Rovibrational Theory of Isotope Effects on Molecular Electronic Properties

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ROVIBRATIONAL THEORY of ISOTOPE EFFECTS on MOLECULAR ELECTRONIC PROPERTIES

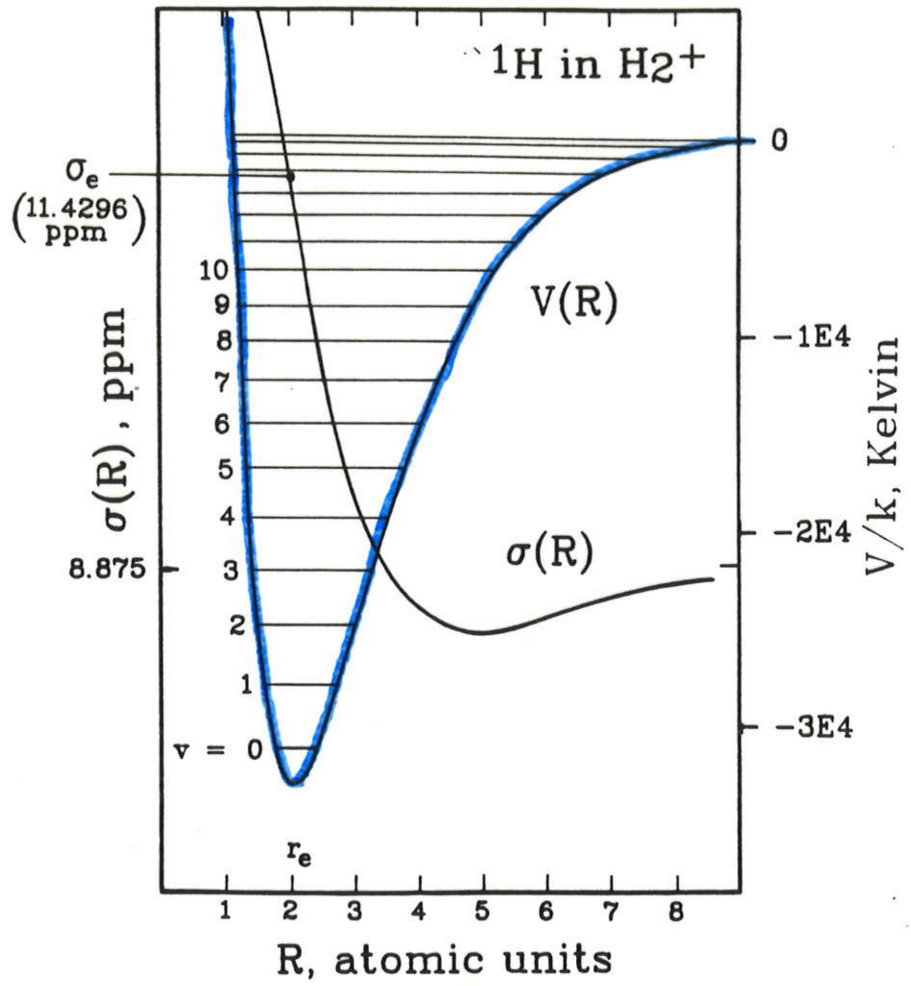
OUTLINE

1. Born-Oppenheimer approximation
2. (Mass-independent) electronic property surfaces
3. The intramolecular potential surface and the probability of finding a molecule at a given nuclear configuration
4. The shape of the surface in the vicinity of the equilibrium geometery
5. Examples of isotope effects
6. The electronic and dynamic factors
7. Estimation of the dynamic factors
8. Polyatomic molecules
9. Summary

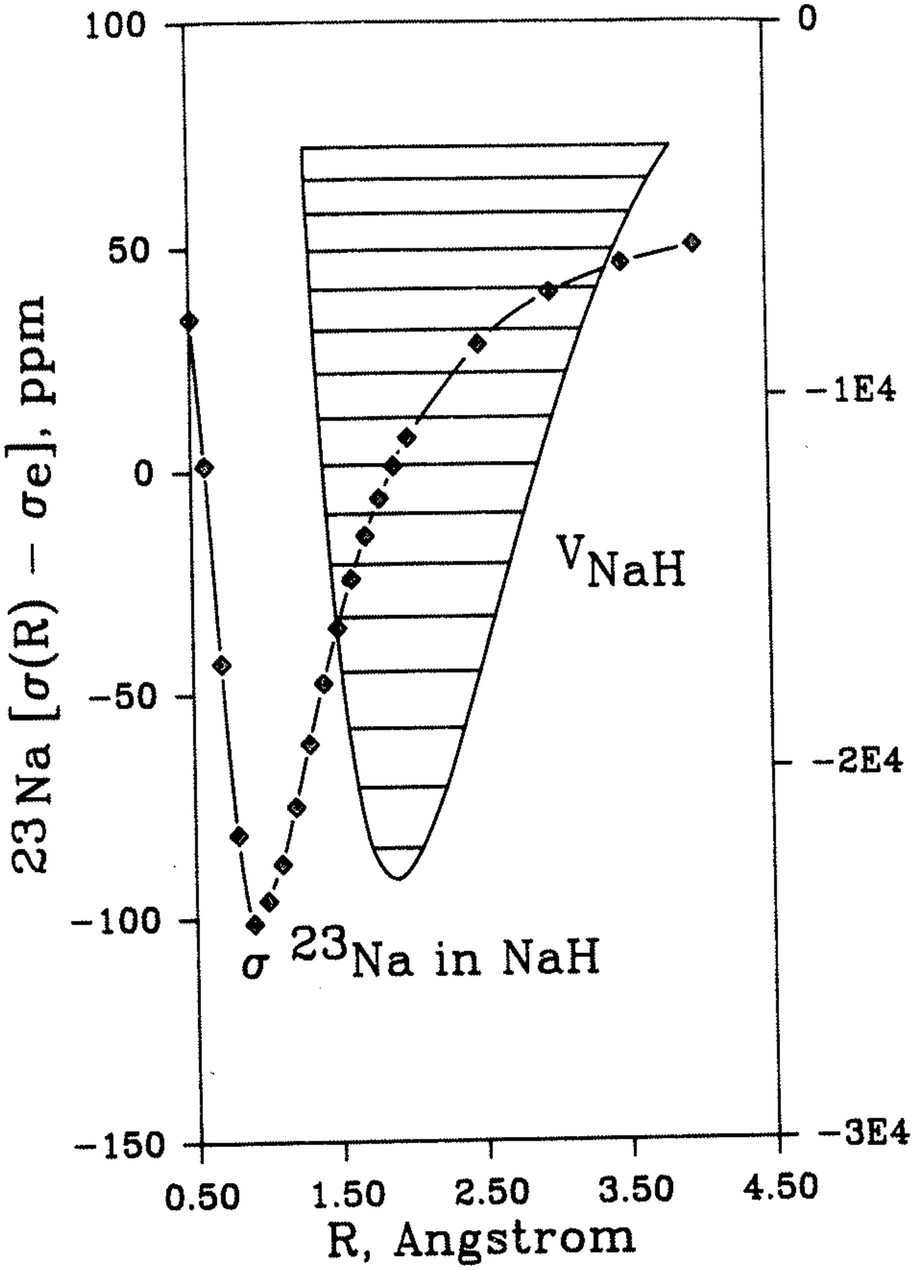
1. Born-Oppenheimer approximation

The separation of electronic and nuclear motion means that a molecular electronic energy and molecular electronic property values can be associated with a particular nuclear configuration.

Potential Energy Surface



Molecular Property Surface

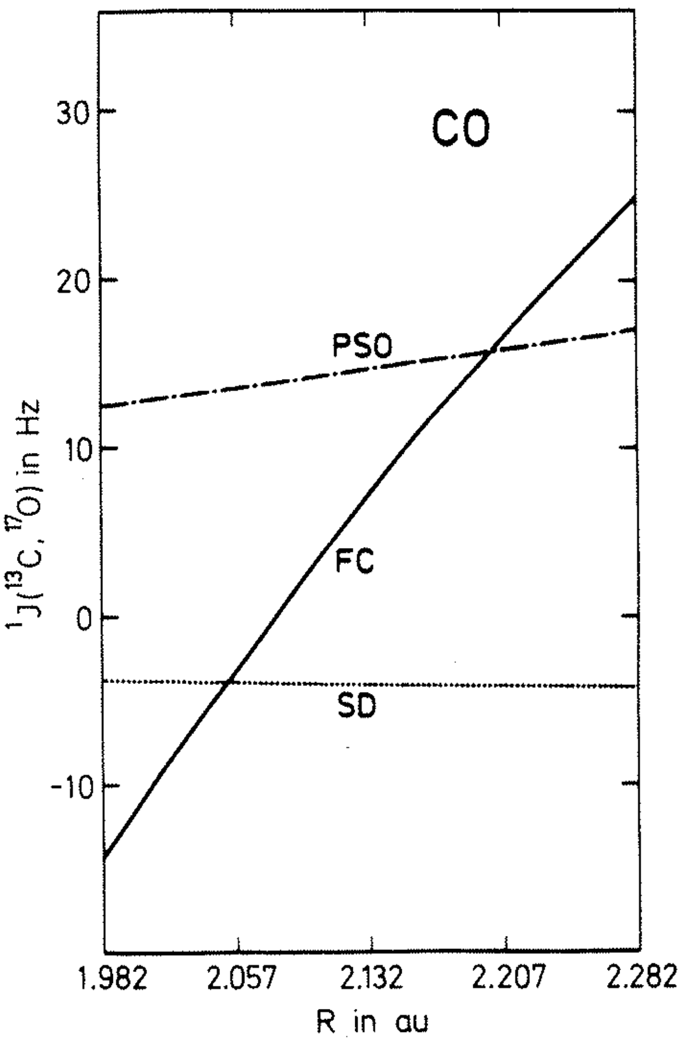


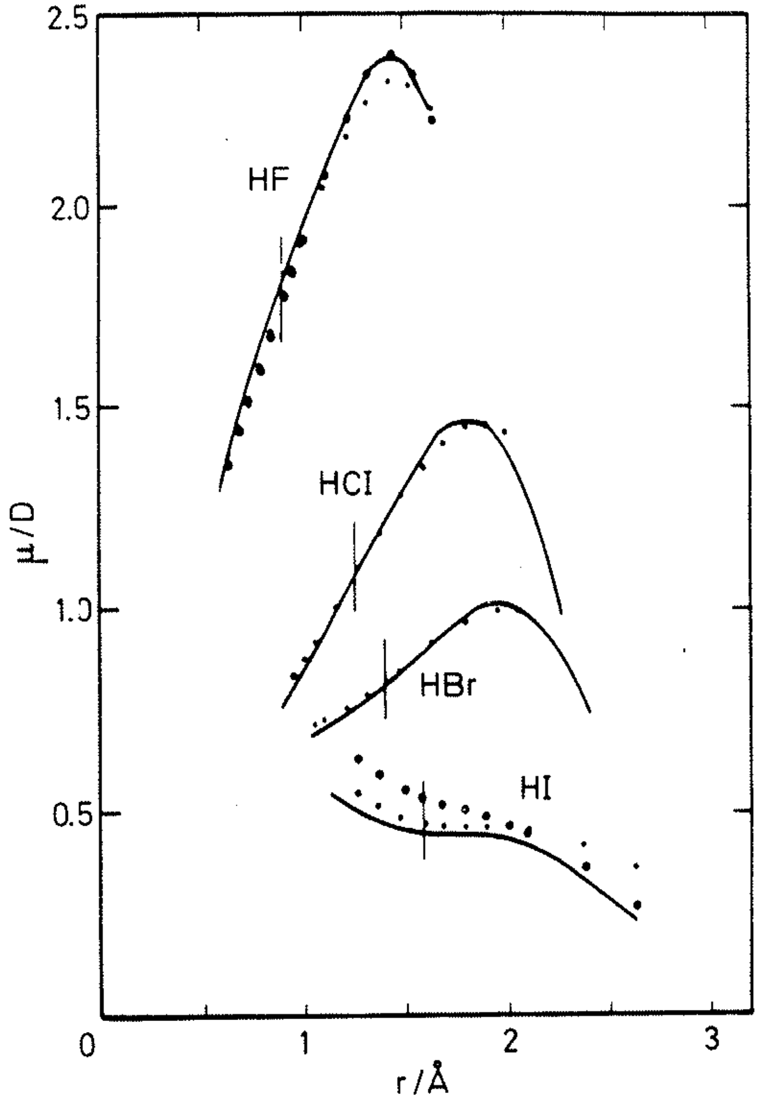
In the context of the Born-Oppenheimer separation both are ***independent of the masses of the nuclei***

2. (Mass-independent) electronic property surfaces

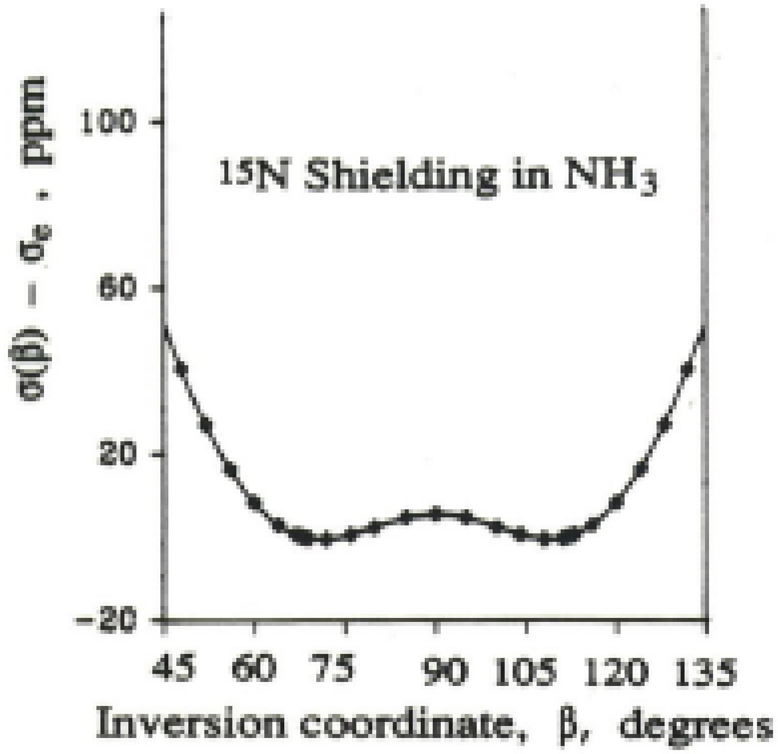
Nuclear spin-spin coupling in CO

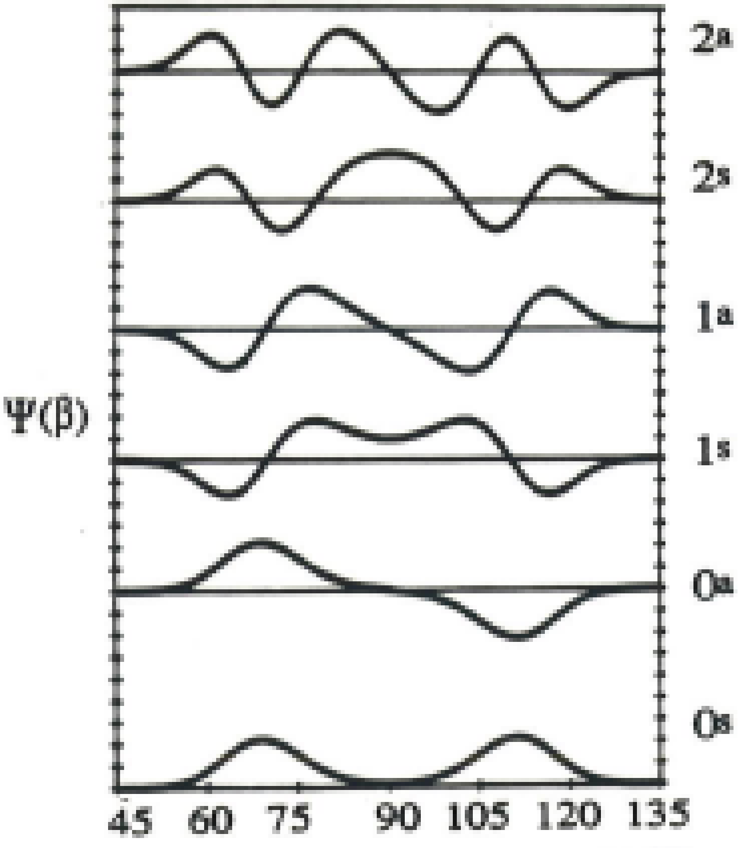
Dipole moment





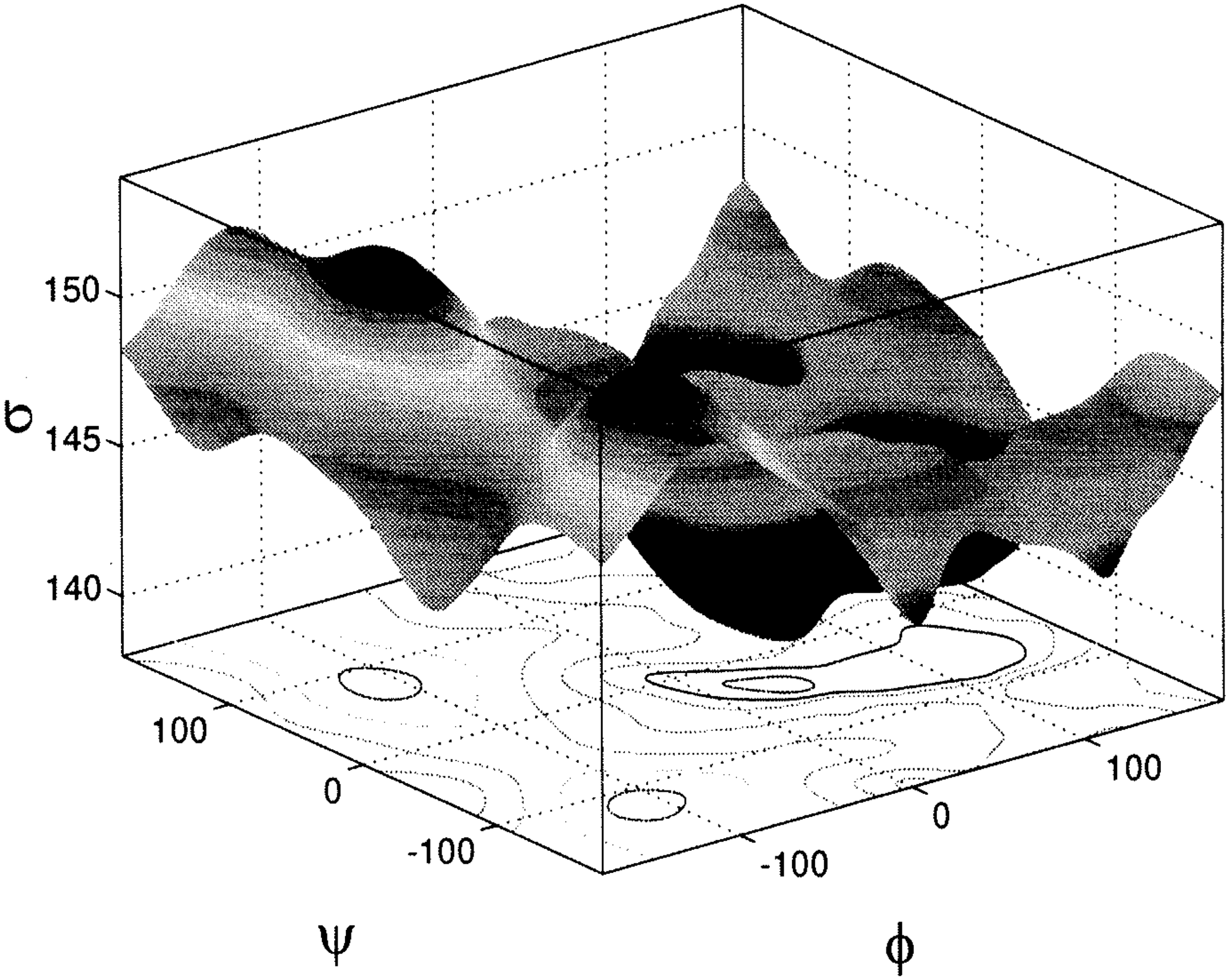
can do the same for angles

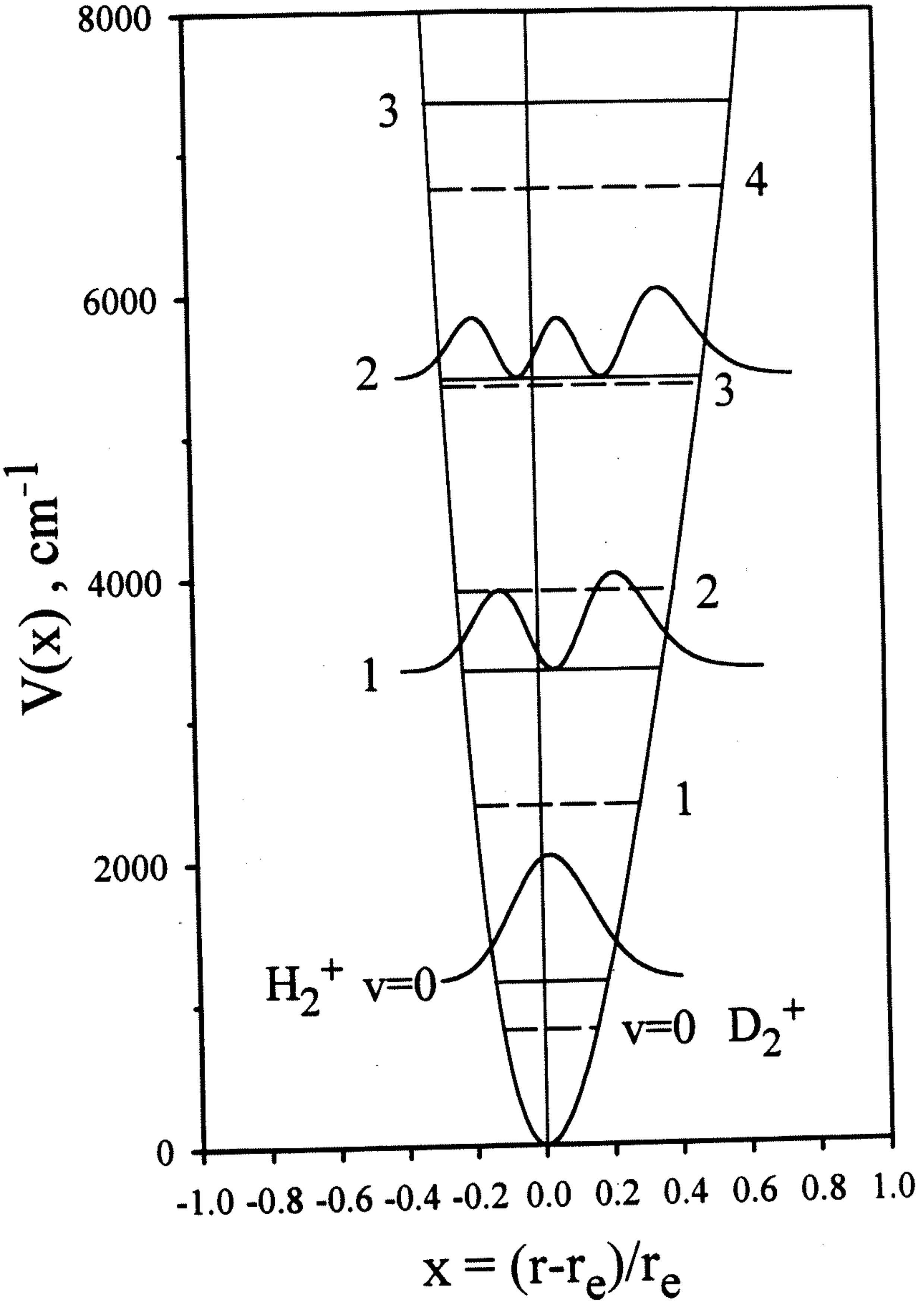




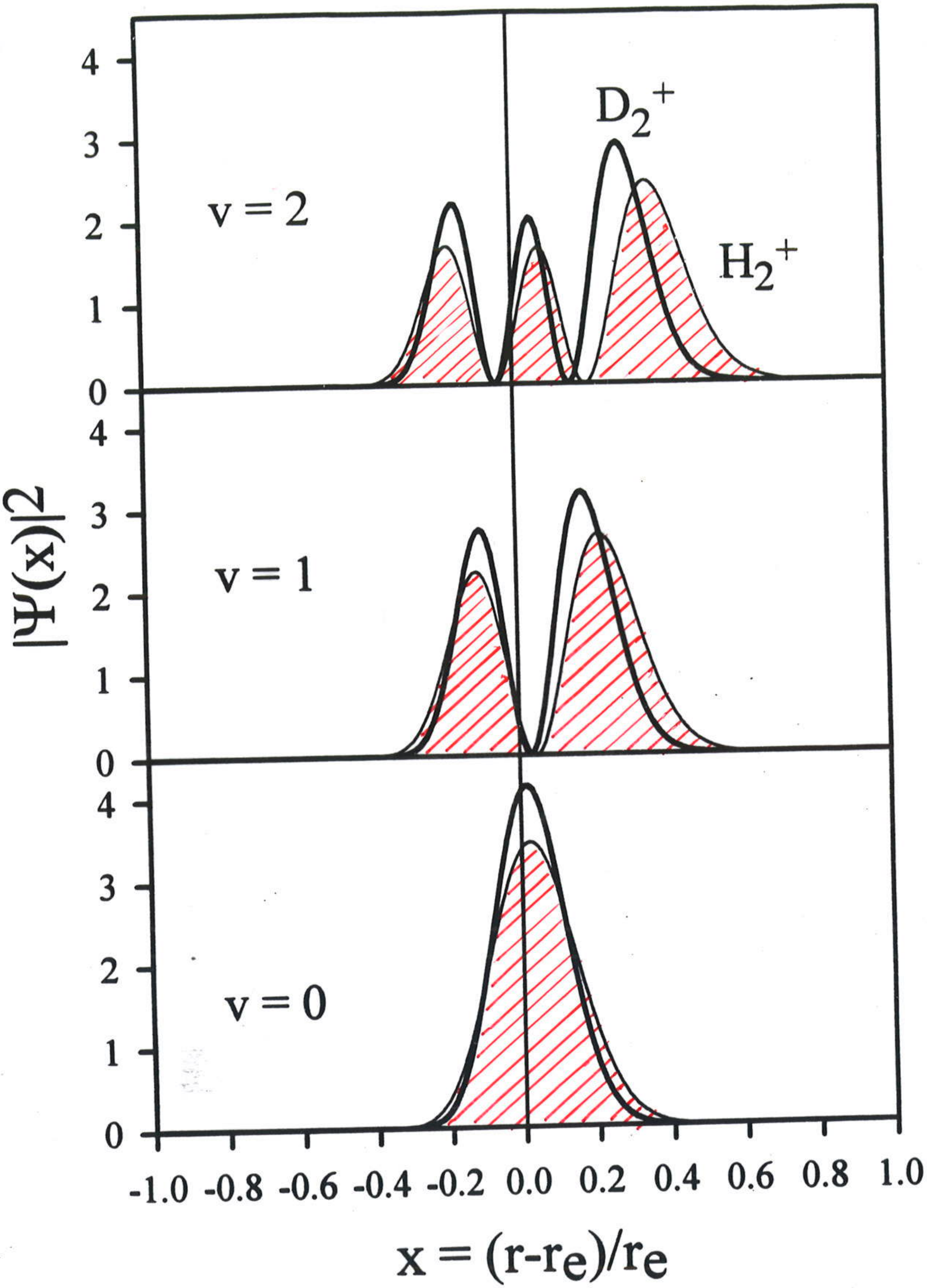
Inversion wavefunctions of NH_3

Some surfaces are hypersurfaces (multidimensional) but we can look at traces on the surface (cuts obtained by fixing some of the nuclear coordinates) which describe how the property depends on one symmetry displacement coordinate or bond angle or torsion angle.





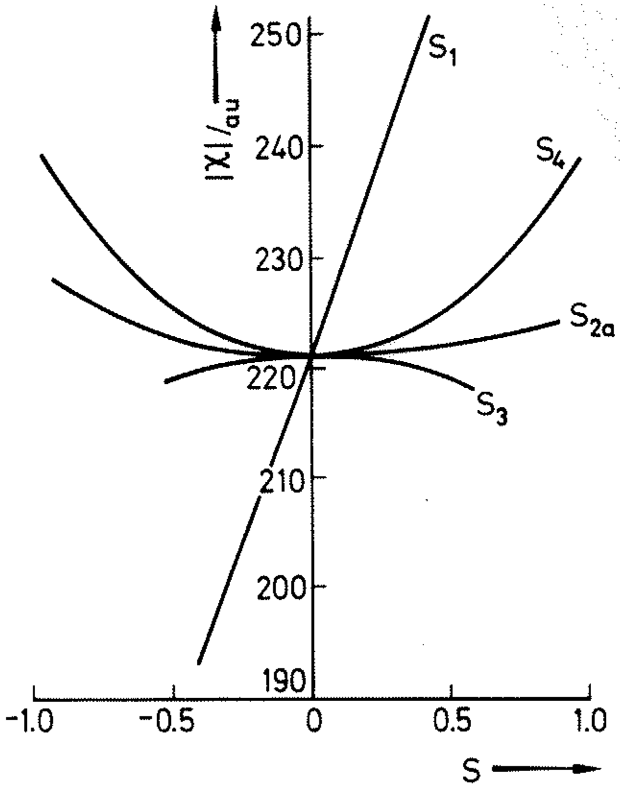
8000
6000
4000
2000
0
$V(x)$, cm^{-1}
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
$x = (r-r_e)/r_e$
3
4
2
3
1
2
1
H_2^+ v=0
v=0 D_2^+



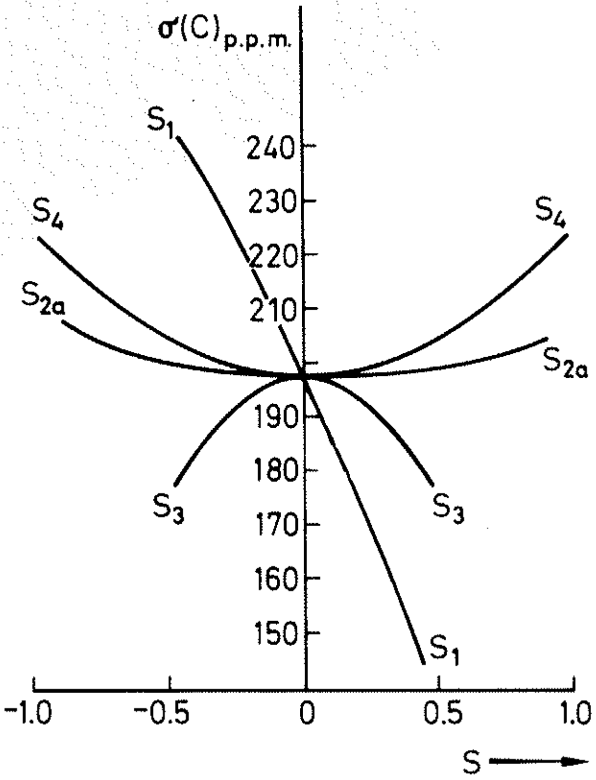
v = 2
D$_2^+$
H$_2^+$
v = 1
v = 0
$|\Psi(x)|^2$
0
1
2
3
4
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
x = (r-r$_e$)/r$_e$

The shape of the surface in the vicinity of the equilibrium geometry is important. The sensitivity to bond extension can be more important than other modes.

Property surfaces of CH_4 molecule.

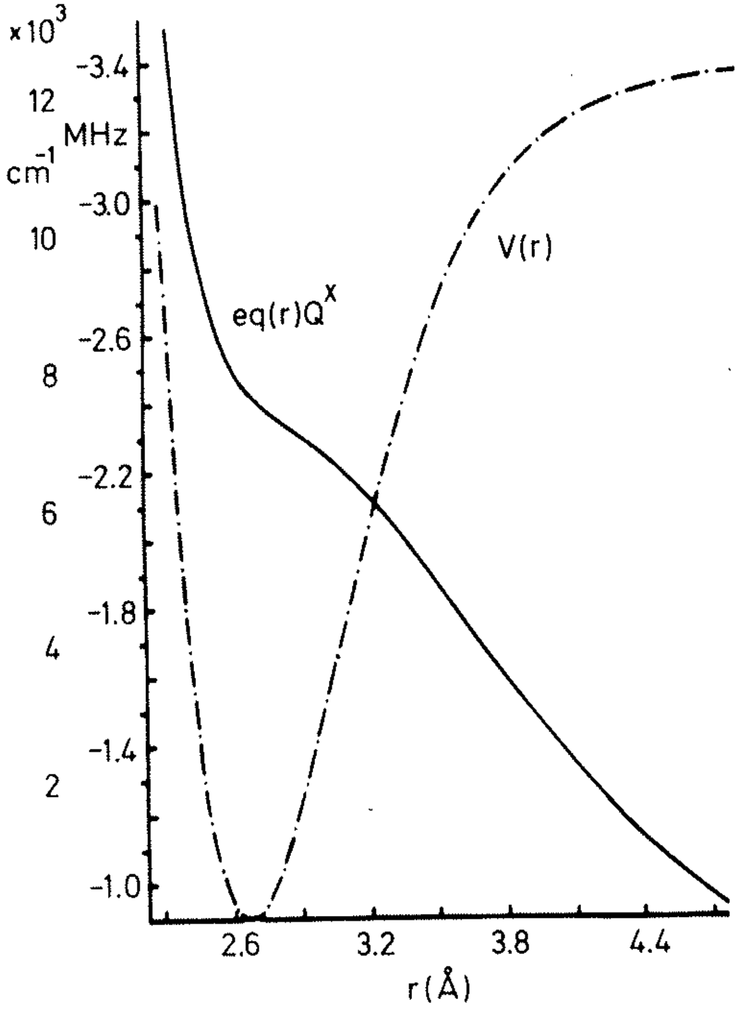


Magnetizability

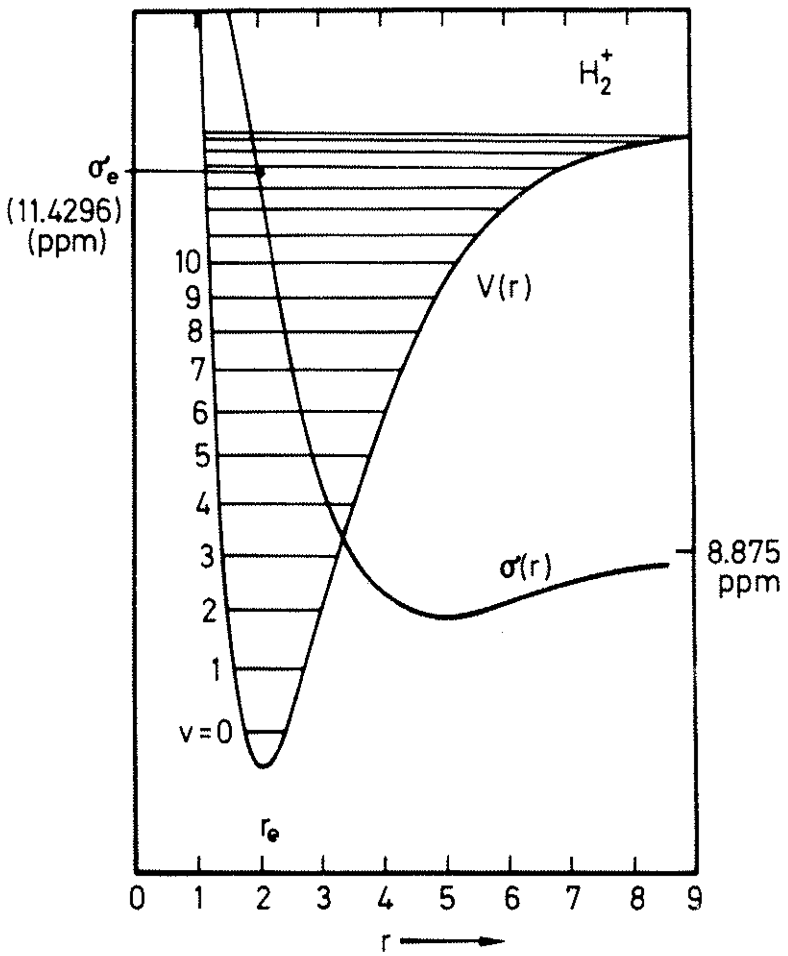


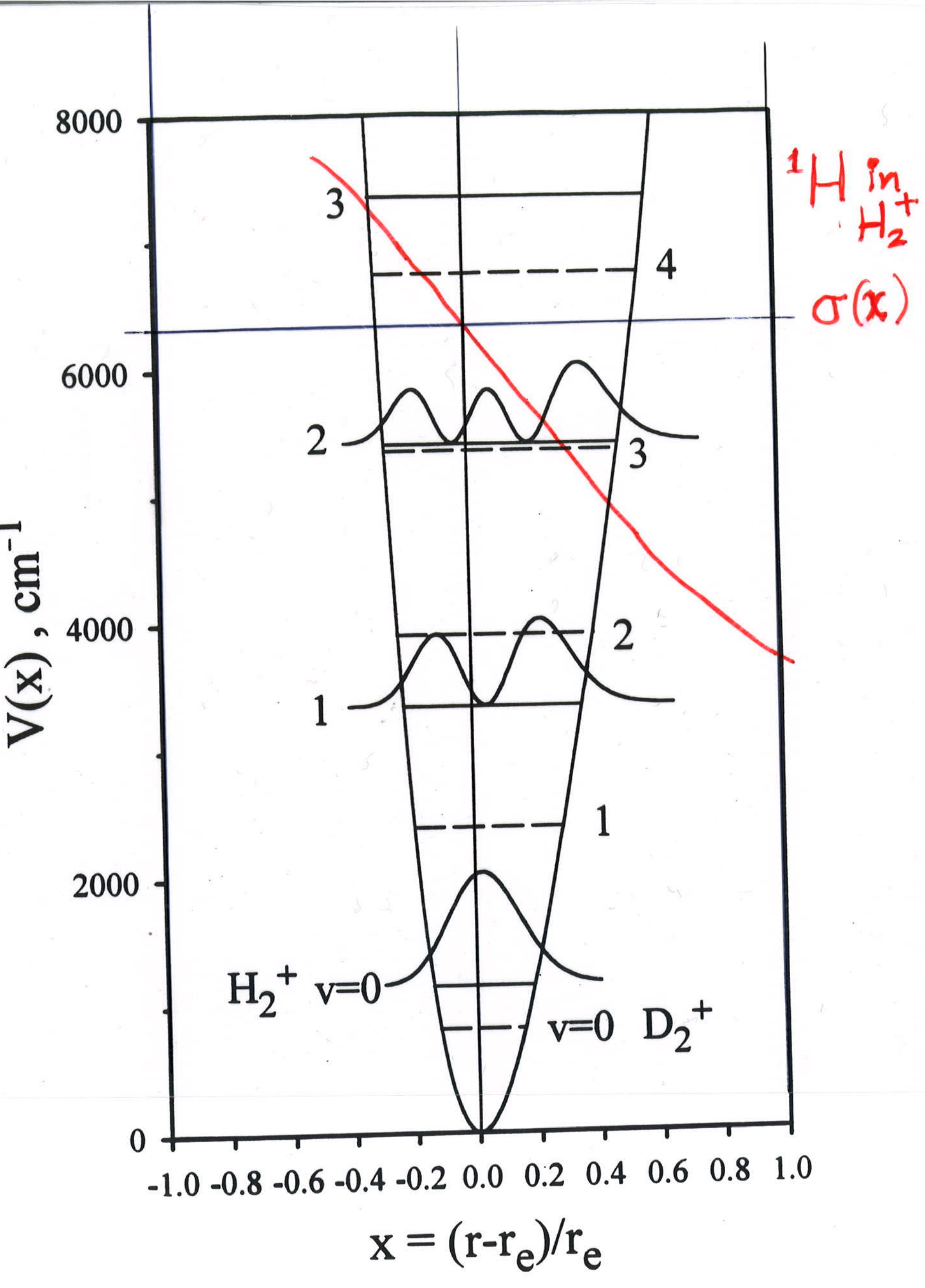
^{13}C chemical shift (shielding)

Nuclear quadrupole coupling in I_2



Proton chemical shift (shielding) in H_2^+




8000
6000
4000
2000
0
V(x) , cm^{-1}
-1.0 -0.8 -0.6 -0.4 -0.2 0.0 0.2 0.4 0.6 0.8 1.0
x = (r-r$_e$)/r$_e$
3
4
2
3
1
2
1
H$_2$$^+$ v=0
v=0 D$_2$$^+$
^{1}H in H$_2^+$
σ(x)

5. Examples of isotope effects

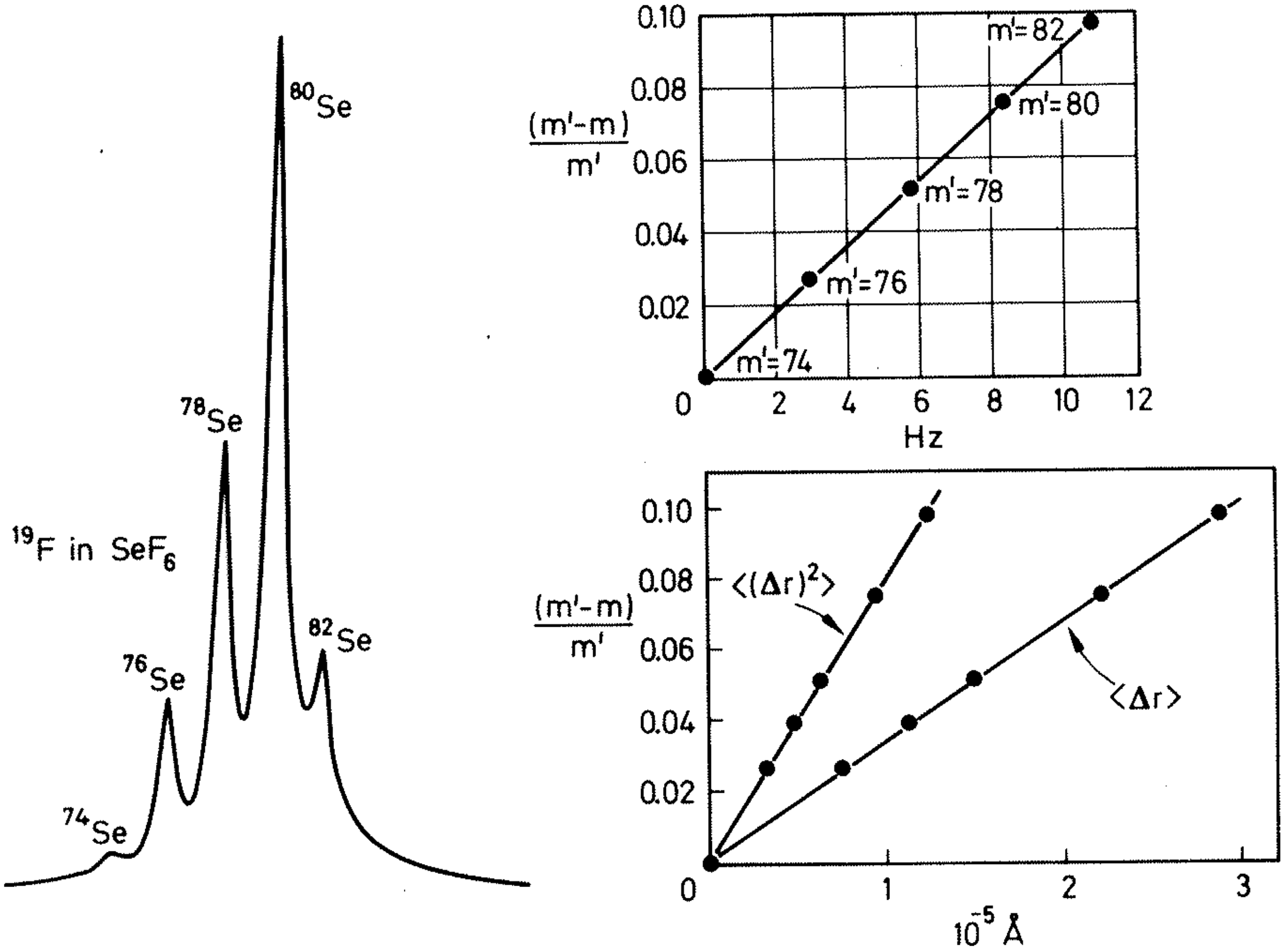


Fig. 1. ^{19}F NMR spectrum in liquid SeF$_6$ at 300 K at 188.3 MHz. The intensities of the peaks for the isotopomers are consistent with the natural abundance of Se isotopes. ^{77}SeF$_6$ satellite peaks (not shown) are split by 1421 Hz. These isotope shifts between $^{m'}$SeF$_6$ and ^{m}SeF$_6$ are plotted for m = 74, also the mean bond displacements and mean square amplitudes (at 300 K) of the Se—F bonds in SeF$_6$ molecule, are proportional to (m′—m)/m′ (see text). Reproduced from Jameson et al. (1986) J. Chem. Phys. 85: 5480, 5484

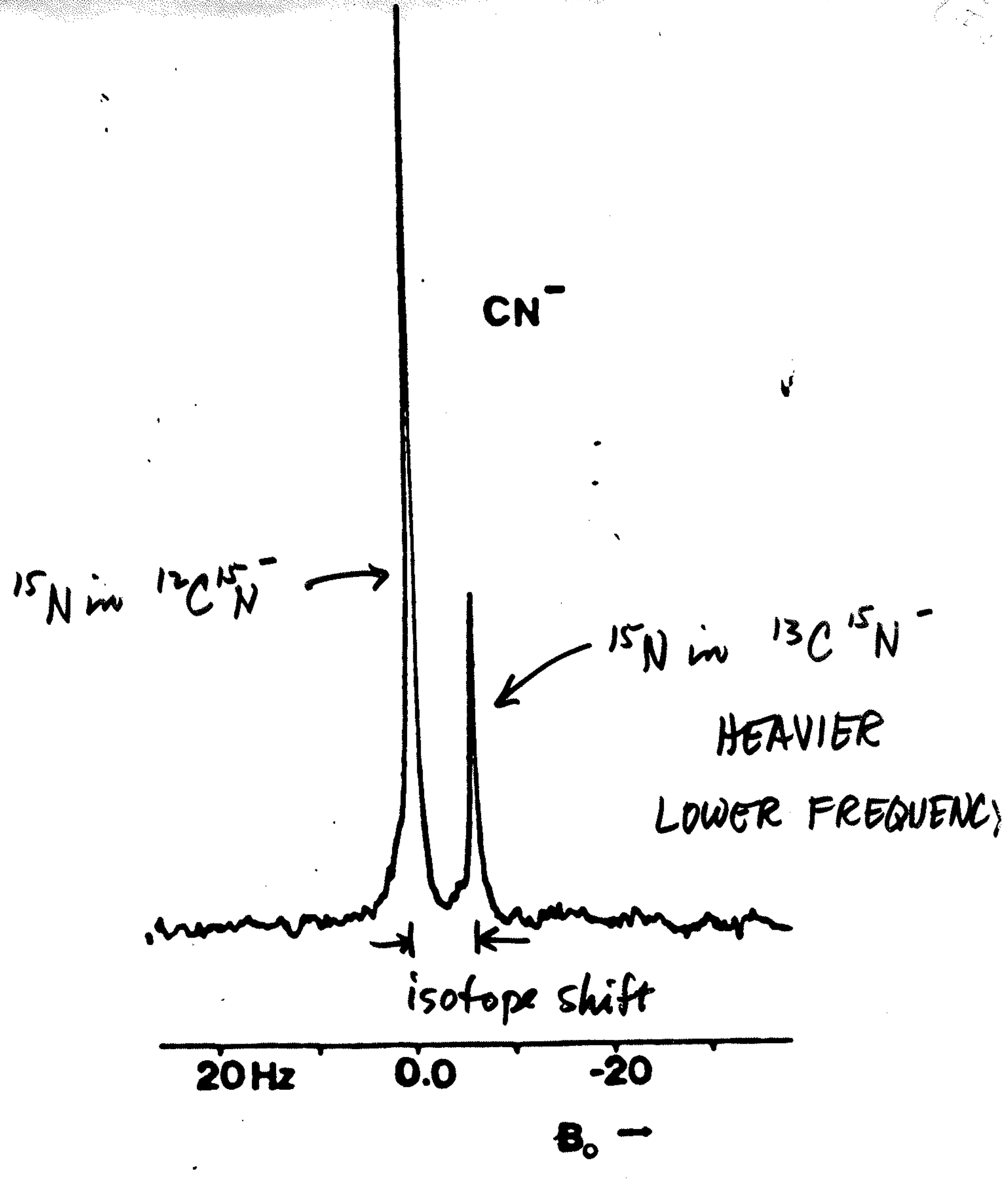
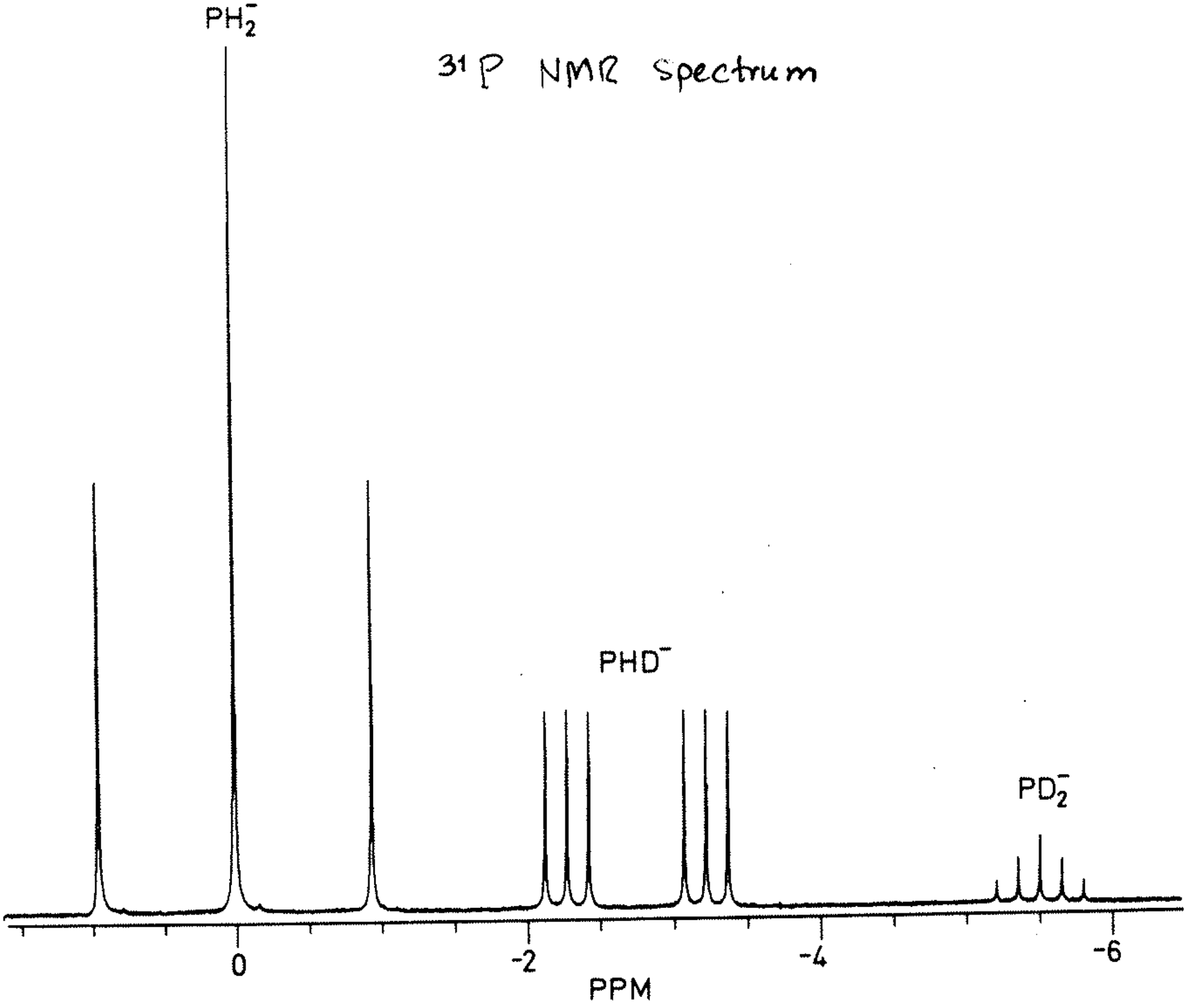
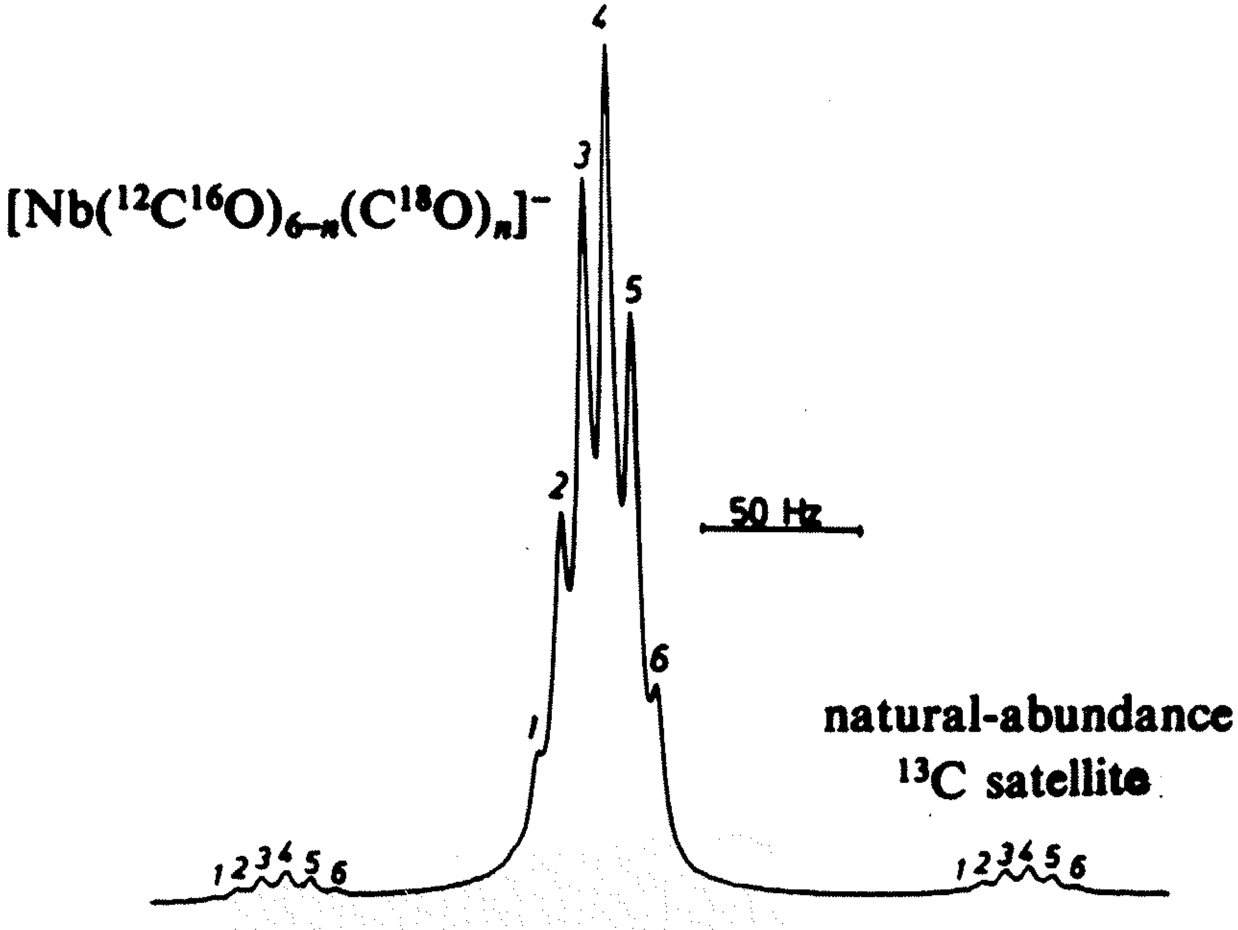


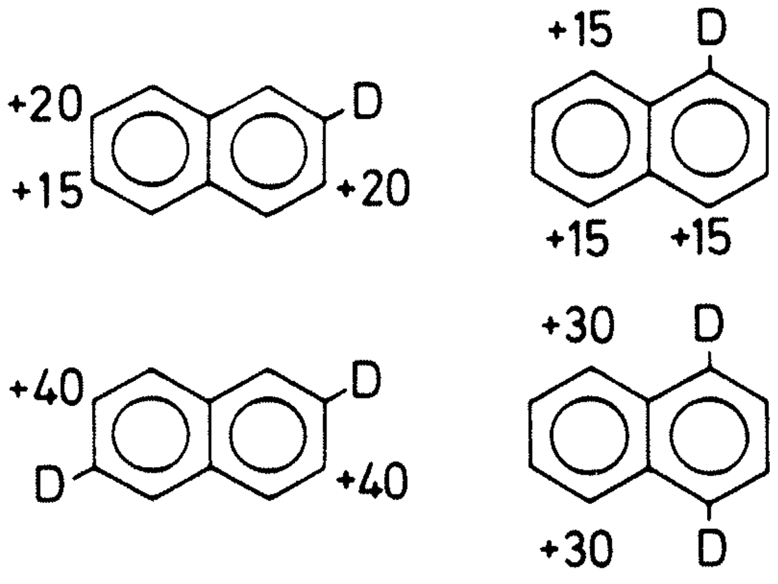
FIG. 1. Nitrogen-15 nmr spectrum of 0.20 *m* $KC^{15}N$ and 0.20 *m* $K^{13}C^{15}N$ in D_2O at 40.55 MHz. All frequencies are relative to the chemical shift of $^{12}C^{15}N^-$.



^{31}P NMR Spectrum



^{93}Nb NMR spectra of $[Nb(CO)_6]^-$ ion
enriched in $C^{18}O$ taken at 88.29 MHz in acetone solution.



splittings in the naphthalene-d anion in milligauss

Secondary isotope effects in the gas phase
quadrupole coupling constants of symmetric tops

Nucleus	Heavy-Light	$\lvert eqQ\rvert_{\mathrm{Heavy}} - \lvert eqQ\rvert_{\mathrm{Light}}$
^{35}Cl	$^{13}CD_3Cl-CD_3Cl$	-1.373 MHz
^{75}As	AsD_3-AsH_3	$+2.12$
^{121}Sb	SbD_3-SbH_3	$+5.01$
^{35}Cl	$DCl-HCl$	-0.226
^{79}Br	$^{13}CD_3Br-CD_3Br$	-1.76
^{79}Br	$DBr-HBr$	-1.673
^{127}I	$DI-HI$	-4.912
^{127}I	CD_3I-CH_3I	-5.36
^{79}Br	CD_3Br-CH_3Br	-1.42
^{79}Br	$SiD_3Br-SiH_3Br$	-0.823
^{35}Cl	CD_3Cl-CH_3Cl	-0.1802
^{14}N	$DCN-HCN$	-0.0061
^{14}N	CD_3CN-CH_3CN	$+0.0049$
^{35}Cl	$DC\equiv CCl-HC\equiv CCl$	-0.01
^{79}Br	$DC\equiv CBr-HC\equiv CBr$	-0.04
^{127}I	$^{13}CH_3I-CH_3I$	-0.016

6. The electronic and dynamic factors

Usually we observe thermal averages rather than individual vibrational states.

Usually we do not have the entire property surface. We still would like to understand isotope effects even in cases where such details are not available.

Except where low barriers to inversion or torsion are important, what determines the isotope effects is the shape of the property surface in the vicinity of the equilibrium molecular geometry since the lowest vibrational states are the most populated. In such cases we can consider a Taylor series expansion of both the property surface and the potential energy surface and we need only the derivatives of both surfaces at the equilibrium geometry.

For a diatomic molecule

$$P = P_e + (dP/dr)_e(r\text{-}r_e) + (1/2)(d^2P/dr^2)_e(r\text{-}r_e)^2 + (1/6)(d^3P/dr^3)_e(r\text{-}r_e)^3 + \ldots$$

$$\langle P\rangle^T = P_e + (dP/dr)_e\langle\Delta r\rangle^T + (1/2)(d^2P/dr^2)_e\,\langle(\Delta r)^2\rangle^T + \ldots$$

For an anharmonic diatomic molecule $\langle\Delta r\rangle^T$ and $\langle(\Delta r)^2\rangle^T$ are related to each other

$$\langle\Delta r\rangle^T = (3a/2)\,\langle(\Delta r)^2\rangle^T$$

a is the Morse parameter, which is mass-independent and related to the ratio of the cubic and the quadratic force constants.

If we stop after the third term we have

$$\langle P\rangle^T = P_e + [(dP/dr)_e + (1/3a)(d^2P/dr^2)_e]\,\langle\Delta r\rangle^T + \text{order}\,\langle(\Delta r)^3\rangle^T + \ldots$$

What do we need to know?

a) The mass-independent property surface has a value at the equilibrium geometry P_e and derivatives $(dP/dr)_e$, $(d^2P/dr^2)_e$, ... These are purely electronic quantities.

b) The mass dependence is entirely in $\langle \Delta r \rangle^T$ or $(3a/2)\langle (\Delta r)^2 \rangle^T$.

$$\langle \Delta r \rangle^T = \langle \Delta r \rangle^T_{rot} + \langle \Delta r \rangle^T_{vib}$$

$$\langle \Delta r \rangle^T_{rot} = \frac{4B_e r_e}{hc\omega_e^2} kT$$

$$\langle \Delta r \rangle^T_{vib} = (3/2)a \, (B_e/\omega_e) r_e^2 \coth(hc\omega_e/2kT)$$

$$\langle (\Delta r)^2 \rangle^T_{vib} = (B_e/\omega_e) r_e^2 \coth(hc\omega_e/2kT)$$

a is mass-independent

$$\omega_e^* = (\mu/\mu^*)^{1/2}\omega_e$$

$$B_e^* = (\mu/\mu^*)B_e$$

$$\langle \Delta r \rangle - \langle \Delta r \rangle^* = (3/2)a \, r_e^2 \{(B_e/\omega_e) \coth(hc\omega_e/2kT) - (\mu/\mu^*)^{1/2}(B_e/\omega_e) \coth[hc(\mu/\mu^*)^{1/2}\omega_e/2kT]\}$$

$$\langle \Delta r \rangle - \langle \Delta r \rangle^* \approx [1 - (\mu/\mu^*)^{1/2}]\langle \Delta r \rangle$$

$$\langle (\Delta r)^2 \rangle - \langle (\Delta r)^2 \rangle^* \approx [1 - (\mu/\mu^*)^{1/2}]\langle \Delta r^2 \rangle$$

$A^{m}X$ and its isotopomer $A^{m'}X$

$[1 - (\mu/\mu^{*})^{1/2}]$ can be further approximated by $(\mu^{*} - \mu)/2\mu^{*}$ so that

$$\langle\Delta r\rangle - \langle\Delta r\rangle^{*} \approx \langle\Delta r\rangle\left(\frac{\mu^{*} - \mu}{2\mu^{*}}\right) = \langle\Delta r\rangle\frac{1}{2}\left(\frac{m' - m}{m'}\right)\left(\frac{m_A}{m_A + m}\right)$$

$$\langle(\Delta r)^2\rangle - \langle(\Delta r)^2\rangle^{*} \approx \langle(\Delta r)^2\rangle\left(\frac{\mu^{*} - \mu}{2\mu^{*}}\right) = \langle(\Delta r)^2\rangle\frac{1}{2}\left(\frac{m' - m}{m'}\right)\left(\frac{m_A}{m_A + m}\right)$$

$$\underset{\text{in } A^{m}X}{\langle P\rangle} \quad - \quad \underset{\text{in } A^{m'}X}{\langle P\rangle^{*}}$$

$$\cong \left\{\left(\frac{dP}{dr}\right)_e \langle\Delta r\rangle_{vib} + \frac{1}{2}\left(\frac{d^2P}{dr^2}\right)_e \langle\Delta r^2\rangle\right\} \cdot \frac{1}{2}\left(\frac{m' - m}{m'}\right)\left(\frac{m_A}{m_A + m}\right)$$

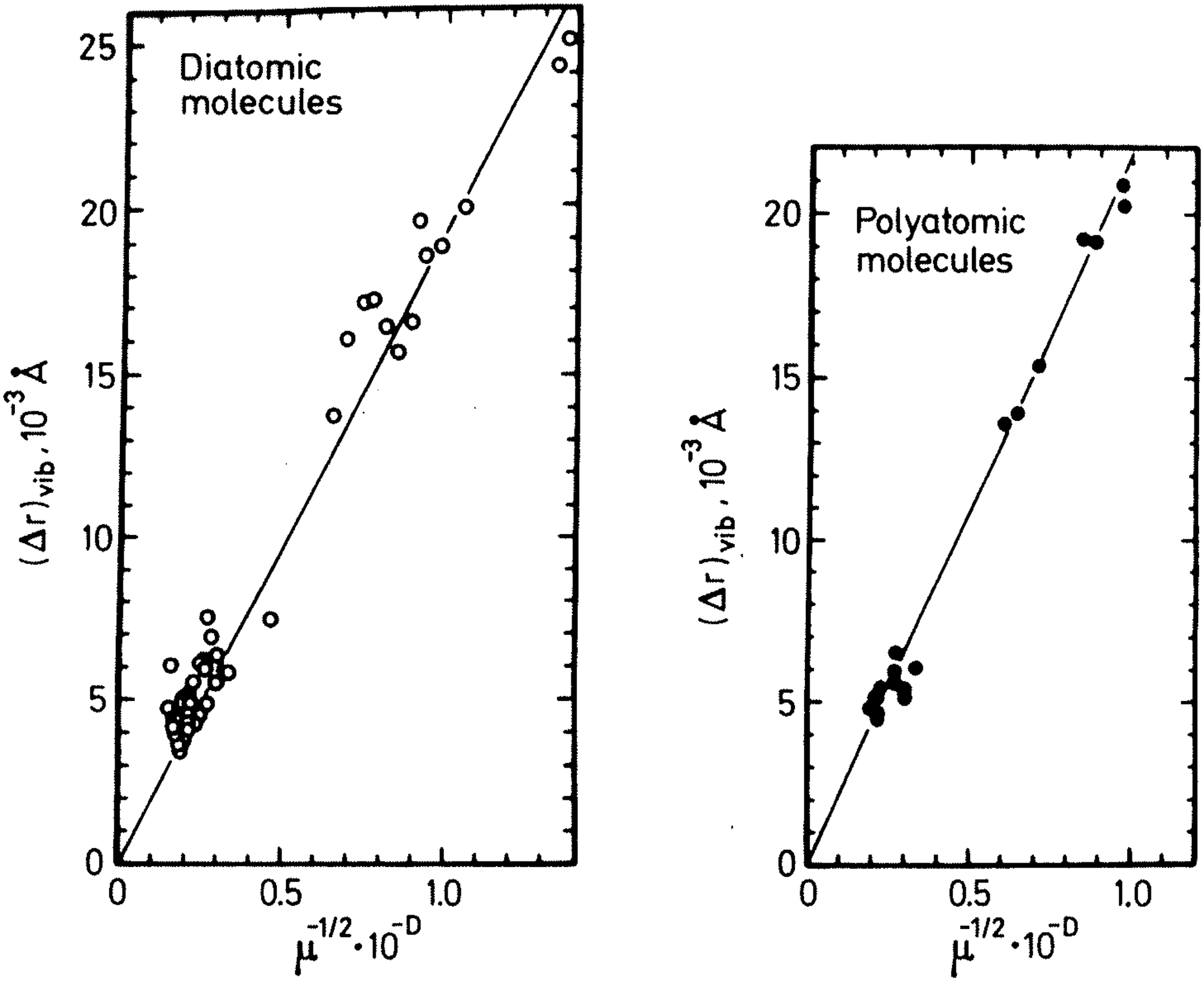
vibrational correction

$$\langle P\rangle - P_e$$

7. Estimation of the dynamic factors

It has been shown that it is possible to estimate the quantities $\langle \Delta r \rangle^T$ entirely from the general relations that have been discovered for the force constants in diatomic molecules,

Reproduced from Jameson CJ, Osten HJ (1948) J. Chem. Phys. 81: 4300,



$$V = D_e\{1 - \exp[-a(r - r_e)]\}^2$$

$$\frac{1}{3}(d^3V/dr^3)_e/(d^2V/dr^2)_e = -a$$

$$\langle\Delta r\rangle^T{}_{vib} = (3/2)a\langle(\Delta r)^2\rangle^T$$

$$\langle\Delta r\rangle_{vib} \approx \left(\frac{3h}{8\pi}\right)(-F_3F_2^{-3/2})\mu^{-1/2}$$

$$F_2 \equiv (\partial^2V/\partial r^2)_e$$

$$(-1)^nF_n = 10^{-(r_e - a_n)/b_n}$$

$$F_3 \equiv (1/3)(\partial^3V/\partial r^3)_e$$

Discovered by Herschbach + Laurie

$$\langle\Delta r\rangle_{vib} \cong (3h/8\pi)\mu^{-1/2}10^{-D}$$

$$D \equiv (r_e - a_3)/b_3 - 3(r_e - a_2)/2b_2$$

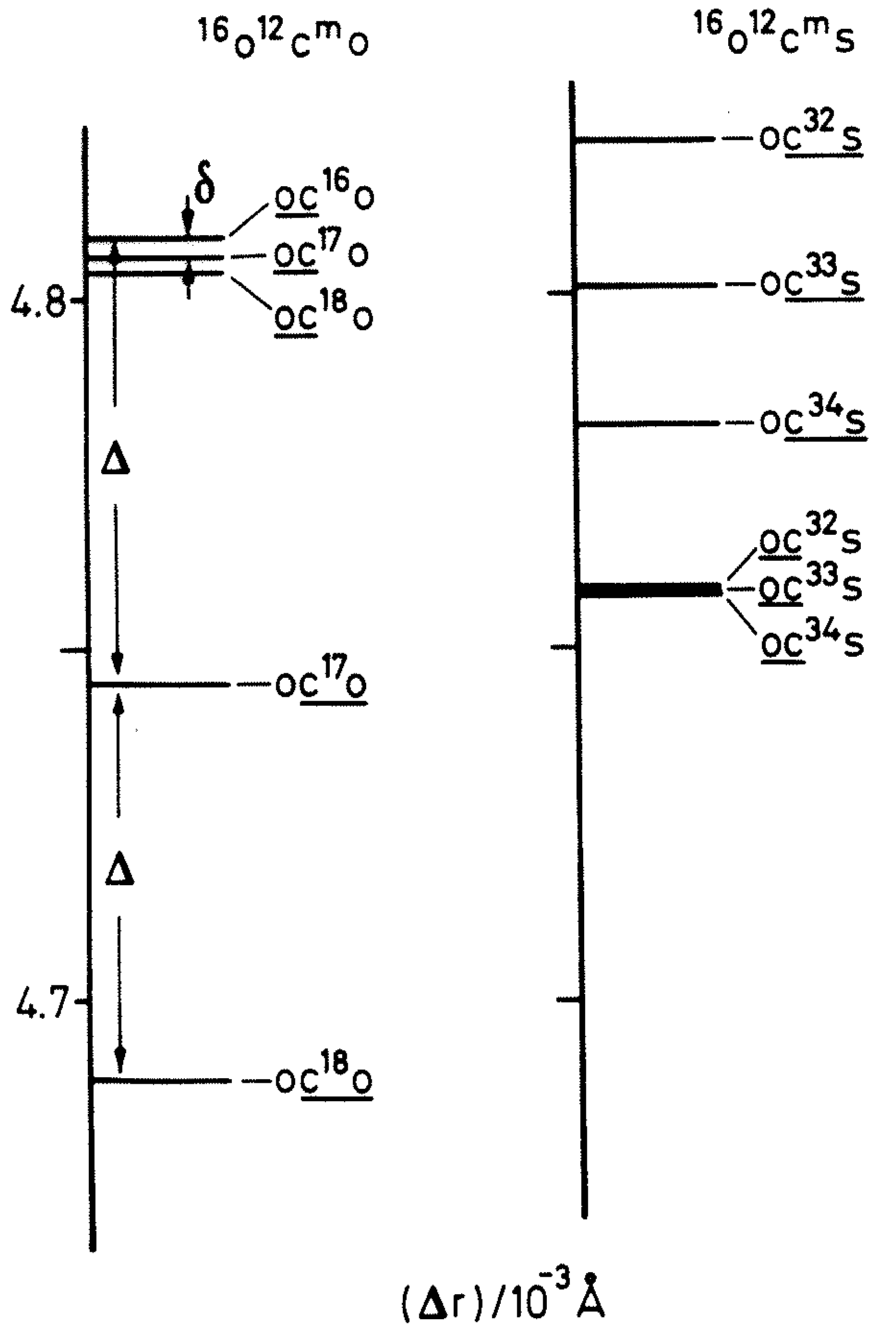
$$\langle(\Delta r)^2\rangle = (h/4\pi)\mu^{-1/2}10^{+d}$$

$$d \equiv (r_e - a_2)/2b_2$$

8. Polyatomic molecules

For a polyatomic molecule isotopic substitution at one site leads to changes in all the dynamic averages.

(1) Some changes are larger than others.



(2) Effects become additive when the cross terms are small, for example

$$\langle P\rangle = P_e + \sum_i \left(\frac{\partial P}{\partial r_i}\right)_e \langle \Delta r_i\rangle^T + \frac{1}{2}\sum_{ij}\left(\frac{\partial^2 P}{\partial r_i^2}\right)_e \langle \Delta r_i^2\rangle^T + \ldots$$

when $\left(\frac{\partial P}{\partial r_i}\right)_e$ are all equal, the n terms can be combined,

$$\langle P\rangle = P_e + n\left[\left(\frac{\partial P}{\partial r_1}\right)_e \langle \Delta r_1\rangle^T + \frac{1}{2}\left(\frac{\partial^2 P}{\partial r_1^2}\right)_e \langle \Delta r_1^2\rangle^T\right] + \ldots$$

ignore various others such as

$$(n-1)\left(\frac{\partial^2 P}{\partial r_1\,\partial r_2}\right)_e [\langle \Delta r_1\,\Delta r_2\rangle - \langle \Delta r_1\,\Delta r_2\rangle^*]$$

$$\left(\frac{\partial^2 P}{\partial r_1\,\partial \alpha}\right)_e [\langle \Delta r_1\,\Delta \alpha\rangle - \langle \Delta r_1\,\Delta \alpha\rangle^*]\ldots$$

With successive isotopic substitution

$$\underset{\text{in } A^mX_n}{\langle P\rangle} \quad - \quad \underset{\text{in } A^mX_{n-s}{}^{m'}X_s}{\langle P\rangle^*} \cong s\left\{\begin{aligned} &\left(\frac{\partial P}{\partial r_1}\right)_e [\langle \Delta r_1\rangle - \langle \Delta r_1\rangle^*] \\ &+\frac{1}{2}\left(\frac{\partial^2 P}{\partial r_1^2}\right)_e [\langle (\Delta r_1)^2\rangle - \langle (\Delta r_1)^2\rangle^*]\end{aligned}\right\}$$

(3) When locally centered electronic properties are being considered (efg or NQCC, chemical shifts, hyperfine coupling, J coupling) the electronic factors are also large or small *depending on the remoteness of the isotopic substitution site* from the local site of the property. For example, the secondary electronic factor $(\partial\sigma^F/\partial r_{CH})_e$ in CH_3F is expected to be smaller than the primary $(\partial\sigma^F/\partial r_{FC})_e$. However, the primary dynamic factor

$\Delta = \{\langle\Delta r\rangle_{CH} - \langle\Delta r\rangle_{CD}\}$ is much larger than the secondary dynamic factor

$\delta = \{\langle\Delta r_{FC}\rangle_{CH3F} - \langle\Delta r_{FC}\rangle_{CDH2F}\}$.

The orders of magnitude of the dynamic quantities are:

$d = \langle\Delta r\rangle_{CH} \approx 20\times10^{-3}$ Å in CH_4

upon D substitution in CH_4, we get

$\langle\Delta r\rangle_{CD} \approx (d - \Delta)$ where $\Delta \approx 5\times10^{-3}$ Å and

$\langle\Delta r\rangle_{CH} \approx (d \pm\delta)$ where $\delta \approx 1\times10^{-5}$ Å

It was predicted that the observed isotope effects from *remote sites are dominated by the primary dynamic quantity together with the secondary electronic factor*. This has been verified by theoretical calculations.

A nice example which permits the distinction between *primary and secondary electronic factors* is the J coupling in NMR. We use the reduced form which is purely electronic and has no dependence on the γ of the coupled spins. In the various deuterated versions of SnH_4 the SnH and SnD couplings can be observed:

$$\langle K(SnH_1)\rangle = K_e + P_r\langle\Delta r_1\rangle + P_s\left\{\langle\Delta r_2\rangle + \langle\Delta r_3\rangle + \langle\Delta r_4\rangle\right\}$$

$$+ \text{ terms in } P_{rr'}, P_{ss'}, P_{rs'}, P_{st'}, P_\alpha \text{ etc} \ldots$$

where the primary derivative is $P_r \equiv \left(\dfrac{\partial K(SnH_1)}{\partial r_{SnH_1}}\right)_e$

and the secondary derivative is $P_s \equiv \left(\dfrac{\partial K(SnH_1)}{\partial r_{SnH_2}}\right)_e$.

If we let $d \equiv \langle\Delta r_{SnH}\rangle$ in SnH_4 and $d\text{-}\Delta \equiv \langle\Delta r_{SnD}\rangle$ in SnD_4, then

$d \approx 17.80\times10^{-3}$ Å and $\Delta \approx 5.161\times10^{-3}$ Å for $r_e = 1.70$ Å

K_e is the reduced coupling constant at the equilibrium geometry.

The leading terms are:

SnH_4: $\langle K(SnH)\rangle = K_e + [P_r+3P_s]d + \ldots$

SnH_3D: $\langle K(SnH)\rangle = K_e + [P_r+2P_s]d + P_s(d\text{-}\Delta) + \ldots$

$\langle K(SnD)\rangle = K_e + P_r(d\text{-}\Delta) + 3P_s d + \ldots$

SnH_2D_2: $\langle K(SnH)\rangle = K_e + [P_r+P_s]d + 2P_s(d\text{-}\Delta) + \ldots$

$\langle K(SnD)\rangle = K_e + [P_r+P_s](d\text{-}\Delta) + 2P_s d + \ldots$

$SnHD_3$: $\langle K(SnH)\rangle = K_e + P_r d + 3P_s(d\text{-}\Delta) + \ldots$

$\langle K(SnD)\rangle = K_e + [P_r+2P_s](d\text{-}\Delta) + P_s d + ..$

SnD_4: $\langle K(SnH)\rangle = K_e + [P_r+3P_s](d\text{-}\Delta) + \ldots$

the primary isotope effect

$$\Delta_p {}^1K(\mathrm{Sn}^{2/1}\mathrm{H}) = |{}^1K(\mathrm{SnD})\,|^{*}_{\mathrm{SnH_3D}} - |{}^1K(\mathrm{SnH})\,|_{\mathrm{SnH_4}} \approx -P_r \cdot \Delta$$

The primary isotope effect may also be taken from $|{}^1K(\mathrm{SnD})|_{\mathrm{SnH_2D_2}} - |{}^1K(\mathrm{SnH})|_{\mathrm{SnH_3D}}$, or $|{}^1K(\mathrm{SnD})|_{\mathrm{SnHD_3}} - |{}^1K(\mathrm{SnH})|_{\mathrm{SnH_2D_2}}$, or $|{}^1K(\mathrm{SnD})|_{\mathrm{SnD_4}} - |{}^1K(\mathrm{SnH})|_{\mathrm{SnHD_3}}$,

At the same time, the secondary isotope effect

$$\Delta_s {}^1K(\mathrm{SnH})\,[{}^{1/2}\mathrm{H}] = |K(\mathrm{SnH})\,|^{*}_{\mathrm{SnH_3D}} - |K(\mathrm{SnH})\,|_{\mathrm{SnH_4}} \approx -P_s \cdot \Delta$$

may be taken from $|{}^1K(\mathrm{SnH})|_{\mathrm{SnH_2D_2}} - |K(\mathrm{SnH})|_{\mathrm{SnH_3D}}$, etc.

leading to

$P_r = (\partial K(\mathrm{SnH_1})/\partial r_{\mathrm{SnH_1}})_e \approx 200$ reduced units per Å.

$P_s = (\partial K(\mathrm{SnH_1})/\partial r_{\mathrm{SnH_2}})_e \approx 75$ reduced units per Å

SUMMARY

- When a heavier isotope replaces an atom in a molecule the changed mass causes changes in the rovibrational averaging of all electronic properties of the molecule.
- These isotope effects are intimately related to both the molecular potential energy surface which governs the vibrational motion and the electronic property surface which is the mathematical surface describing the value of the electronic property as a function of nuclear coordinates such as bond distances, bond angles, torsion angles.
- Considering intrinsic isotope effects in terms of a combination of two factors provides insight into their magnitudes and signs. One is the dynamic factor which has to do with the slight change in the rovibrationally-averaged geometry of the molecule upon substitution of

SUMMARY

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- These isotope effects are intimately related to both the molecular potential energy surface which governs the vibrational motion and the electronic property surface which is the mathematical surface describing the value of the electronic property as a function of nuclear coordinates such as bond distances, bond angles, torsion angles.
- Considering intrinsic isotope effects in terms of a combination of two factors provides insight into their magnitudes and signs. One is the dynamic factor which has to do with the slight change in the rovibrationally-averaged geometry of the molecule upon substitution of

an atom by a heavier isotope; the dynamic average bond lengths tend to become shorter, for example. The other, an electronic factor, has to do with the sensitivity of the chemical shift, spin spin coupling or other electronic property to a change in molecular geometry.

- In the particular case of the local electronic properties such as NMR chemical shift, spin-spin coupling, nuclear hyperfine constant, or nuclear quadrupole coupling of a probe nucleus, the chemical shift (for example) of the probe nucleus is affected to a larger or smaller extent dependent on its location in the molecule relative to the site of the mass change. That is, we can use the isotope effects on these electronic quantities as a way of arriving at the location of the mass-label. All resonant nuclei linked to the label site by some efficient electronic transmission path report on its location, providing a multiplicity of useful information.

- The magnitudes of intrinsic isotope effects on electronic properties depend on the fractional mass change at the isotope substitution site. This is common to various electronic properties.
- The sign of the isotope effect, its dependence on the remoteness of the substitution site, its dependence on the observed probe nucleus depends on which electronic property is being measured and the electronic structure of the molecule.

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