**PERSPECTIVES: COMPUTATIONAL ANALYSIS**

# $Y_2K$

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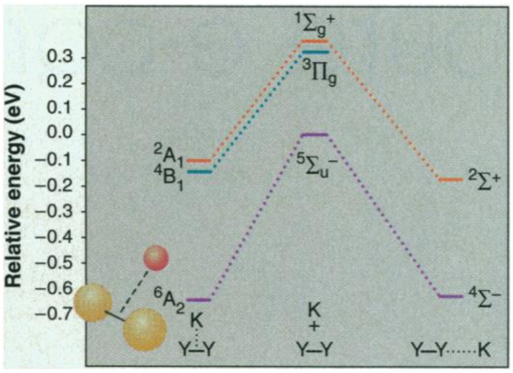
Few subjects in 1999 have received greater press coverage than $Y_2K$. It is with some shock that we have found the chemical literature to contain no references to this obviously critically important molecule. To alleviate this situation, we performed a quantum chemical analysis of diyttrium potassium ($Y_2K$) to characterize its likely molecular and electronic structure (*1*) and to better address the "$Y_2K$ problem." [Other key yttrium-containing molecules, such as YOY and YNOT (radioactive), also remain to be characterized; these may concern future investigators.]

How does the computational chemist approach $Y_2K$? The task can proceed faster (and in the case of the $Y_2K$ problem, timely solutions are obviously critical) if we apply some chemical intuition to the problem. $Y_2K$ may reasonably be expected to be either linear or T shaped, with a potassium atom bound to an yttrium dimer. We thus take a building block approach, starting with the $Y_2$ dimer and then introducing a K atom. We compute energies for different electronic states for both linear and T-shaped geometries.

We first tested the level of electronic structure theory used in our study (referred to hereafter as the MPW1/DZVP level) (*2*) by computing properties of the related scandium dimer. The calculated properties of $Sc_2$ [hyperfine splitting (hfs), vibrational frequency, and dissociation energy] are in good agreement with experiments (*3*, *4*), lending confidence in the utility of the MPW1/DZVP level of theory for studying the $Y_2K$ problem.

We characterized three different electronic states for $Y_2$; these states correlate with low-energy states of $Y_2K$. The lowest energy (that is, ground) state is predicted to be a high-spin (pentet) state, in agreement with assignments based on photoelectron spectroscopy (*5*) and previous calculations (*5*, *6*). Some experimentalists, however, have suggested that the singlet is the ground state (*7*). Our predicted hfs value for the pentet (*8*) may prove useful for future experiments using electron spin resonance to resolve this controversy.

Armed with these results for $Y_2$, we now consider the linear and T-shaped isomers of $Y_2K$ (see the figure). For each case, we have characterized three likely low-energy states (see the table). The T-shaped isomers are best thought of as weak to moderate charge-transfer complexes between a K atom and $Y_2$. The magnitudes of the interaction energies between K and $Y_2$ in the different states are directly reflected in their molecular dipole moments (see the table). Charge transfer is facilitated in all cases by the availability of a relatively low-energy empty orbital of $Y_2$ of appropriate symmetry.



**Explosion: unlikely.** Energies (in electron volts) for different $Y_2K$ isomers relative to infinitely separated ground state $Y_2$ and K. The lowest energy structure computed for $Y_2K$ is shown on the left.

One of the linear states, the $^6\Sigma^-$ state, is a hilltop on the potential energy surface (a degenerate bending motion transforms this structure to the $^6A_2$ T-shaped isomer). The predicted interaction energies between K and $Y_2$ in the other two linear isomers are similar to those for the T shaped isomers, suggesting that they can also be classified as weak or moderate charge-transfer complexes.

The above results do not allow us to determine whether $Y_2K$ will be linear or T shaped (*9*). However, we are gratified to note that, given the modest range of isomeric binding energies, the ultimate arrival of $Y_2K$ is unlikely to be the explosive event of which some prognosticators have warned (*10*). One caveat remains, however: Our analysis has been focused on molecular $Y_2K$, but the phase diagram for Y/K remains to be determined. We suspect that solid $Y_2K$ could be the material of the millenium.

**COMPUTED PROPERTIES FOR ISOMERS/STATES OF $Y_2K$ AT THE MPW1/DZVP LEVEL**

| Electronic state | Binding energy (eV)* | $r$Y – Y (Å) | $r$Y – K (Å)† | Dipole moment (D) | Vibrational frequencies ($cm^{-1}$) |
|---|---|---|---|---|---|
| **T shape** | | | | | |
| $^6A_2$ | −0.64‡ | 2.909 | 4.039 | 4.0 | 58 ($a_1$), 91 ($b_2$), 181 ($a_1$) |
| $^4B_1$ | −0.13 | 2.693 | 4.181 | 1.3 | 80 ($a_1$), 105 ($b_2$), 215 ($a_1$) |
| $^2A_1$ | −0.10 | 2.666 | 4.173 | 3.3 | 77 ($a_1$), 120 ($b_2$), 221 ($a_1$) |
| **Linear** | | | | | |
| $^6\Sigma^-$ | −0.17 | 2.985 | 4.360 | 2.0 | 17$i$ ($\pi$), 51 ($\sigma$), 184 ($\sigma$) |
| $^4\Sigma^-$ | −0.62 | 2.957 | 3.927 | 6.8 | 21 ($\pi$), 88 ($\sigma$), 191 ($\sigma$) |
| $^2\Sigma^+$ | −0.09 | 2.639 | 3.951 | 6.0 | 31 ($\pi$), 75 ($\sigma$), 225 ($\sigma$) |

*Energy relative to $^5\Sigma_u^-$ $Y_2$ + $^2S$ K atom; negative sign indicates energy lower than asymptote. †In linear case, distance is to nearest Y atom. ‡$E$ ($h$) = −7266.639 95.

## References and Notes

1. We acknowledge the formal bias for the molecular formula $KY_2$ but prefer to blithely ignore it.
2. For the nonspecialist, we emphasize the general rule: the longer the acronym, the better the level of theory. For the specialist: We used density functional theory, in particular the Becke-style (*11*) one-parameter functional of Adamo and Barone (*12*) that makes use of the gradient-corrected exchange and correlation functionals of Perdew and Wang (*13*, *14*). We used the polarized valence double-zeta basis set of Godbout *et al.* (*15*).
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8. The predicted hfs value is $^{89}Y = -33.3$ G.
9. To facilitate identification of $Y_2K$ in possible matrix ESR experiments, we note that the predicated isotropic hfs values for T-shaped $^6A_2$ are $^{89}Y = -29.5$ G and $^{39}K = 5.9$ G; for linear $^4\Sigma^-$, the predicted values are $^{89}Y = -20.5$, −2.2 G, and $^{39}K = -2.3$ G.
10. Happily, no computer software (*16*) or hardware failures were experienced in the course of these studies.
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17. We thank D. Leopold for stimulating discussions.

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