How do we know basic chemical quantities?
Ionization Energies
Electron Affinities
Bond Lengths
Bond Dissociation Energies

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Ionization Energies

Ionization energies

The currently accepted values of ionization energies of the atoms are found at the NIST website: https://www.nist.gov/pml/ground-levels-and-ionization-energies-neutral-atoms.

These values are known to incredible precision! Excluding highly radioactive elements, they are **all known** to better than 1 part in 6000 accuracy. For atomic cesium, the ionization energy is known to an accuracy of 1 part in 20 billion.

How can we possibly know this things so precisely?

NIST Atomic Spectra Database Ionization Energies Data

Example of how to reference these results:
Kramida, A., Ralchenko, Yu., Reader, J., and NIST ASD Team (2021). *NIST Atomic Spectra Database* (ver. 5.9), [Online]. Available: https://physics.nist.gov/asd [2022, September 23]. National Institute of Standards and Technology, Gaithersburg, MD. DOI: https://doi.org/10.18434/T4W30F

BibTex Citation (new window)

Multiple spectra
108 Data Rows Found

At. Num.	El. name	Ground Shells [a]	Ground Level	Ionization Energy (eV)	Uncertainty[b] (eV)	References
1	Hydrogen	$1s$	$^2S_{1/2}$	(13.598434599702)	0.000000000012	HDEL
2	Helium	$1s^2$	$^1S_0$	24.587389011	0.000000025	L17714
3	Lithium	$1s^2 2s$	$^2S_{1/2}$	5.391714996	0.000000022	L12261
4	Beryllium	$1s^2 2s^2$	$^1S_0$	9.322699	0.000007	L5964
5	Boron	$1s^2 2s^2 2p$	$^2P^\circ_{1/2}$	8.298019	0.000003	L12312
6	Carbon	$1s^2 2s^2 2p^2$	$^3P_0$	11.2602880	0.0000011	L20057
7	Nitrogen	$1s^2 2s^2 2p^3$	$^4S^\circ_{3/2}$	14.53413	0.00004	L1411
8	Oxygen	$1s^2 2s^2 2p^4$	$^3P_2$	13.618055	0.000007	L74,L3760
9	Fluorine	$1s^2 2s^2 2p^5$	$^2P^\circ_{3/2}$	17.42282	0.00005	L7481,L526
10	Neon	$1s^2 2s^2 2p^6$	$^1S_0$	21.564541	0.000007	L8826,L1407
11	Sodium	[Ne]$3s$	$^2S_{1/2}$	5.13907696	0.00000025	L10921,L9648
12	Magnesium	[Ne]$3s^2$	$^1S_0$	7.646236	0.000004	L10635,L6969
13	Aluminum	[Ne]$3s^2 3p$	$^2P^\circ_{1/2}$	5.985769	0.000003	L7215,L10321
14	Silicon	[Ne]$3s^2 3p^2$	$^3P_0$	8.15168	0.00003	L5815

The key to measuring ionization energies is SPECTROSCOPY!

We can measure the wavelength (or frequency) of light to very high precision, and the energy of a photon is related to its wavelength (or frequency).

Remember:

$E_{photon} = h\upsilon$ where $h = 6.62607015 \times 10^{-34}$ J-s

and υ = frequency (cycles per second)

Also, $\upsilon = \frac{c}{\lambda} = \frac{299792458\ m{-}s^{-1}}{\lambda}$

So if you can measure the wavelength of light precisely, you can know the photon energy precisely.

Common energy units:

Joule (J) – the standard SI unit of energy 1 J = 1 kg-m^2-s^{-2}

electron volt (eV) – the amount of energy gained by an electron when it is accelerated through a potential difference of 1 Volt. 1 eV = 1.602177 $\times$ 10^{-19} J

cm^{-1} (usually called "wavenumbers" or "reciprocal centimeters".

This is a weird unit of energy, and in fact, it's only proportional to energy.

Since $E = h\upsilon, E = h\frac{c}{\lambda} = \frac{hc}{\lambda}$ and $\frac{1}{\lambda}$ is proportional to energy. Spectroscopists nearly always measure this in cm^{-1} (wavenumbers).

1 cm^{-1} = 1.986302458 $\times$ 10^{-23} J

Energy Levels of the Hydrogen Atom

Bohr's theory of the hydrogen atom and the more correct theory that was developed by Schrödinger and Heisenberg give an exact formula for the energy levels of the hydrogen atom that precisely agrees with experimental measurements:

$$E_n = -\frac{\mu\, e^4}{8\,{\epsilon_0}^2 h^2}\ \frac{1}{n^2}\ , \qquad n = 1, 2, 3, \ldots$$

Here the constants are:

μ = reduced mass of the proton-electron pair = 9.104425×10^{-31} kg

e = charge of the electron = 1.60217663× 10-19 C

ϵ_0 = permittivity of free space = $8.85418782 \times 10^{-12}\ \frac{C^2 s^2}{kg\ -m^3}$

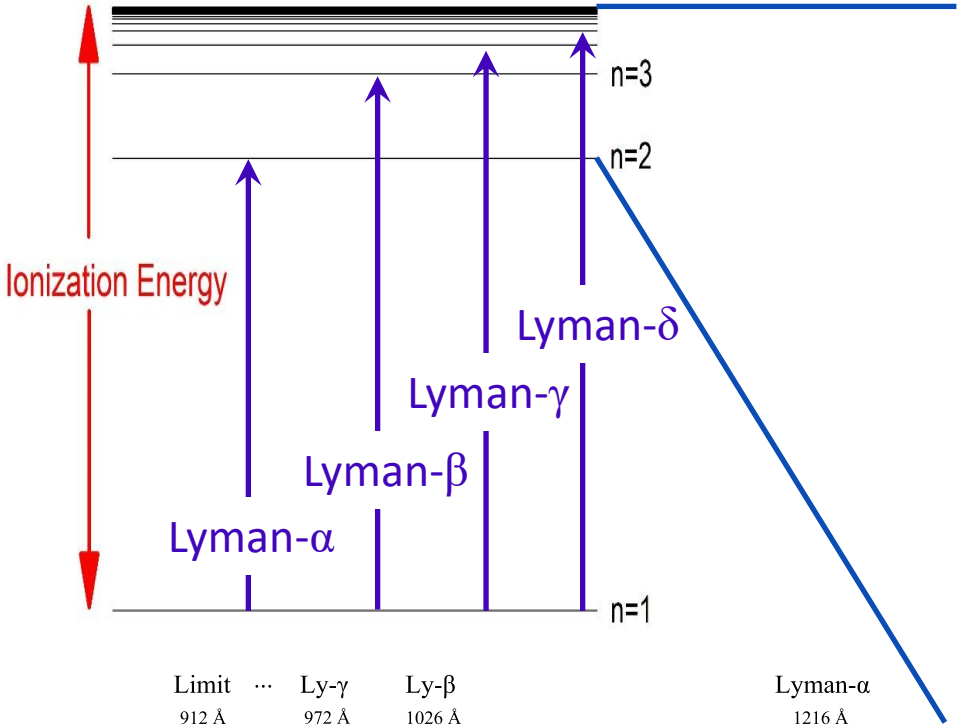
h = Planck's constant = $6.62607015 \times 10^{-34}$ J-s

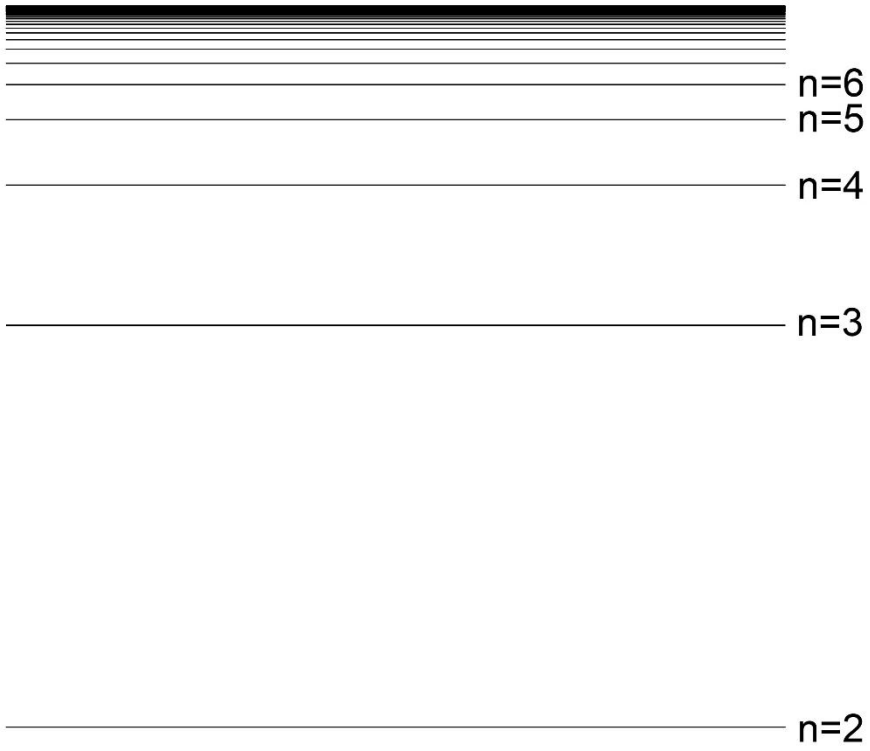
$$\frac{E_n}{hc} = -\frac{109678.77\ cm^{-1}}{n^2}$$

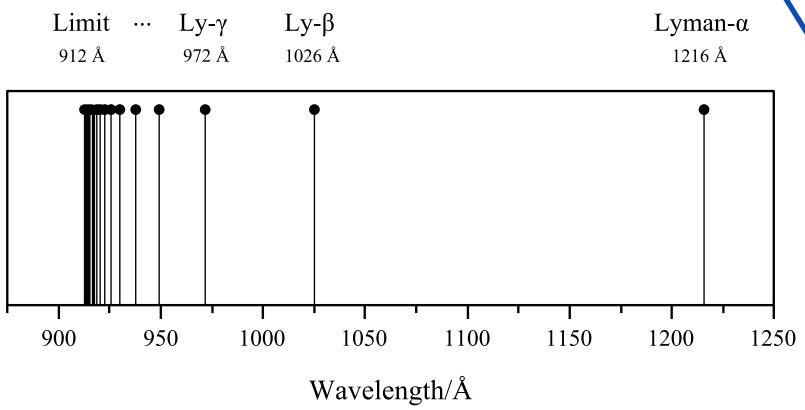
This number is called the *Rydberg constant* for hydrogen.

These energy levels are known to extremely high precision!

Energy Levels of the Hydrogen Atom







https://commons.wikimedia.org/w/index.php?curid=10530212

The Lyman series of lines in the UV spectrum of atomic hydrogen was discovered in 1906 by Theodore Lyman, physicist at Harvard.

Ionization Energy of the Hydrogen Atom

How do you obtain the ionization energy from the energy levels?

The ionization energy is given by the energy difference between the ground level and the limit as n$\longrightarrow \infty$.

$$IE(H) = \lim_{n\to\infty} E_n - E_{n=1}$$

$$IE(H) = \lim_{n\to\infty}\left(-\frac{109678.77\ cm^{-1}}{n^2}\right) - \left(-\frac{109677.58.77 cm^{-1}}{1^2}\right)$$

$$\boxed{IE(H) = 109678.77\ cm^{-1}}$$

The key to using spectra to obtain the ionization energies precisely is having a formula for the energy levels.

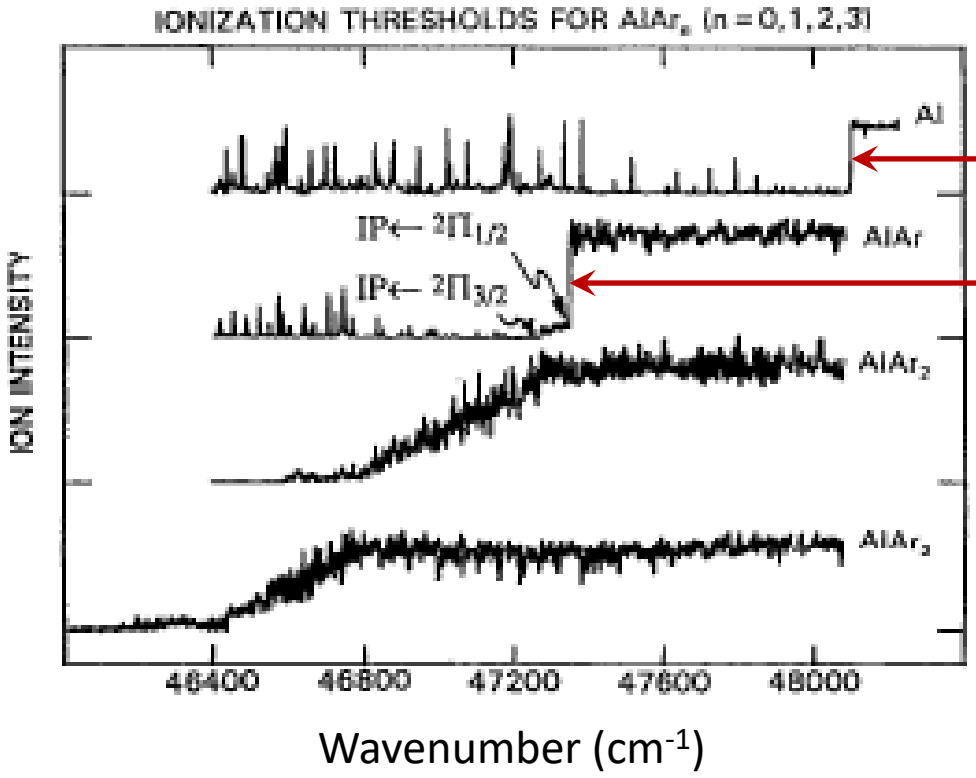
An exact formula for all of the energy levels is only available for hydrogen.

How can we measure the ionization energy for other atoms?

A Direct Method: Scan the spectrum and detect the wavelength where ions are first produced.

Need:

1. Atoms must be in the gas phase
2. Atoms must be in their ground state (this is tough to achieve for atoms that are electronically complex).
3. Must be able to scan the spectrum in the deep ultraviolet region.
4. Must be able to detect when ions are produced.



Ionization threshold for atomic Al

Ionization threshold for the weakly-bound AlAr complex

Problem: To extract and detect the ions, you need an electric field to pull them to the detector. And an added electric field shifts the ionization energy to lower values.

From: Scott A. Heidecke, Zhenwen Fu, John R. Colt, and Michael D. Morse, "Spectroscopy of AlAr and AlKr from 31,000 cm-1 to the ionization limit," J. Chem. Phys. **97**(3), 1692-1710 (1992).

A More Precise Method: Fitting a Rydberg Series

Consider an atom with one electron excited to a high energy level.

Classically, that electron orbits the cation at a long distance, and doesn't really feel the other electrons that are orbiting that nucleus very strongly. The excited electron "thinks" that it's orbiting a +1 point charge – which is the hydrogen atom! So these highly excited states, which consist of a ground state atomic cation with one electron orbiting at long distance should have energy levels that are similar to the hydrogen atom. Maybe they'll have an energy level structure given by:

$$E_n = IE - \frac{R^*}{n^2}$$

Here we'll have to use a slightly different Rydberg constant, because the reduced mass for our atom will be slightly different than for the hydrogen atom.

As it turns out, this isn't quite right. The electron that is highly excited spends most of its time far away from the other electrons, but part of the time it is located closer to the nucleus where it feels a stronger attraction. This pulls the energy levels down compared to the hydrogenic energy levels. A more detailed analysis shows that the correct formula (only for the case when just one electron is excited to high energy levels) is:

$$E_n = IE - \frac{R^*}{(n - \delta)^2}$$

δ is called the quantum defect and is related to how deeply the excited electron penetrates into the electron cloud of the other electrons.

Fitting a Rydberg Series

For a series of Rydberg states that have the same value of the angular momentum quantum number, ℓ, the value of δ should be constant.

So we can solve the quantum defect equation for δ:

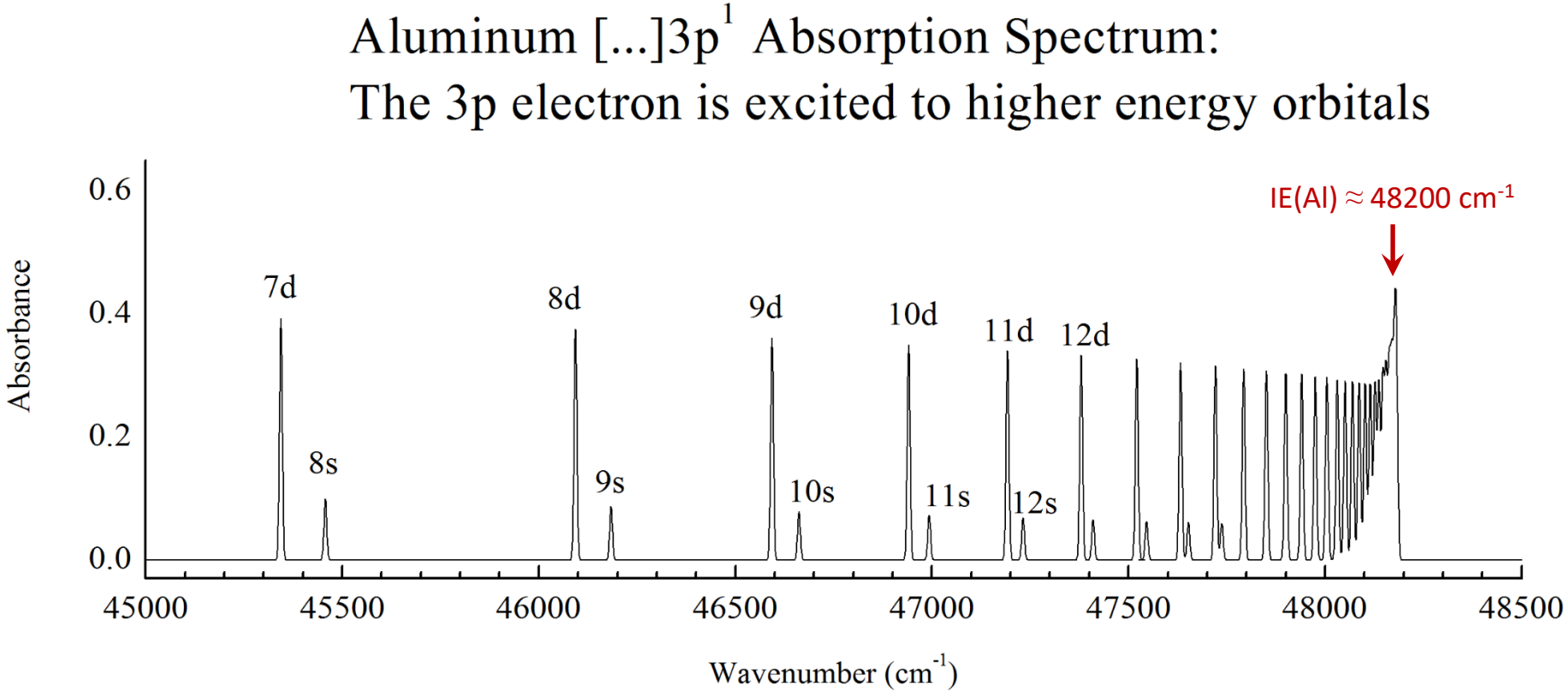
$$E_n = IE - \frac{R^*}{(n - \delta)^2}$$

Solving for δ, we get:

$$\delta = n - \sqrt{\frac{R^*}{IE - E_n}}$$

Now, if we have a series of measured Rydberg levels (E_n), we can guess different values of the IE, and see what value causes the calculated values of δ to be the closest to staying constant. Let's see how this works in practice!

Absorption Spectrum of Atomic Aluminum



Aluminum has the electronic structure [Ne]3s^2 3p^1. The 3p electron can be excited to higher lying ns or nd orbitals, leading to two series of absorption lines. The energies of these lines can be measured very precisely. The quantum defect formula can be used to deduce the ionization energy.

Electron Affinities

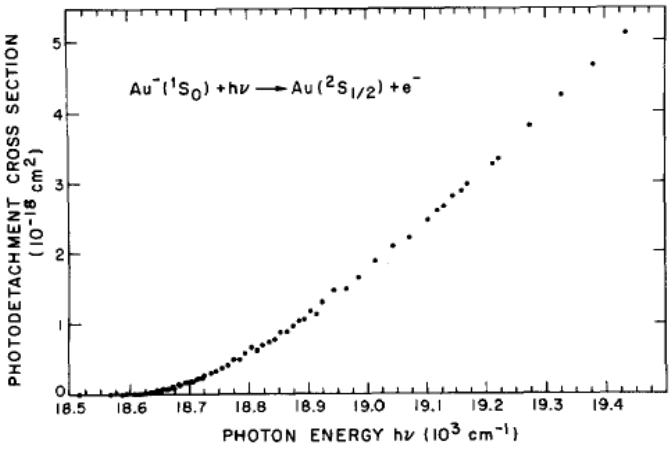
How do we know the electron affinities of the elements?

The electron affinity is the amount of energy required to remove an electron from a gas phase anion. Again, this is most precisely done using a photon, because we can measure the photon's energy from its wavelength or wavenumber.

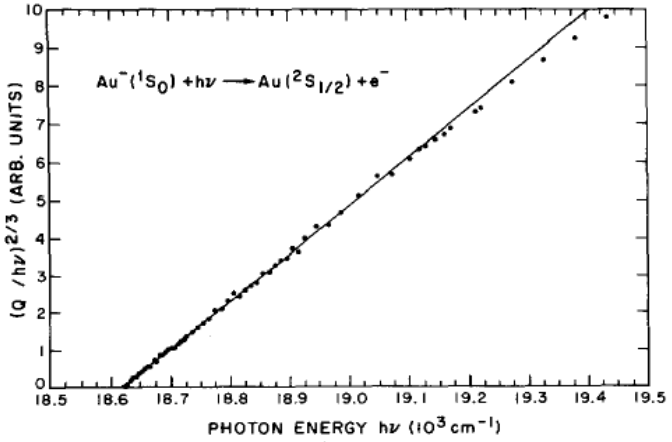
Neutral atoms have a series of Rydberg levels at high energies. Anions don't because there's no long-range force between a neutral atom and an electron. Many anions don't have states where an electron has been excited, but remains bound. So we can't fit a Rydberg series like we did for ionization energies.

A simple, direct method: Threshold electron detachment. Make the gas-phase anion, scan a light source, and measure the detached electron current. A theoretical model gives the photoelectron intensity as a function of the excess energy of the detaching photon.

Data for the detachment of an electron from Au^-



Raw Data



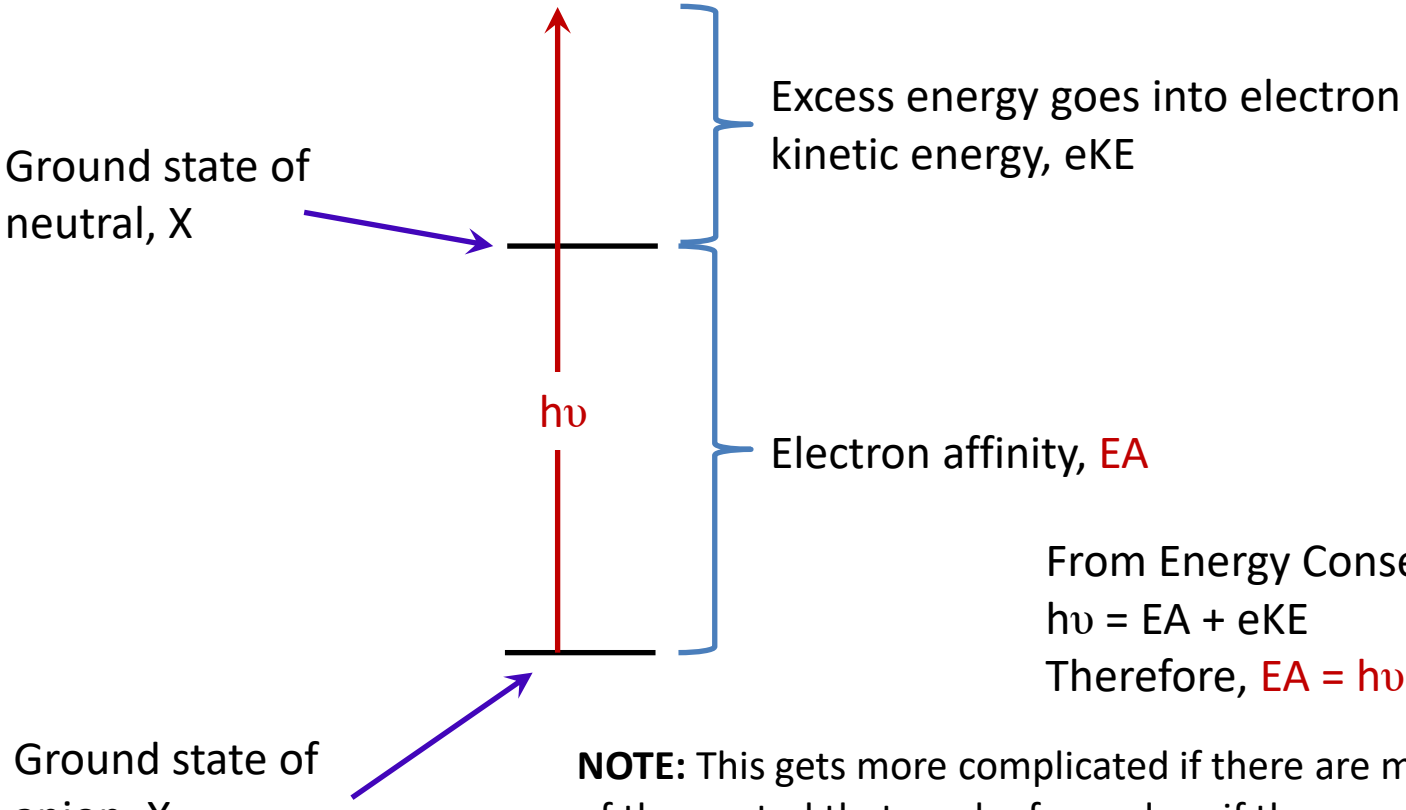
Fitted to the Theoretical Model

From: H. Hotop and W. C. Lineberger, "Dye-laser photodetachment studies of Au^-, Pt^-, PtN^-, and Ag^- ions," J. Chem. Phys. **58**, 2379 (1973).

From this study, the electron affinity of atomic gold was determined to be 2.3086 eV. This is greater than sulfur, 2.0771 eV.

Another Method: Photoelectron Spectroscopy

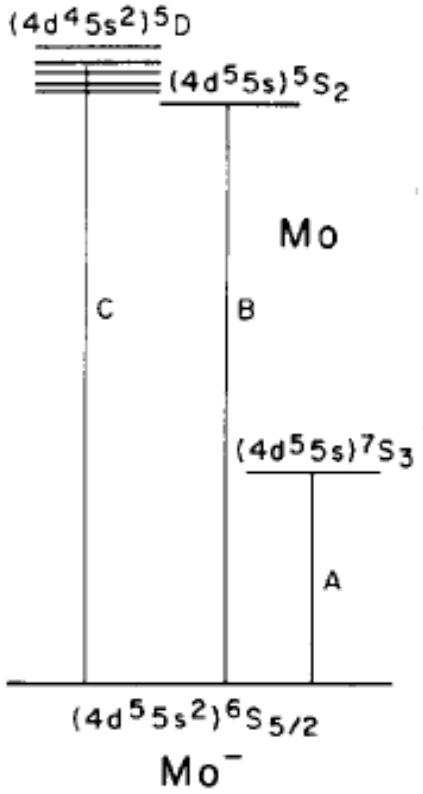
Make the gas phase anion, irradiate it with light of a known photon energy, and measure the kinetic energies of the ejected photoelectrons.

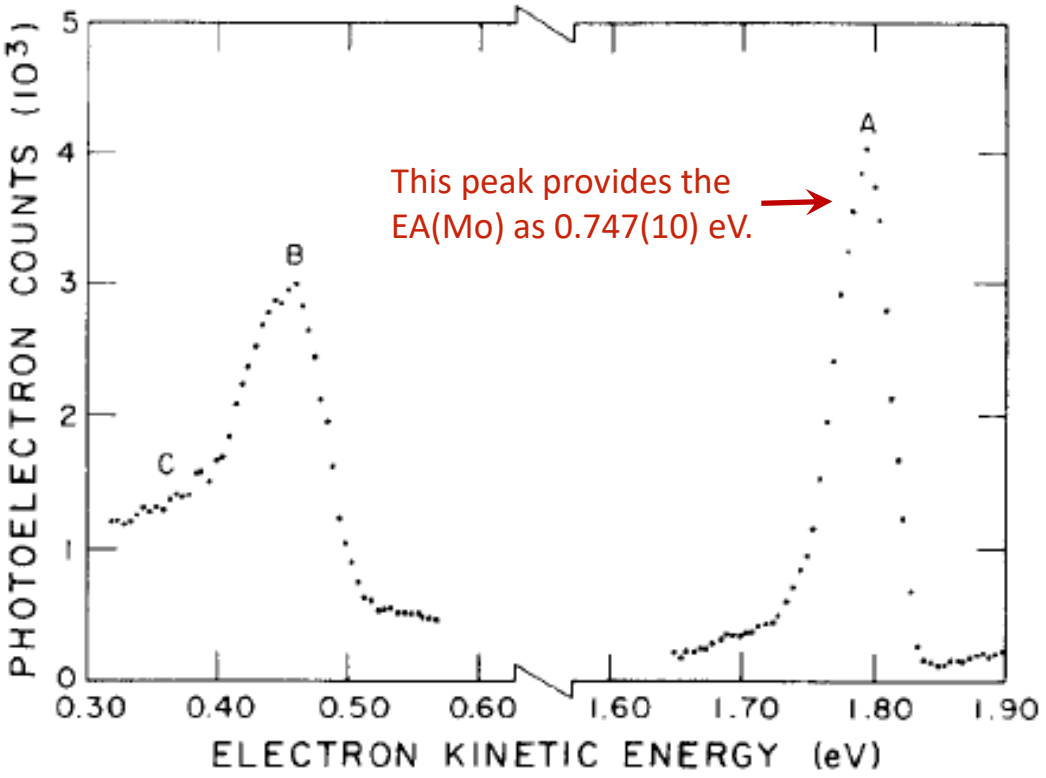


From Energy Conservation,
$h\upsilon = EA + eKE$
Therefore, $EA = h\upsilon - eKE$

NOTE: This gets more complicated if there are multiple states of the neutral that can be formed, or if there are multiple electronic orbitals the electron can be ejected from.

Photoelectron Spectroscopy in Action: The EA of Molybdenum (Mo)





Using 488 nm photons to detach the electron, the photon energy is 2.541 eV. The fastest, highest energy electrons have an eKE of 1.794 $\pm$ 0.010 eV, so the electron affinity of Mo is 2.541-1.794 = 0.747(10) eV.

The slower photoelectrons (peaks B and C) leave the neutral Mo atom in an excited electronic state.

From: C. S. Feigerle, R. R. Corderman, S. V. Bobashev, and W. C. Lineberger, "Binding energies and structure of transition metal negative ions," J. Chem. Phys. **74**(3), 1580 (1981).

Bond Lengths

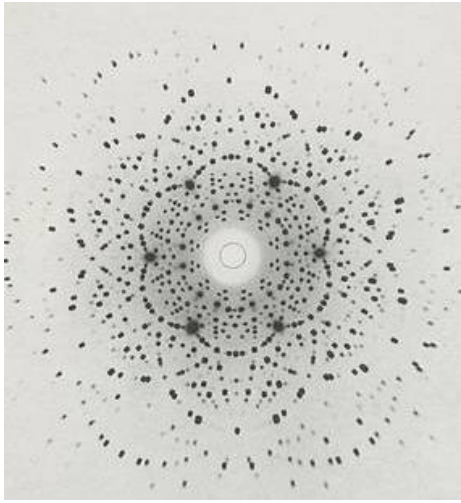
X-ray Diffraction

X-rays are scattered by electrons MUCH more effectively than from nuclei. They're primarily scattered from regions close to the nucleus, which is where the electron density is highest. Each atom can be thought of as a scattering center, and the scattered X-ray waves from all the different scattering centers can add up constructively if they're propagating in the right direction. There are specific angles where the X-rays add up constructively, leading to spots. By analyzing the intensities of the scattered X-rays, a map of the electron density (with peaks at the positions of the nuclei) can be derived. (This is a complicated problem, but is now highly automated.) From the positions of the atoms, you can deduce bond lengths between atoms.

Issues:

1. For large numbers of atoms in the unit cell, you need single crystals. Powders work for simple structures.
2. Because the X-rays scatter from regions of high electron density, heavy atoms are easier to locate than light atoms. Hydrogen atoms can't be located precisely with X-rays.
3. Structures are always perturbed by packing forces.
4. Can never be used for molecules that react or dimerize. Radicals are generally impossible to study.

Beryl, $Be_3Al_2Si_6O_{18}$



A Crystal Of Beryl Fragments A Beam.
A photograph by Science Source

Measuring Bond Lengths with Spectroscopy

For linear molecules, quantum mechanics tells us there are quantized rotational levels that follow the formula:

$$E_{rotation}(J) = \frac{J(J+1)\hbar^2}{2I} \equiv BJ(J+1).$$

Here J is a quantum number with the possible values of J = 0, 1, 2, …, and I is the moment of inertia. If you imagine the atoms laid out on the z-axis with coordinates z_1, z_2, z_3, …, then the moment of inertia is

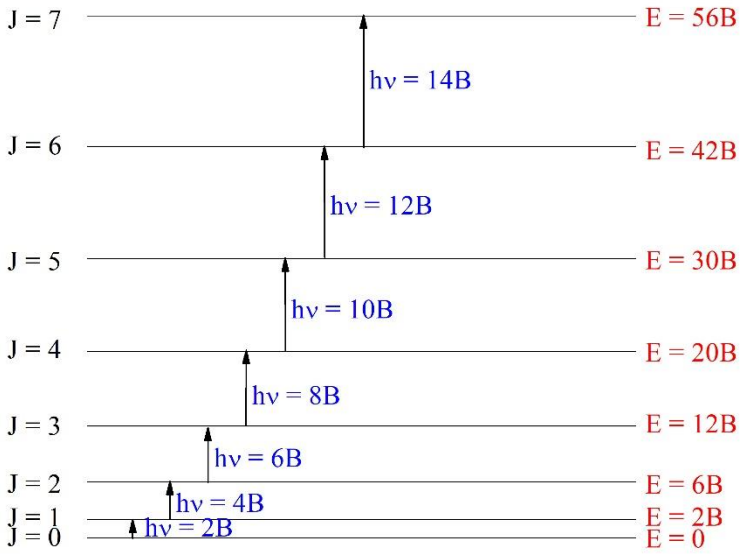
$$I = \sum_i m_i (z_i - z_{CM})^2 \ .$$

This means that if you can measure the rotational energy levels, you can get the moment of inertia of the molecule!

If the molecule is diatomic, then $I = \mu R^2$, where μ is the reduced mass ($\mu = \frac{m_1 m_2}{m_1 + m_2}$) and R is the bond length.

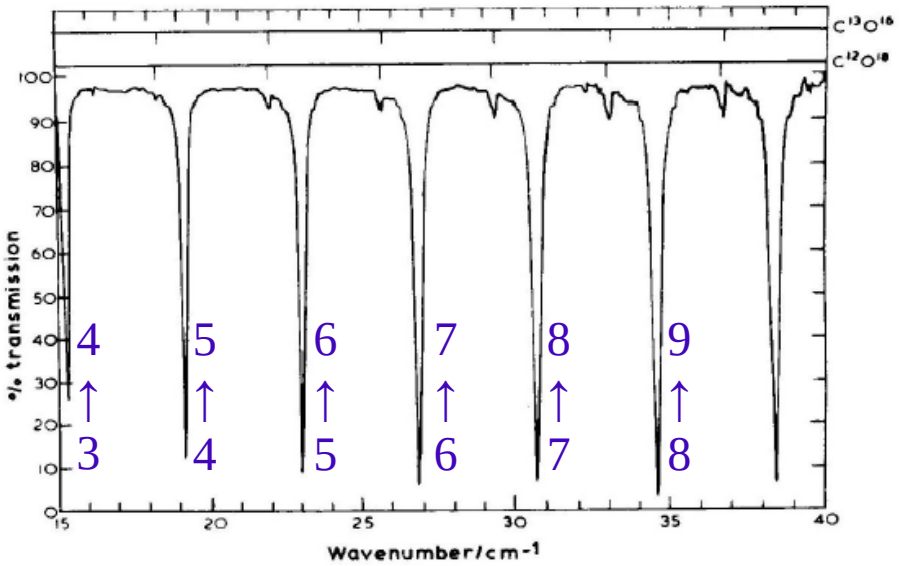
The quantum number J designates the rotational angular momentum of the molecule. Because a photon has a spin of 1, J can only increase by 1 when the molecule absorbs a photon.

Measuring Bond Lengths using Spectroscopy



The $\Delta J = +1$ selection rule leads to a series of equally spaced lines with a separation of 2B.

A portion of the pure rotational spectrum of CO



This is actually a very poor quality spectrum, because the lines are so broad. In a carefully designed study, the lines can be measured so precisely that the rotational constant of $^{12}C^{16}O$ is known to incredible precision: $B(^{12}C^{16}O) = 1.92252867\ cm^{-1}$, giving the bond length as 1.12823 Å.

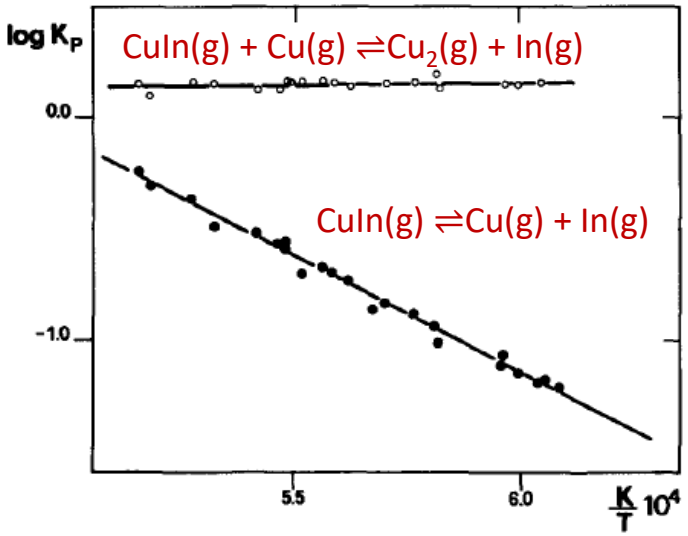
From: J. W. Fleming and J. Chamberlain,"High resolution far infrared fourier transform spectrometry using Michelson interferometers with and without collimation," Infrared Phys., **14**, 277 (1974).

Bond Dissociation Energies

Method 1. Measure the Equilibrium Constant

Suppose you wanted to know the bond dissociation energy of the diatomic gas phase molecule composed of copper and indium, CuIn. How could you measure it?

- Seal a sample of solid copper and solid indium in a container that can withstand high temperatures, and poke a tiny hole in the container.
- Put the whole thing in a vacuum system and evacuate it to low pressures
- Heat the system until a pressure of gaseous Cu and In exists above the solid materials, allowing the equilibrium Cu(g) + In(g) ⇌ CuIn(g) to form.
- Measure the amount of Cu(g), In(g) and CuIn(g) emerging from the small hole using electron impact mass spectrometry
- Back-calculate the pressure of each substance in the reaction cell, and calculate the equilibrium constant, K_p.
- Use $-RT\ \ln K = \Delta H - T\Delta S$ to determine the ΔH and ΔS values for the dissociation process.
- Extrapolate to 0K to get the ΔH value at absolute zero, which is the bond dissociation energy



This is a tough experiment. The temperature range plotted corresponds to 1500 - 2000K (white hot).

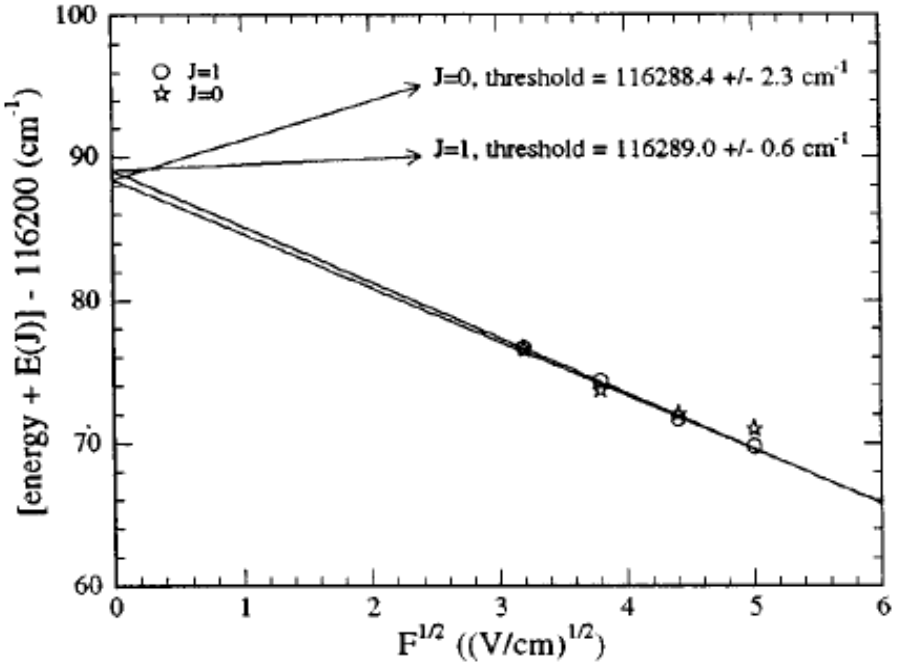
From these data the bond dissociation energy of CuIn is measured as 1.90 ± 0.08 eV.

From: G. Balducci, P. E. Di Nunzio, G. Gigli, and M. Guido, "Dissociation energies of the intermetallic molecules CuIn, AgIn, and AuIn," J. Chem. Phys. **90**(1), 406 (1989).

Method 2: Threshold Ion-Pair Production

- Create a molecular beam of the molecule (for example HCl) in a vacuum system.
- Scan a laser light source over the region where the expected for production of ions ($H^+ + Cl^-$) is expected. Above the threshold, the ions will fly apart quickly.
- Slightly below the threshold, the molecule will remain bound, but may be pulled apart by a small electric field. Pulse this field on after the directly produced ions have flown away.
- Detect the delayed ion production as the laser is scanned at various applied fields, looking for the threshold. Extrapolate to zero applied field and you'll have the energy required for the reaction $HCl(g) \rightarrow H^+(g) + Cl^-(g)$

Extrapolation to zero applied electric field



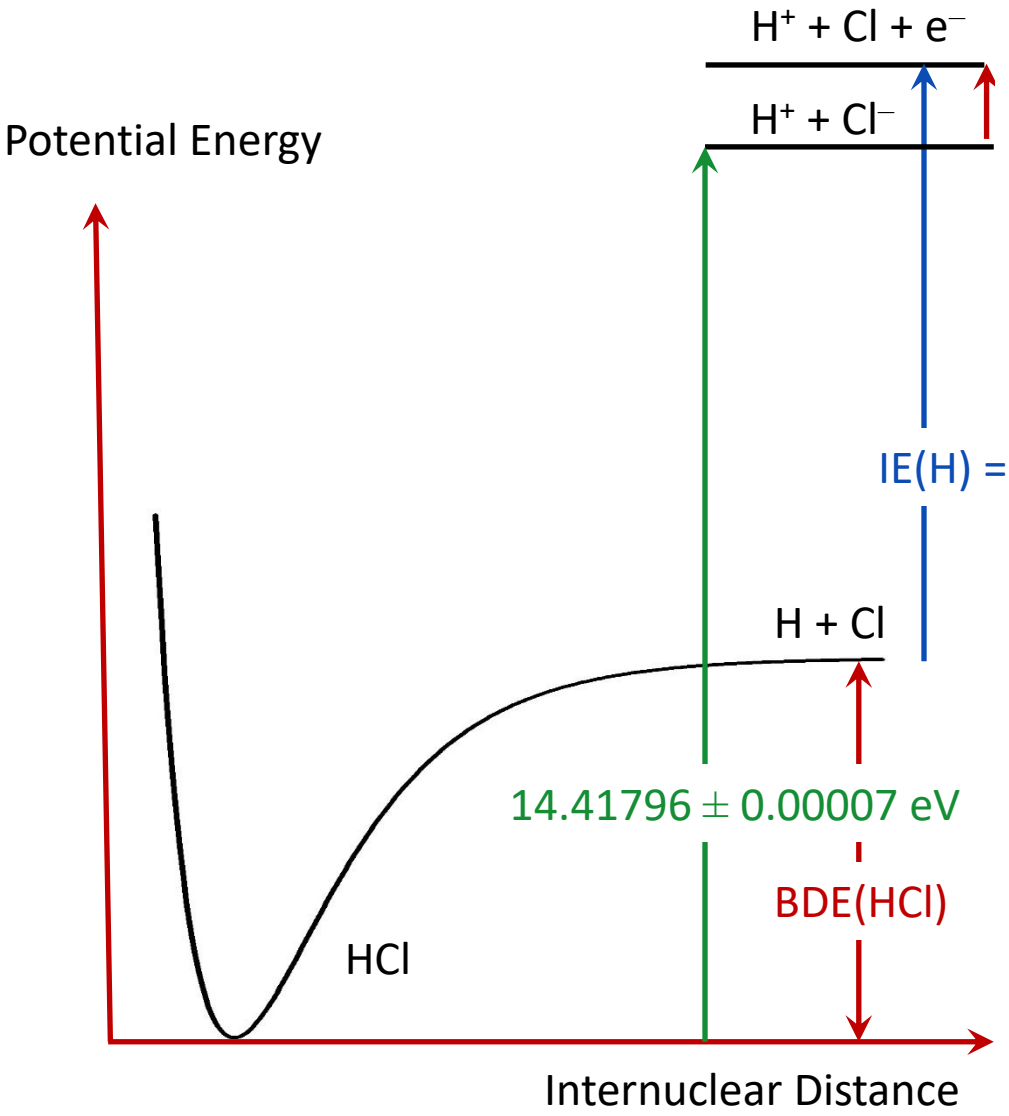
From this investigation, the energy required for the reaction $HCl(g) \rightarrow H^+(g) + Cl^-(g)$ at 0K is $116{,}288.7 \pm 0.6\ cm^{-1}$, or 14.41796 ± 0.00007 eV.

That's amazingly precise!

But HCl dissociates into H + Cl atoms, not into ions. How can we deduce the bond dissociation energy into neutral atoms?

From J. D. D. Martin and J. W. Hepburn, "Determination of bond dissociation energies by threshold ion-pair production spectroscopy: An improved D_0(HCl)," J. Chem. Phys. **109**(19), 8139 (1998).

Obtaining the Bond Dissociation Energy from the Ion-Pair Threshold

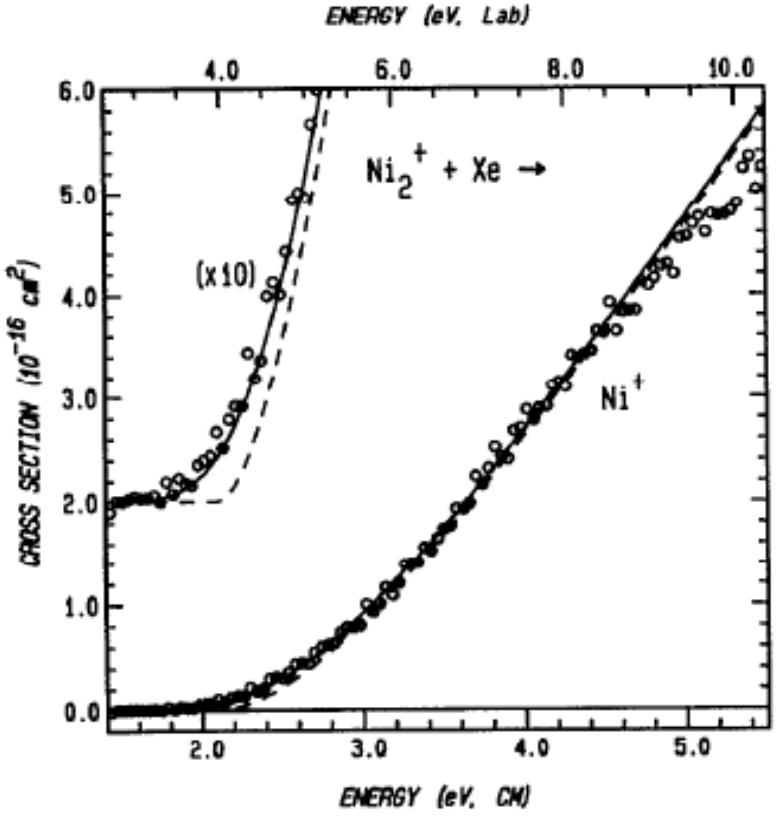


BDE(HCl) = 14.41796 eV
+ 3.61268 eV
– 13.5984346 eV

BDE(HCl) = 4.4322 ± 0.0001 eV

Method 3. Collision-Induced Dissociation of Ions

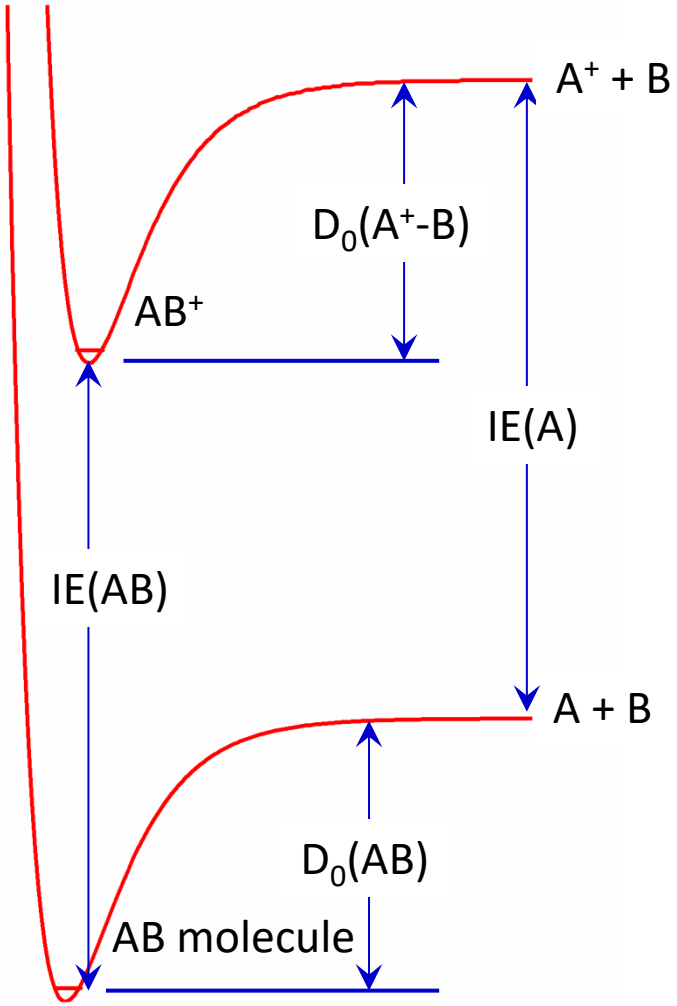
- Use a mass spectrometer to select a particular ion.
- Make sure it's internally cold.
- Accelerate it to a precisely controlled kinetic energy, and collide it with an unreactive collision partner (Xe is a good choice).
- Measure the fragmentation yield as a function of collision energy and fit the data to a model.



From these data, the bond dissociation energy of Ni_2^+ is measured to be 2.08 ± 0.07 eV.

From: L. Lian, C.-X. Su, and P.B.Armentrout, "Collision-induced dissociation of Ni_n^+ (n=2-18) with Xe: Bond energies, geometrical structures, and dissociation pathways," J. Chem. Phys. **96**(10), 7542 (1992).

Converting bond energies of ions to bond energies of neutrals



Thermochemical Cycle:

$IE(AB) + D_0(A^+\text{-}B) = D_0(AB) + IE(A)$

so

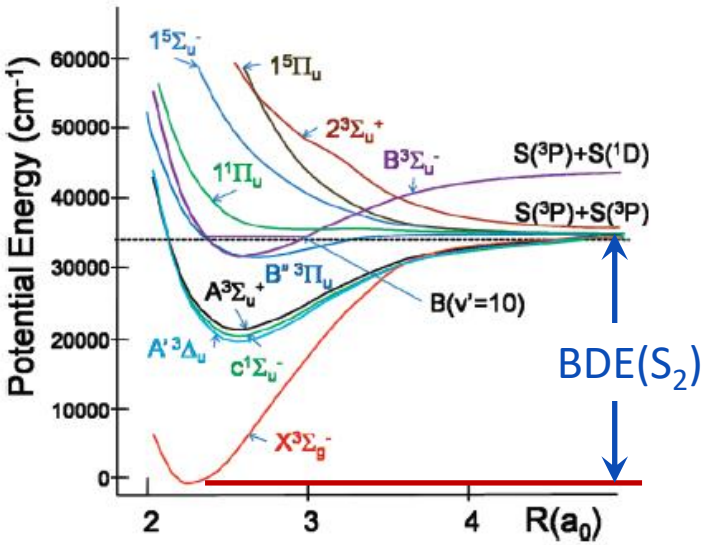
$D_0(AB) = IE(AB) + D_0(A^+\text{-}B) - IE(A)$

Conclusion: You can convert the bond dissociation energy of a cation, $D_0(A^+\text{-}B)$, to the bond dissociation energy of the corresponding neutral molecule, $D_0(AB)$, if you know the ionization energy of the atom, IE(A), and of the neutral molecule, IE(AB).

Method 4. Velocity Map Imaging – Measuring the kinetic energy of the separating fragments

Example: The bond dissociation energy of S_2, the stable gaseous form of sulfur.

Ground and excited states of S_2



Method: Excite S_2 with a laser above its dissociation limit, and measure how fast the departing sulfur atoms fly apart.

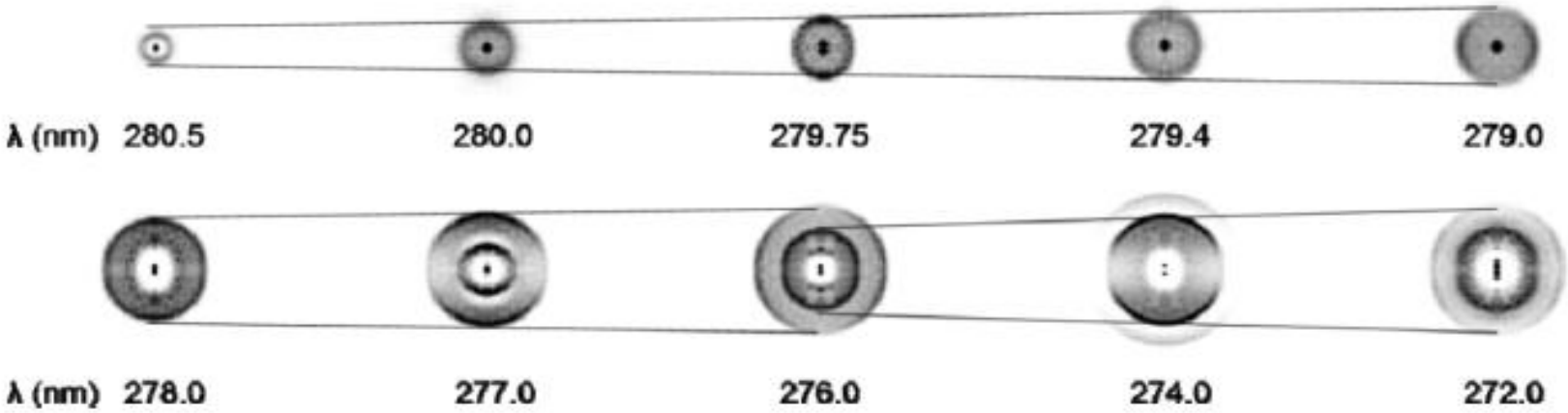
More details: Use one laser to dissociate S_2 and use a second one to ionize the departing S atoms, because ions are MUCH easier to detect than neutral atoms.

Use an electric field to accelerate the S^+ ions to a position sensitive detector after a fixed time, and see how large the scatter plot is. The bigger the area that they hit, the greater the kinetic energy between them.

Velocity Map Imaging – Measuring the kinetic energy of the separating fragments

Example: The bond dissociation energy of S_2, the stable gaseous form of sulfur.

Detector images as a function of the dissociation laser wavelength:



As the wavelength gets shorter (higher photon energy), the image gets larger because the S atoms separate with greater kinetic energy. It looks like 280.5 nm (35,650 cm^{-1}) is pretty close to the amount of energy required to break the S_2 bond.

A more careful analysis gives the S_2 bond dissociation energy to be

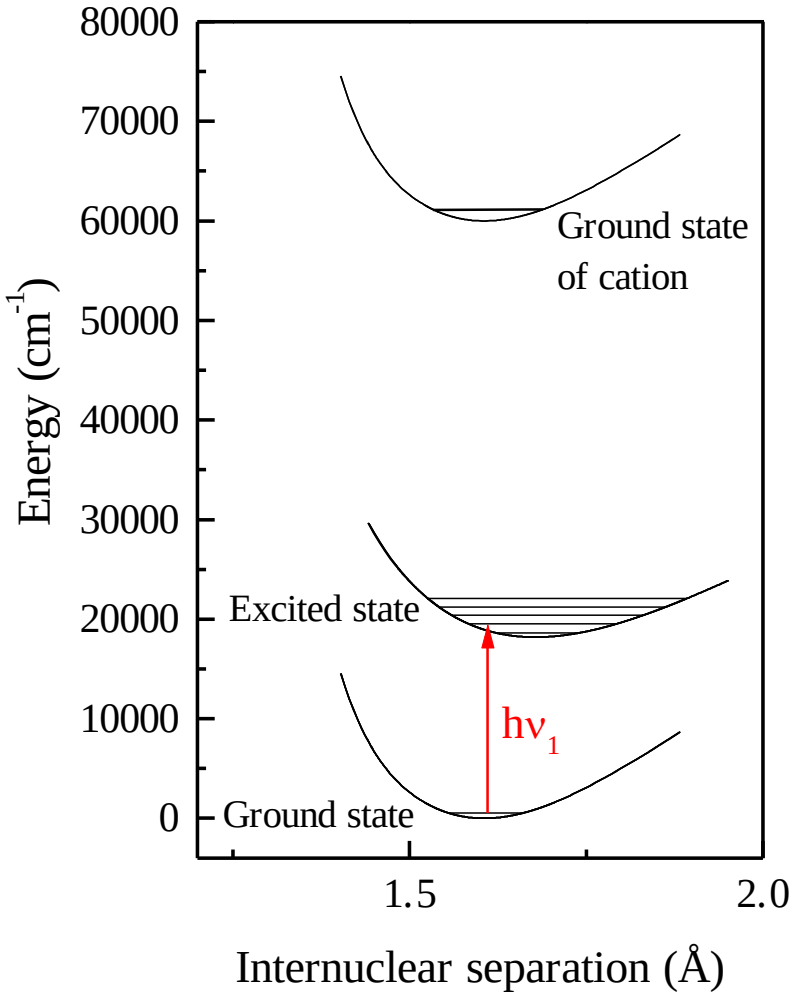
$35{,}636.9 \pm 2.5$ cm-1 or 4.4184 ± 0.0003 eV

AMAZING PRECISION, don't you think?

P.W.J.M. Frederix, C-H Yang, G. C. Groenenboom, D. H. Parker, K. Alnama, C. M. Western, and A. J. Orr-Ewing, "Photodissociation Imaging of Diatomic Sulfur (S2)," J. Phys. Chem. A, **113**, 14995 (2009).

Method 5. Observing a sharp dissociation threshold in a highly congested set of states

The resonant two-photon ionization process:



Step 1: Excite the molecule with a laser to an excited electronic state.

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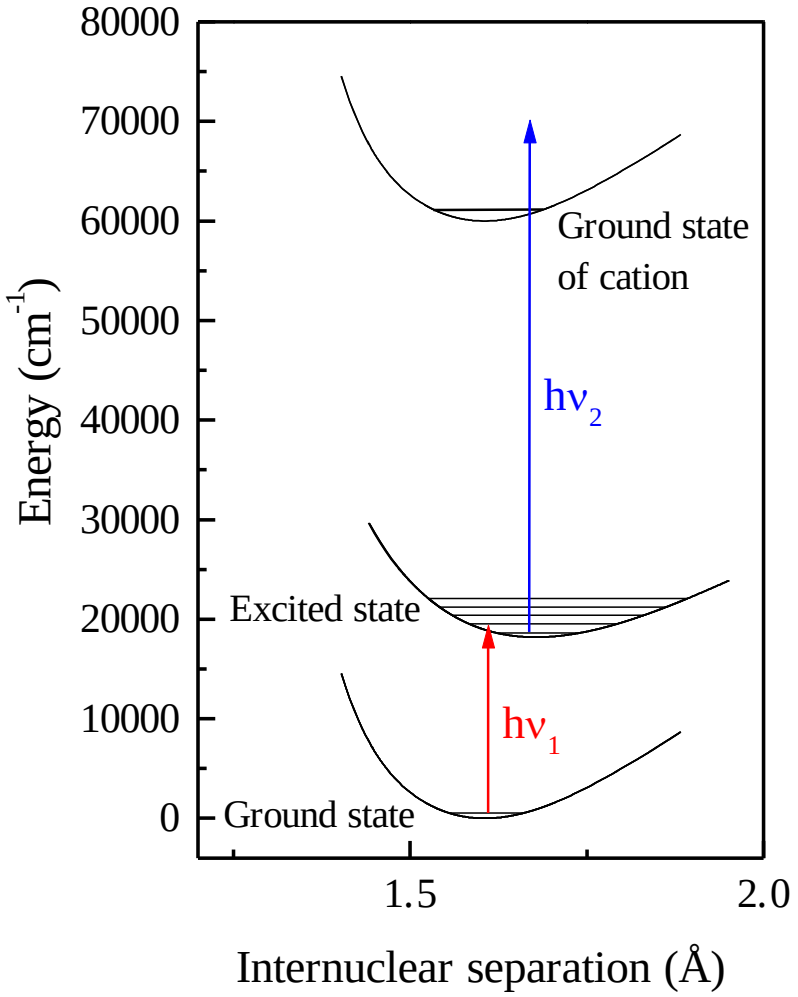
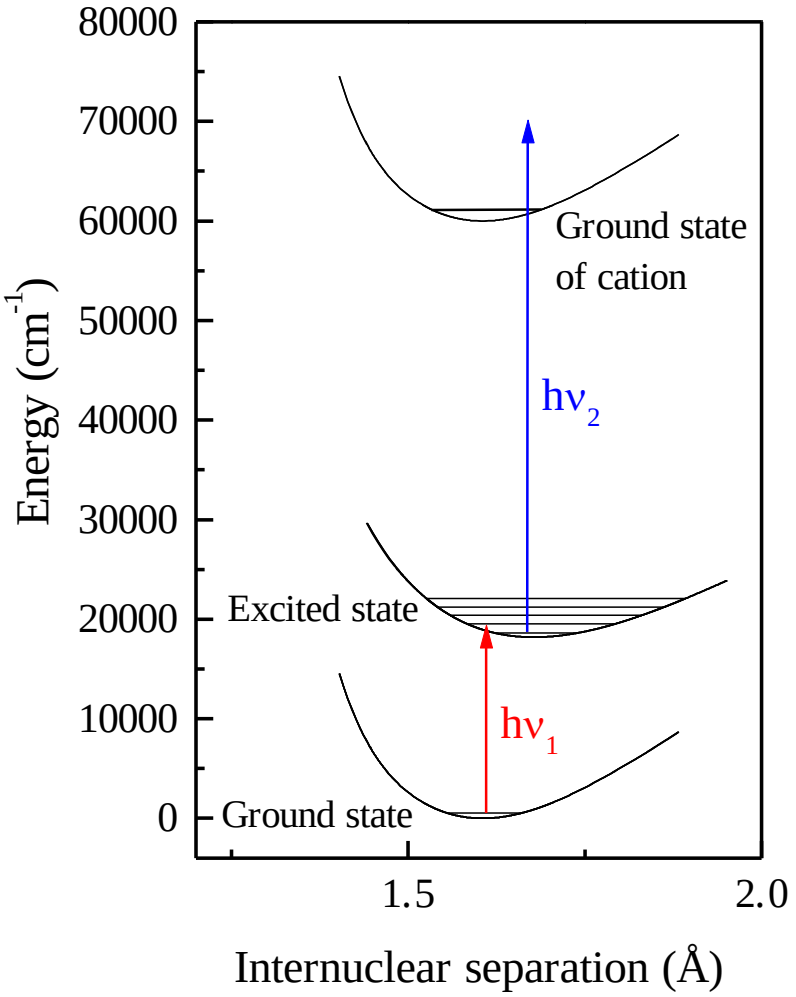


Step 1: Excite the molecule with a laser to an excited electronic state.

Step 2: A short time later, ionize the molecule with a second laser pulse that can ionize the excited state but not the ground state.

Method 5. Observing a sharp dissociation threshold in a highly congested set of states

The resonant two-photon ionization process:



Step 1: Excite the molecule with a laser to an excited electronic state.

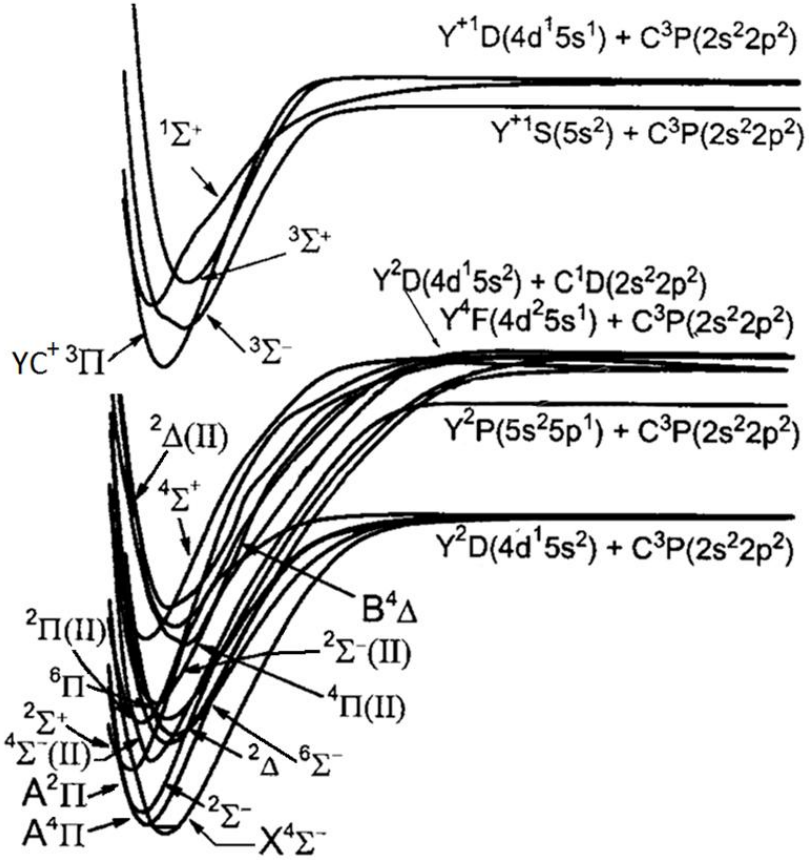
Step 2: A short time later, ionize the molecule with a second laser pulse that can ionize the excited state but not the ground state.

Step 3: Detect the ions in a mass spectrometer.

Step 4: Scan the laser ($h\upsilon_1$) and plot ion signal vs. υ_1 to get a spectrum.

Method 5. Observing a sharp dissociation threshold in a highly congested set of states

But what if the molecule has a LOT of excited states?



From: B. Suo and K. Balasubramanian, J. Chem. Phys. **126**, 224305 (2007).

Method 5. Observing a sharp dissociation threshold in a highly congested set of states

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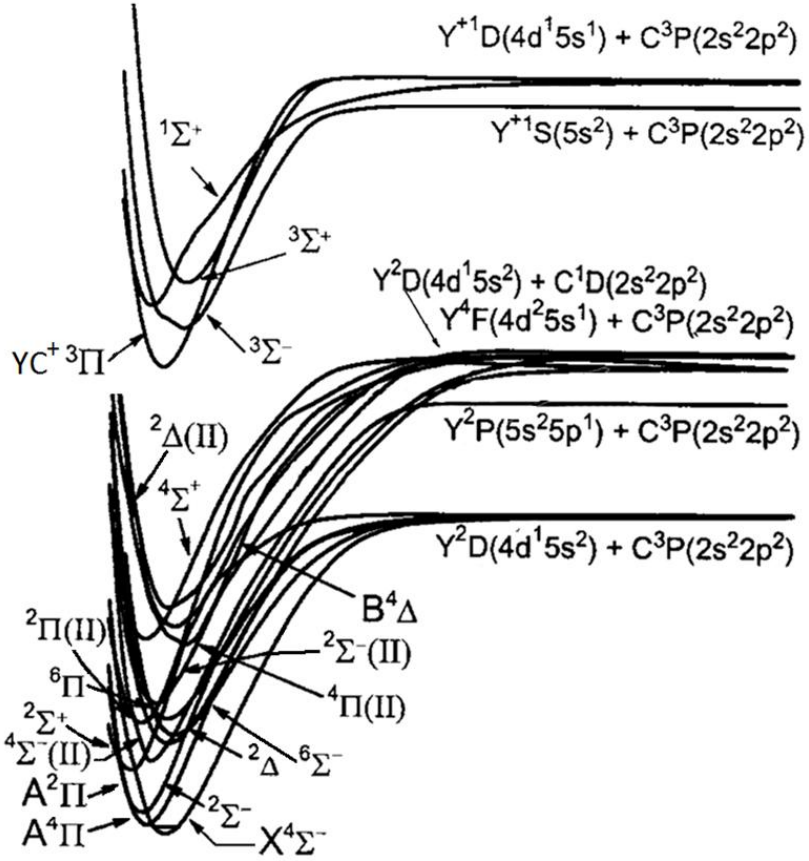
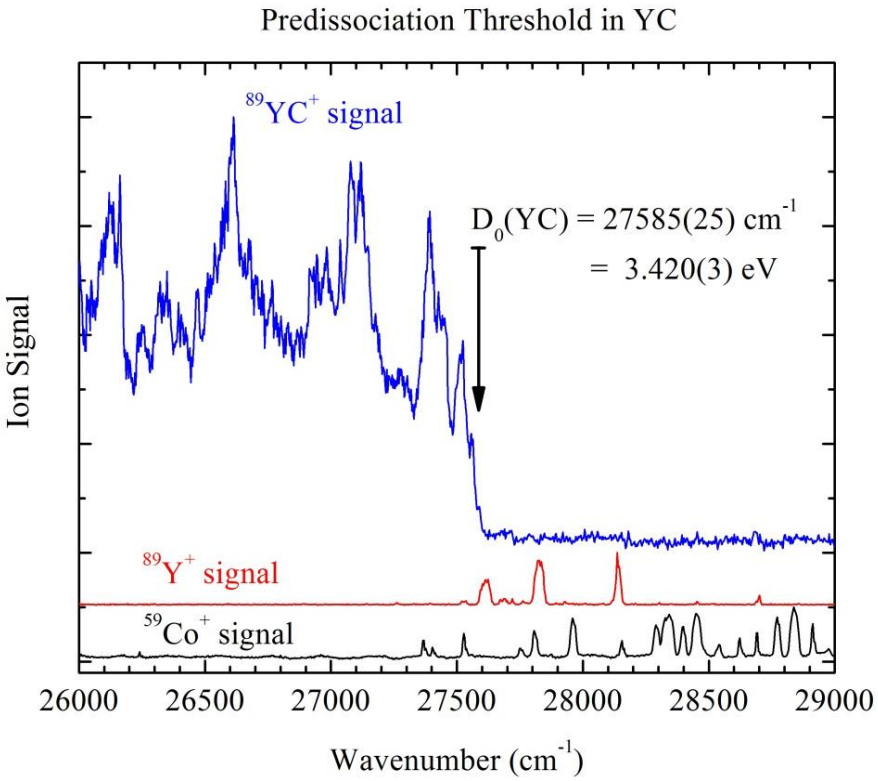


From: B. Suo and K. Balasubramanian, "Spectroscopic constants and potential energy curves of YC," J. Chem. Phys. **126**, 224305 (2007).



From: A. Sevy, D. M. Merriles, R. S. Wentz, and M. D. Morse, "Bond dissociation energies of ScSi, YSi, LaSi, ScC, YC, LaC, CoC, and YCH," J. Chem. Phys. **151**, 024302 (2019).

TM-Main Group BDEs Measured by in the Morse Group (eV):

Sc	Ti	V	Cr	Mn	Fe	Co	Ni
B 1.72(6)	B 1.956(16)	B 2.150(16)	B	B	B 2.43(2)	B 2.954(3)	B 3.431(4)
C 3.042(10)	C 3.857(4)	C 4.109(3)	C	C	C 3.961(19)	C 3.899(13)	C 4.167(3)
N 3.905(29)	N 5.015(12)	N 4.997(2)	N	N	N	N	N
O	O	O 6.545(2)	O 4.649(5)	O	O	O	O
Si 2.015(3)	Si 2.201(3)	Si 2.234(3)	Si	Si	Si 2.402(3)	Si 2.862(3)	Si 3.324(3)
S 4.852(10)	S 4.690(4)	S 4.535(3)	S	S	S 3.240(3)	S 3.467(5)	S 3.651(3)
Cl	Cl	Cl	Cl	Cl	Cl	Cl	Cl
Se 4.152(3)	Se 3.998(6)	Se 3.884(3)	Se	Se	Se 2.739(6)	Se 2.971(6)	Se 3.218(3)
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
B 2.057(3)	B 2.573(5)	B 2.989(12)	B	B	B 4.815(3)	B 5.252(3)	B
C 3.420(3)	C 4.892(10)	C 5.620(4)	C 5.136(3)	C	C	C	C
N 4.125(24)	N	N	N 5.220(4)	N	N 4.905(3)	N 3.659(32)	N
O	O	O	O 5.414(19)	O	O 4.863(3)	O 4.121(3)	O
Si 2.450(2)	Si 2.950(3)	Si 3.080(3)	Si	Si	Si 4.132(3)	Si 4.169(3)	Si
S 5.391(3)	S 5.660(4)	S 5.572(3)	S 3.932(4)	S	S 4.071(8)	S 3.611(3)	S
Cl	Cl	Cl 4.48(2)	Cl	Cl	Cl	Cl	Cl
Se 4.723(3)	Se 4.902(3)	Se 4.834(3)	Se	Se	Se 3.482(3)	Se 3.039(9)	Se
La	Hf	Ta	W	Re	Os	Ir	Pt
B 2.086(18)	B 2.593(3)	B 2.700(3)	B 2.730(4)	B	B 4.378(3)	B 4.928(10)	B 5.235(3)
C 4.718(4)	C 4.426(3)	C 4.975(3)	C 5.289(8)	C 5.731(3)	C	C	C
N	N 5.374(4)	N	N	N 5.635(3)	N 5.732(3)	N 5.115(4)	N
O	O	O	O	O 5.510(3)	O	O	O
Si 2.891(5)	Si 2.871(3)	Si 2.999(3)	Si 3.103(3)	Si	Si 4.516(3)	Si 4.952(3)	Si 5.325(9)
S	S 5.780(20)	S 5.542(3)	S 4.935(3)	S 3.947(3)	S 4.277(3)	S 4.110(3)	S 4.144(8)
Cl	Cl	Cl	Cl 3.818(6)	Cl	Cl	Cl	Cl
Se	Se 5.154(4)	Se 4.705(3)	Se 4.333(6)	Se	Se 3.613(3)	Se 3.591(3)	Se 3.79(3)

Color Code: Published or accepted work (91 TM molecules). Unpublished results (15 TM molecules).
Also, 6 published triatomic BDEs (Sc-B_2, Ti-B_2, V-B_2, Y-B_2, Mo-B_2, and Y-CH)

Thanks for listening!

Anytime you'd like to ask me a question:

morse@chem.utah.edu

This and all previous presentations can be found at my website:
https://chem.utah.edu/directory/morse/research-group/ap_chemistry_powerpoints.php

Or better still, just ask me for them in an email.