Bond dissociation energies for transition metal silicides accurately determined

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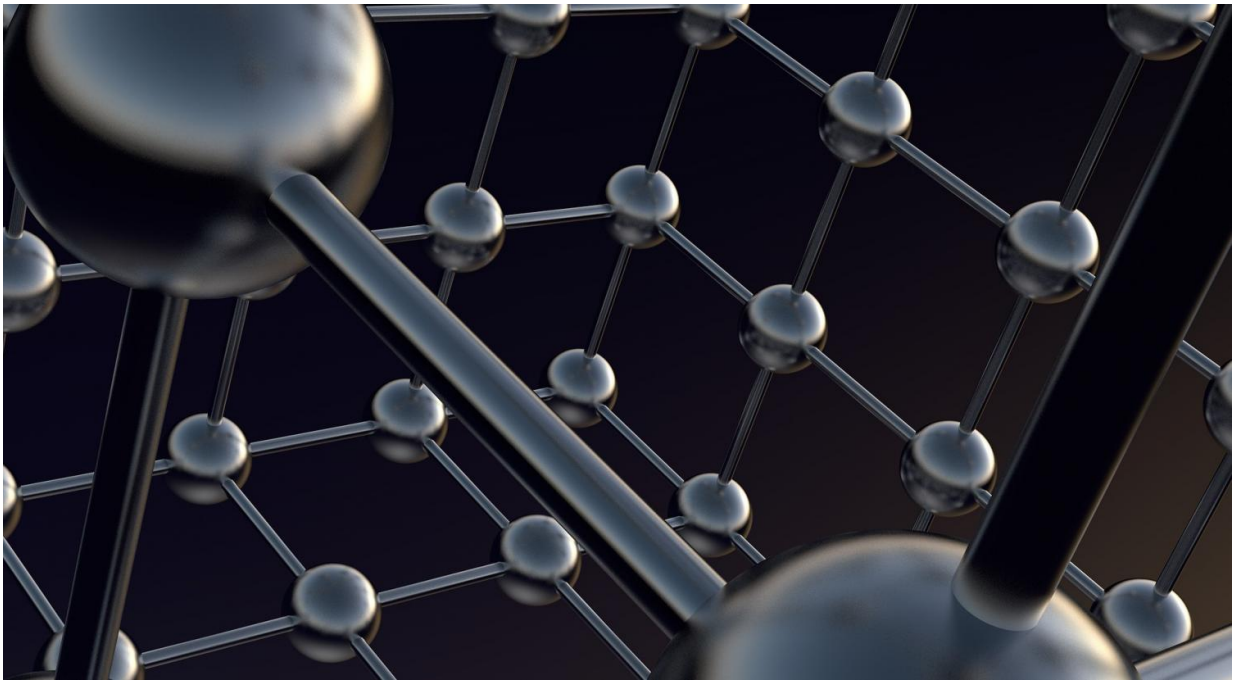

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Transition metal silicides, a distinct class of semiconducting materials that contain silicon, demonstrate superior oxidation resistance, high temperature stability and low corrosion rates, which make them promising for a variety of future developments in electronic devices. Despite their relevance to modern technology, however, fundamental aspects of the chemical bonding between their transition metal atoms

and silicon remain poorly understood. One of the most important, but poorly known, properties is the strength of these chemical bonds—the thermochemical bond dissociation energy.

With funding from the National Science Foundation, a team of researchers from the University of Utah has investigated this property, and in this week's *The Journal of Chemical Physics*, from AIP Publishing, they present their valuable findings for a number of specific compounds. These include precise values of the bond dissociation energies of the group four and five transition metal silicide molecules: TiSi, ZrSi, HfSi, VSi, NbSi and TaSi.

"The team measured the energy at which the diatomic silicides fall apart more quickly than they can be ionized by absorption of a second photon. This amount of energy is called the predissociation threshold. It provides an upper limit to the bond dissociation energy. However, the researchers have found that for molecules with certain electron configurations, if the molecule is cold, then the observation of a sharp predissociation threshold provides an accurate value of the thermochemical bond dissociation energy, and not simply an upper limit."

"What I'm so pleased about with this new technique that we've developed is that it's not just applicable to a small set of molecules," said Michael Morse, one of the work's authors. "It's based on the fact that these small transition metal molecules have a density of electronic states that increases very rapidly as you get close to the dissociation limit, and that's key in causing the molecule to fall apart as soon as you get above that limit [...] The peculiarities of the transition metals make the method broadly applicable to that entire class of molecules, which are quite difficult to investigate by other means."

This sharp threshold observation in a dense vibronic spectrum provides a new and highly effective means of estimating the bond dissociation

energy for transition metals bonded to other p-block elements. According to the researchers, the uncertainties using this new method are much smaller than those seen with previous approaches.

Along with measuring the bond dissociation values for these molecules, the researchers were also able to use the predissociation thresholds to determine other fundamental values for certain molecules using thermochemical cycles, namely enthalpies of formation and ionization energies.

The data acquired can be used by chemists to develop more accurate computational methods regarding transition metal chemical bonding, along with bettering our understanding of these bonds.

"Quantum chemists are trying to develop new, efficient and accurate means of calculating these systems, and they've been quite successful with main group systems, and especially organic compounds," Morse said. "But, the transition metals are much more difficult because there are so many more ways the electrons can be arranged. Another problem is that in the past, there hasn't been as much highly accurate data available that can be used to compare theory and experiment. Without accurate data, it's hard to tell how good a computational method may be."

The research team has plans to work with other diatomic molecules containing transition metals. In fact, they already have results for the bond dissociation energies of TiC, ZrC, HfC, VC, NbC, TaC, WC, WSi, WS, WSe, and WCl that are in preparation for publication. By examining series of chemically related molecules, like these studies of the metal-carbon and tungsten-halogen molecules, the team intends to develop a broad picture of chemical bonding in the transition metal molecules.

"There's a big advantage that comes from this sort of wide-ranging, systematic study. It allows us to develop what I like to call 'chemical intuition' about chemical bonds," said Morse.

More information: Andrew Sevy et al, Bond dissociation energies of TiSi, ZrSi, HfSi, VSi, NbSi, and TaSi, *The Journal of Chemical Physics* (2017). DOI: 10.1063/1.4986213