(^{-1}\), a \( \sigma_u - \sigma_v \) combination mode at 2944.9 cm\(^{-1}\), and a zero-order Renner–Teller average for the bending frequency of 472.7 cm\(^{-1}\). The spin–orbit coupling constant is 71.3 cm\(^{-1}\),\(^\text{6}\) whereas the \( A\,^2\Sigma_u^+ \) state has a \( T_e \) of 36811 cm\(^{-1}\).\(^\text{7}\)

The dissociation energy is not very accurately known. The most recent value was obtained by Pellerite \textit{et al.}\(^\text{5}^{\text{6}}\) using ion cyclotron resonance, which yielded \( \Delta H_0 = 112.5 \pm 2 \) kcal/mol, which corresponds to \( \Delta H_0 = \Sigma D_0 = 725.6 \pm 5 \) kcal/mol (from \( \Delta H_0 = 112.5 \pm 2 \) kcal/mol).\(^\text{5}^{\text{6}}\) Some work yielded \( \Delta H_0 = 12.5 \pm 2 \) kcal/mol, or \( \Sigma D_0 = 237.9 \pm 5 \) kcal/mol. In our own paper on boron–nitrogen clusters,\(^\text{10}^{\text{10}}\) we obtained \( \Delta H_0 = 210.9 \) kcal/mol from CCSD(ST)/6-31G* energies and a scaling procedure as proposed by Raghavachari,\(^\text{11}^{\text{11}}\)\(^\text{12}^{\text{12}}\) which is expected to be accurate to 0.2 eV. The only other theoretical determination was a paper by Petrongolo,\(^\text{13}^{\text{13}}\) who computed \( D_e = 2.25 \) eV for the lowest dissociation products \( \text{N}_2 \) and \( \text{N}(^2\text{D}) \) using a \( [5s3p2d] \) basis set, augmented by \( (spd) \) bond functions, and the MRD–CI procedure\(^\text{14}^{\text{14}}\) with 9 reference configurations and energy extrapolation. Combining this with the \( D_e (\text{N}_2) = 9.90 \) eV,\(^\text{15}^{\text{15}}\) \( T_e (\text{D} = \text{S}) = 19 \) 2244.464 cm\(^{-1}\),\(^\text{17}^{\text{17}}\) and a zero-point energy (ZPE) from the experimental frequencies of \( 5.6 \) kcal/mol, a \( \Sigma D_0 = 219.6 \) kcal/mol is obtained, in marginal agreement with the newer experimental result. However, an accurate \textit{ab initio} determination is apparently desirable to settle the issue.

All calculations were carried out at the experimental \( r_0 \)\(^\text{2}^{\text{2}}\) using the GAUSSIAN 88 package\(^\text{18}^{\text{18}}\) running on the IBM 3090/400e VF at the K. U. Leuven, under the MVS/XA operating system.

Standard 6-311G*,\(^\text{17}^{\text{17}}\) 6-311 + \( G^* \),\(^\text{18}^{\text{18}}\) and 6-311G(2df)\(^\text{19}^{\text{19}}\) basis sets were used. Electron correlation was included using the QCISD(T) model,\(^\text{20}^{\text{20}}\) which was very recently shown\(^\text{21}^{\text{21}}\) to be a very good approximation to CCSD(T).\(^\text{22}^{\text{22}}\) (An excellent review of coupled cluster theory is found in Ref. 23.) Single\(^\text{24}^{\text{24}}\) and multiply\(^\text{25}^{\text{25}}\) projected MP2 and MP3 energies, as well as the unprojected MP4(SDQ)\(^\text{26}^{\text{26}}\) energy, are obtained \textit{en passant} in the calculations. Full MP4\(^\text{26}^{\text{26}}\) energies were obtained in separate runs for all three basis sets.

Atomization energies were then obtained using both standard G1 theory,\(^\text{27}^{\text{27}}\) and a variation in which all MP4 energies are replaced by their more accurate QCISD(T) counterparts. This was done because a recent study of the NASA Ames group\(^\text{28}^{\text{28}}\) on the C–H dissociation energy of acetylene has indicated that the regular G1 recipe is perhaps not appropriate for highly spin-contaminated species. It was already shown some time ago\(^\text{29}^{\text{29}}\) on theoretical grounds that the CCSD energy (and, by extrapolation, its QCISD approximation) is not affected by a single spin contaminant.

Because of high spin contamination (\( \langle \hat{S}^2 \rangle > 0.90 \)), singlet excitations will be very important. We therefore evaluated the binding energies of \( \text{N}_2 \) and \( \text{N}_3 \) using the QCISD(T)/6-31G* model from UHF/6-31G* geometries,\(^\text{29}^{\text{29}}\) which yielded 198.5 and 191.6 kcal/mol, respectively. Scaling the binding energy with 1.15 yields a very good value of 228.3 kcal/mol for the \( D_e \) of \( \text{N}_2 \), and a \( D_e \) of 220.4 kcal/mol (\( D_e \) = 214.7 kcal/mol). Thus, the quasiperturbative treatment of single excitations in CCSD(ST) explains part, but not all, of the disagreement between our previously computed value and experiment. [It is perhaps also worth mentioning that the MP4(DQ) and CCD binding energies differ only slightly, and that the MP2 and MP3 values converge smoothly to that value: this indicates that no convergence problem exists as far as the \( T_2 \) effects are concerned.]

Table I presents total and dissociation energies obtained using the three basis sets listed above, as well as from assuming additivity of the effects of diffuse functions and expansion of the polarization space. As these two effects are very different, this assumption should hold quite well.

It is immediately seen that the QCISD total energy for \( \text{N}_3 \) is underestimated by 6 to 7 millihartrees at the MP4(SDQ) level, as well as that the triple excitation effect is significantly overestimated at the MP4 level. Oddly, the two effects compensate each other, leading to a relatively small difference between the full MP4 and the QCISD(T) binding energies (there also exists some cancellation between the separated atoms and the molecule). Furthermore, the differences work in opposite directions for the various basis sets, underestimated the binding energy by 0.11 and 0.77 kcal/mol for the 6-311G* and 6-311G(2df) basis sets respectively, and overestimating it by about 0.24 kcal/mol for the 6-311 + \( G^* \) basis set. For the combined binding energy, this finally results in a net underestimate of 0.42 kcal/mol. The G1 correction amounts to 14.46 kcal/mol; the corrected QCISD(T)/6-311 + \( G(2df) \) binding energy within the basis set additivity approximation, is then 233.95 kcal/mol, compared to 233.64 kcal/mol using the conventional G1 recipe. Apparently the G1 value benefits from the fortuitous cancellation, which might not have been observed if oscillation of the MP series were also present.

Basis set effects are strikingly large, including an in-
TABLE I. Total energies (hartree, minus sign omitted) of 3N and N₃ and total atomization energy (TAE, kcal/mol) of N₃.

<table>
<thead>
<tr>
<th>Method</th>
<th>6-31G*</th>
<th>TAE</th>
<th>6-311G*</th>
<th>TAE</th>
<th>6-311 + G*</th>
<th>TAE</th>
<th>6-311G(2df)</th>
<th>TAE</th>
<th>a</th>
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<tr>
<td>UHF</td>
<td>163.156327</td>
<td>163.193941</td>
<td>163.196678</td>
<td>163.193941</td>
<td></td>
<td></td>
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<td>MP4(SDQ)</td>
<td>163.418412</td>
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<td>163.475959</td>
<td>163.522031</td>
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<td>163.472685</td>
<td>163.477524</td>
<td>163.526664</td>
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<td></td>
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<tr>
<td>QCISD</td>
<td>163.419420</td>
<td>163.471785</td>
<td>163.476796</td>
<td>163.522715</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>QCISD(T)</td>
<td>163.421441</td>
<td>163.474825</td>
<td>163.479607</td>
<td>163.529098</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

| UHF     | 163.245792 | 56.14 | 163.280996 | 54.63 | 163.284143 | 54.89 | 163.296994 | 64.67 | 64.92 |
| MP4(SDQ) | 163.701424 | 177.59 | 163.761350 | 182.32 | 163.766954 | 182.83 | 163.842787 | 201.28 | 201.79 |
| MP4     | 163.724165 | 191.01 | 163.789834 | 199.01 | 163.795913 | 199.79 | 163.874534 | 218.29 | 219.07 |
| QCISD   | 163.707520 | 180.79 | 163.768221 | 186.02 | 163.773728 | 186.33 | 163.848940 | 204.71 | 205.02 |
| QCISD(T) | 163.726744 | 191.58 | 163.791603 | 199.12 | 163.797606 | 199.55 | 163.878199 | 219.06 | 219.49 |

* Using additivity approximation (see text).

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The ZPE as obtained from the UHF/6-31G* harmonic frequencies scaled by a recommended factor of 0.8930 is 5.62 kcal/mol, compared to the 5.56 kcal/mol obtained from the experimental bands. Assuming positive anharmonicity constants (which is the normal situation), the latter value will be a lower bound to the true ZPE. We will therefore use the 5.62 kcal/mol value (in keeping with the G1 model) as a "second best" alternative to the ZPE obtained from a full anharmonic force field. We then finally obtain a ΣD₀ of 228.35 kcal/mol and a heat of formation at 0 K of 109.25 kcal/mol, in excellent agreement with the result of Pellerite et al.

In order to obtain the heat of formation at 298.15 K, we have set up the partition functions using the available experimental data and a RRHO approximation. Except perhaps for the bending frequency, the relatively high frequencies, and the fact that the experimental data correspond to the first vibrational transitions (which will dominate the partition function), the use of this model is certainly warranted. One other term which should be included is the spin-orbit coupling, for which we assumed that the computed ground state splits up in two levels ± 71.3/2 cm⁻¹. At very high temperatures, the levels will have comparable populations and may be treated as degenerate: at room temperature, however, we find an atomization enthalpy increase of 0.119 kcal/mol. The degenerate bending vibration contributes −0.308 kcal/mol, the two others together only −0.009 kcal/mol. The rotational enthalpy using the first four terms of the well-known asymptotic series is indistinguishable from the classical result (−0.592 kcal/mol). Finally, the translation enthalpy difference adds up to −2.962 kcal/mol. Together, the thermal atomization enthalpy is 2.173 kcal/mol. Combining this with ΔH°_298 K[N(g)] = 112.97 kcal/mol, we finally find ΔH°_298 K[N₃(g)] = 108.4 ± 2 kcal/mol.
Radiative lifetimes of the $\tilde{A}^2A_1(ν_3=0–2)$ states of CH$_3$S

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The methylthio radical (CH$_3$S) is an important intermediate in combustion and atmospheric chemistry. Recent kinetic studies on various reactions of CH$_3$S have employed the laser-induced fluorescence technique to monitor the concentration of CH$_3$S. However, published measurements of the lifetimes of the vibrational levels of the $\tilde{A}^2A_1$ state of CH$_3$S vary more than twofold. Our new measurements of the radiative lifetimes were made on CH$_3$S which was generated by either laser photolysis of dimethyl disulfide (CH$_3$SSCH$_3$) or the reaction of F and CH$_3$H in a discharge-flow system.

In the photolysis technique, CH$_3$S was generated from CH$_3$SSCH$_3$ by means of KrF laser emission at 248 nm (5–20 mJ). Two types of experiments were performed using either the low-pressure gas cell or the supersonic expansion technique. In the cell-photolysis experiments, the partial pressures were typically 0.003–0.3 Torr for CH$_3$SSCH$_3$ and 0.6–20 Torr for He. A slow flow with a residence time of ~1 s in the cell was utilized to replenish the reagent. In the supersonic expansion, a pulsed nozzle (of diameter 0.5 mm) with a gate width of 500 μs and a stagnation pressure 2200–2800 Torr was used. In the discharge-flow technique, CH$_3$S was produced by the reaction of F and CH$_3$H. The F atoms were generated in a microwave discharge of a CF$_4$/He mixture in a side-arm of the flow tube. CH$_3$SH was introduced to the flow tube via a sliding injector. Typical experimental conditions for the discharge-flow method are $P_{\text{CH}_3\text{SH}} = (1–5.4) \times 10^{-4}$ Torr, $P_{\text{CF}_4} = (1–19) \times 10^{-3}$ Torr, $P_{\text{He}} = 0.4–2.0$ Torr, and $\overline{v} = 600–1000$ cm$^{-1}$.

The CH$_3$S was excited to various vibrational levels of the $\tilde{A}$ state by means of either an excimer-pumped dye laser (356–400 nm), or a Nd–YAG laser system which emitted in the range 363–380 nm by frequency mixing of the output at 1.06 μm with that from the 532 nm pumped dye laser. The $ν_3 = 0$, 1, and 2 levels of the $\tilde{A}$ state were populated by excitation near 377.0, 371.4, and 366.0 nm, respectively. The fluorescence was collected with a set of quartz lenses, passed through either a 450 nm interference filter (FWHM = 10 nm) or a 0.32 m monochromator, and detected by a photomultiplier (Hamamatsu R928). The output of the photomultiplier was amplified (300 MHz bandwidth) before its signal was averaged by a 125 MHz digital storage oscilloscope. Typically 1000–5000 waveforms were averaged; the averaged waveform was transferred to a microcomputer for analysis. Typically a single exponential fit was carried out over 2–3 decay lifetimes. A digital delay pulse generator was used to trigger the lasers and the oscilloscope. In the photolysis experiments CH$_3$S was usually probed with a delay >25 μs after the photolysis.

The fluorescence decay rate ($τ^{-1}$) for the $ν_3 = 0–2$ levels are shown in Fig. 1. In the cell-photolysis experiments, the decay rates of the $ν_3 = 0$ level increased as the [CH$_3$SSCH$_3$] was increased within the range (2–62) $\times 10^{14}$ molecule cm$^{-3}$, as noted by the symbols ▲ in Fig. 1. The intercept in Fig. 1 gave a radiative lifetime 1070 ± 15 ns, whereas the slope gave (7.8 ± 0.8) $\times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the quenching rate coefficient of this level by CH$_3$SSCH$_3$. The uncertainties represent one standard error. In the discharge-flow experiments, the decay rates of the $ν_3 = 0$ level were approximately constant ($τ = 1170 ± 20$ ns) either as [CF$_4$] was increased within the range (2–61) $\times 10^{13}$ molecule cm$^{-3}$.

FIG. 1. Decay rates of the $ν_3 = 0–2$ levels of CH$_3$S ($\tilde{A}^2A_1$) in the cell photolysis experiments (▲, $ν_3 = 0$; □, $ν_3 = 1$; ○, $ν_3 = 2$). The ordinate for the $ν_3 = 1$ level has been shifted upward by 2 $\times 10^6$ s$^{-1}$. 