

AFRL-MN-EG-TP-2006-7402

## ROTATIONAL DYNAMICS OF SMALL MOLECULES IN QUANTUM SOLIDS AND LIQUIDS (BRIEFING CHARTS)

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### CONFERENCE PAPER

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<b>14. ABSTRACT</b>					
<ul style="list-style-type: none"> <li>• High resolution IR absorption spectra of diatomic dopants in solid pH<sub>2</sub> provide rigorous tests of theories describing molecular rotations in solids.</li> <li>• Leading candidate theories cannot explain strong linear correlation.</li> </ul>					
<b>15. SUBJECT TERMS</b> Molecular Rotational Dynamics in Solids, Matrix Isolation Spectroscopy, IR Absorption Spectra of CO Isotopomers, Center of Interaction, Quantum Liquids, Quantum Solids					
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# Rotational Dynamics of Small Molecules in Quantum Solids and Liquids



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- \* Molecular rotational dynamics in solids
- \* Matrix Isolation Spectroscopy in solid parahydrogen ( $pH_2$ )
- \* IR absorption spectra of CO isotopomers in solid  $pH_2$
- \* "Center-Of-Interaction" (C.I.) for CO in  $pH_2$
- \* Similarities between CO/ $pH_2$  and CO/IHe
- \* Speculations on quantum solids vs. quantum liquids

This paper is published in the interest of the scientific and technical information exchange.

Publication of this report does not constitute approval or disapproval of the ideas or findings.

61st International Symposium on Molecular Spectroscopy, Talk RI03, 22 June 2006, Ohio State University, Columbus, OH

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# Models of Molecular Rotations in the Solid Phase

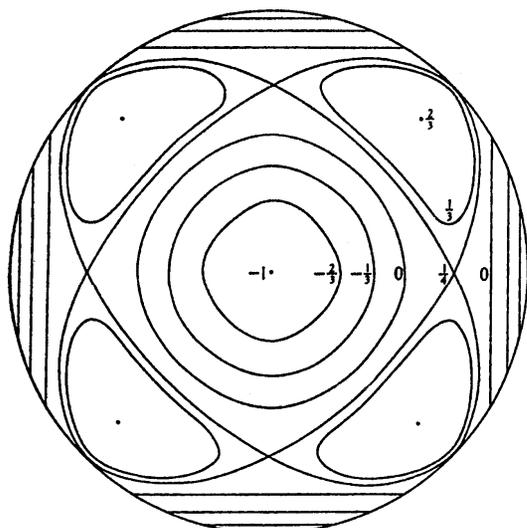
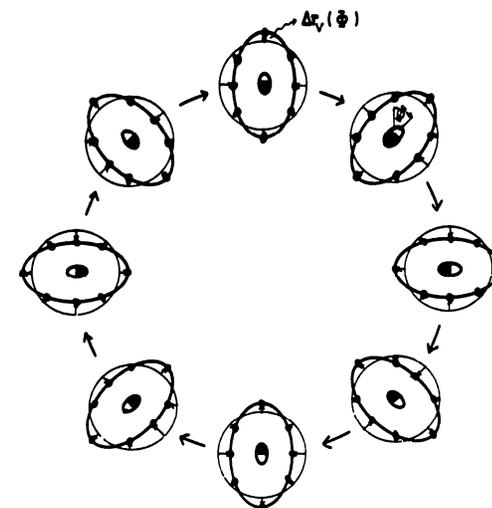
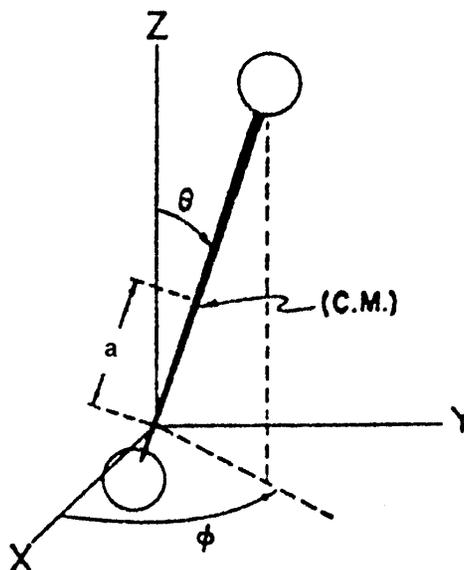


FIG. 1—Equipotential lines for  $K = 1$ .



rotating molecule trapped in pseudo-rotating cage

## Crystal Field Theory:

- \* Molecular center-of-mass (C.M.) remains fixed at trapping site center.
- \* Rigid, undistorted trapping site.

A.F. Devonshire, Proc. Roy. Soc. (London) **A153**, 601 (1936).

## Rotation-Translation Coupling:

- \* Molecular "center-of-interaction" (C.I.) occupies trapping site center at equilibrium.
- \* Molecular C.M. moves relative to trapping site center during rotation.

M.T. Bowers, G.I. Kerley, and W.H. Flygare, J. Chem. Phys. **45**, 3399 (1966).

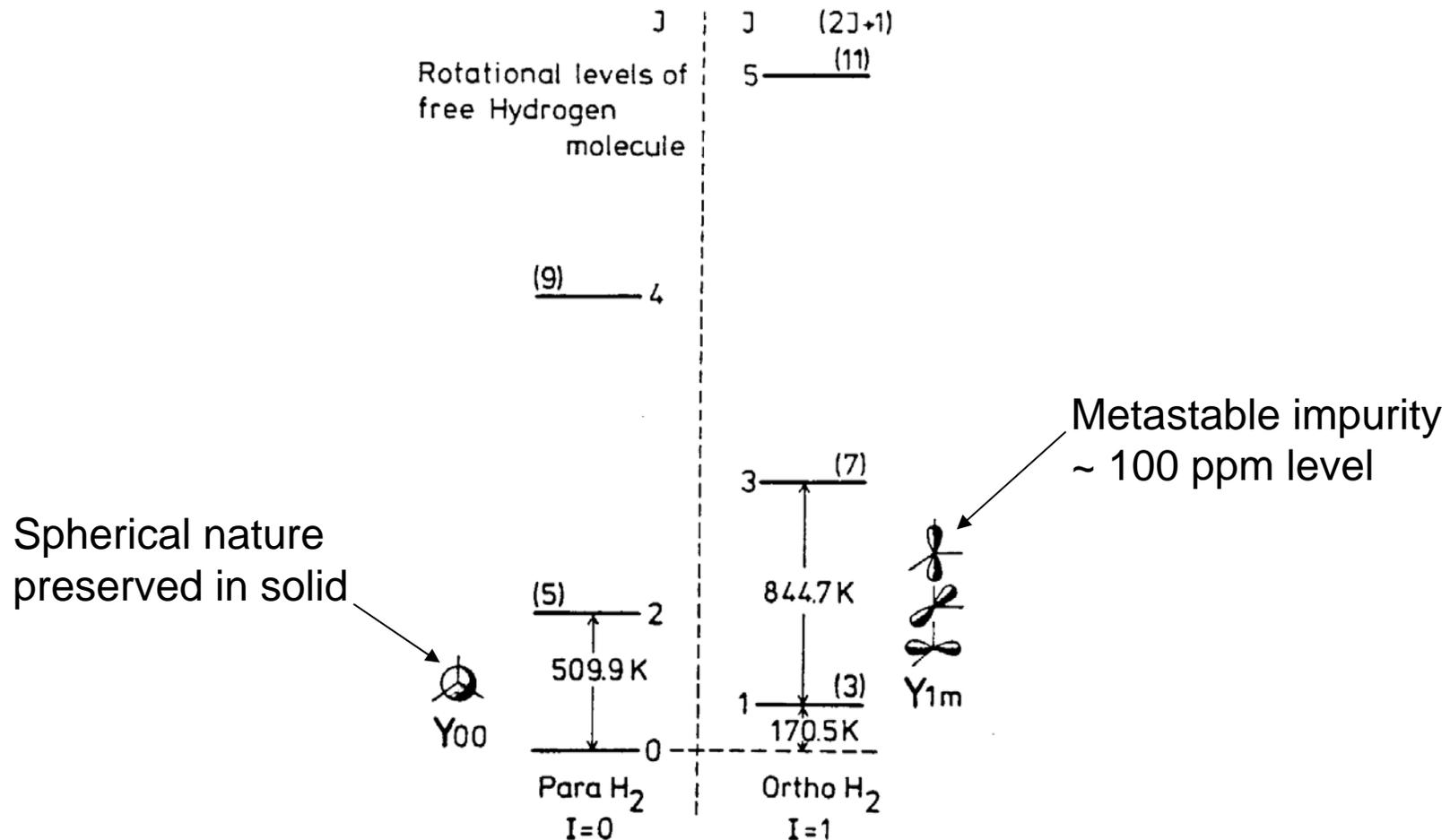
## Pseudorotating Cage Model:

- \* Molecular rotation is coupled to synchronous pseudorotation of matrix cage atoms.

J. Manz, J. Am. Chem. Soc. **102**, 1801 (1980).



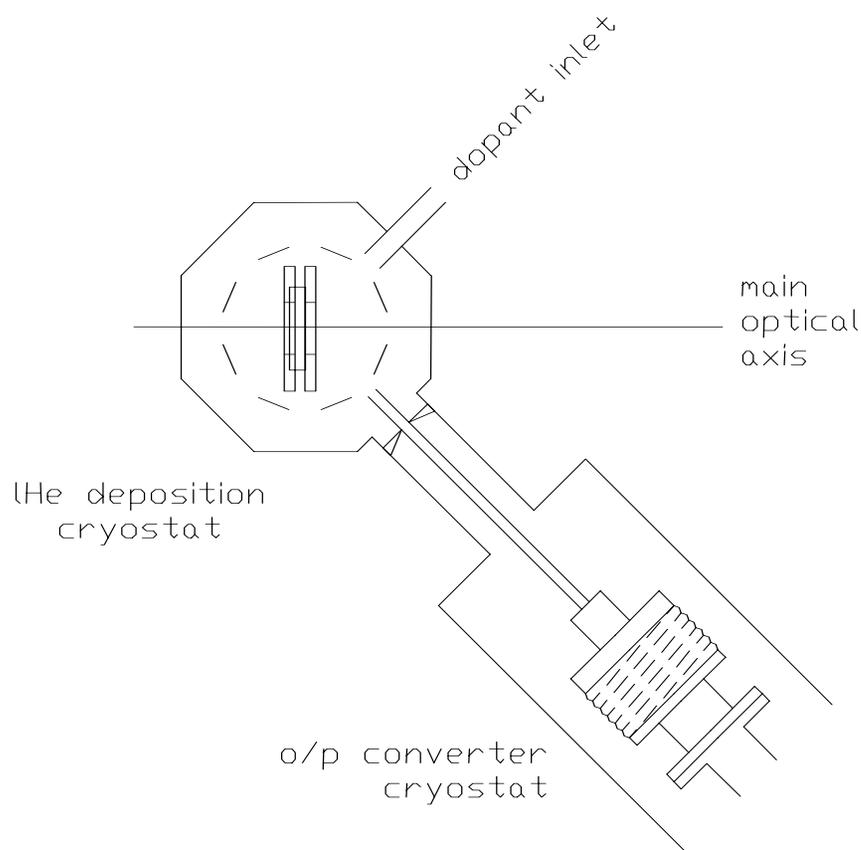
# ortho- and para-hydrogen



I.F. Silvera, Rev. Mod. Phys. **52**, 393 (1980).



# Rapid vapor deposition of solid $p\text{H}_2$



- \* Mixed fcc/hcp microstructure in as-deposited samples; can anneal to nearly pure hcp.

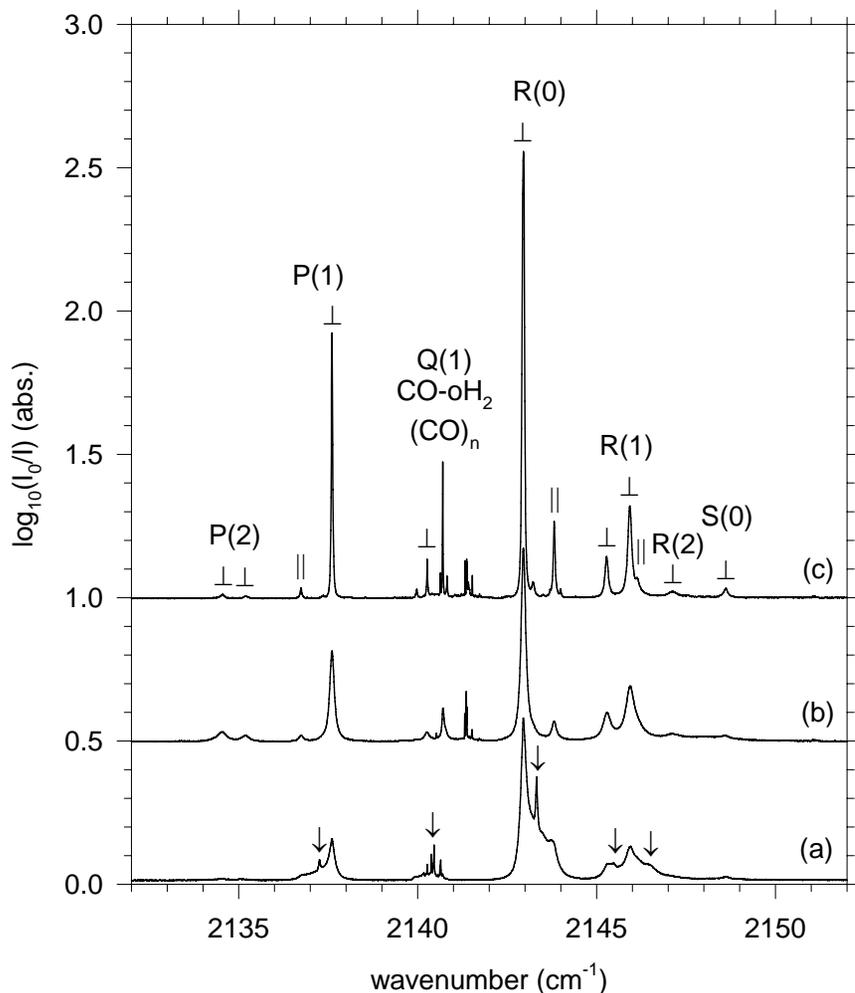
- \* High-symmetry trapping sites in weakly interacting host solid;  
⇒ 1st solid matrix host in which non-hydride dopants ( $\text{CO}$ ,  $\text{N}_2$ ,  $\text{NO}\dots$ ) are observed to rotate!

- \* Small post-annealing residual inhomogeneities;  
⇒ often observe sharp IR absorption lines ( $\sim 0.01 \text{ cm}^{-1}$ ); widths limited by rotational dephasing/relaxation.

M.E. Fajardo and S. Tam, *J. Chem. Phys.* **108**, 4237 (1998).  
S. Tam and M.E. Fajardo, *Rev. Sci. Instrum.* **70**, 1926 (1999).



# $^{12}\text{C}^{16}\text{O}/\text{pH}_2$ IR absorptions



13 ppm  $^{12}\text{C}^{16}\text{O}/\text{pH}_2$ ,  $d=2.9$  mm.

Assignments from Crystal Field Theory analysis (T. Momose) with adjustable  $\omega_e$ ,  $B_e$ ,  $D_e$ ,  $\alpha_e$ ,  $\epsilon_2$ ,  $\epsilon_3$ .

" $\perp$ ", " $\parallel$ "  $\Rightarrow$  polarization vs. hcp c-axis  
" $\downarrow$ "  $\Rightarrow$  CO in metastable fcc sites

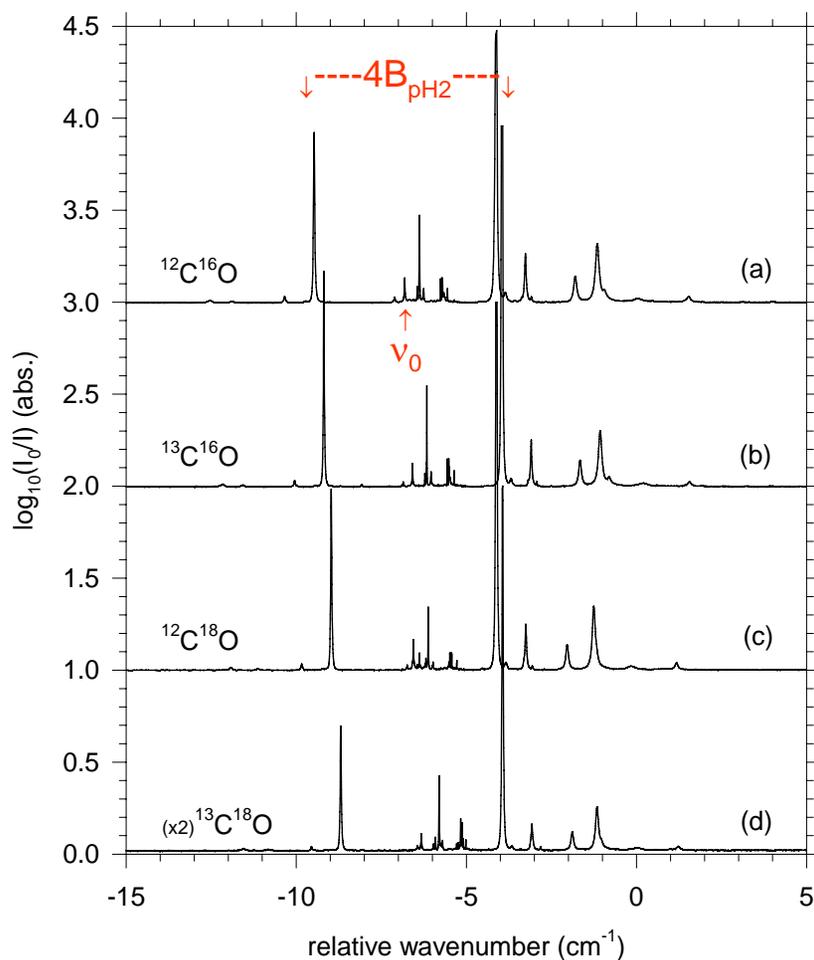
(c)  $T=2.4\text{K}$ , annealed.

(b)  $T=4.8\text{K}$ .

(a)  $T=2.4\text{K}$ , as deposited.



# CO isotopomers in $pH_2$



Annealed samples at  $T = 2.4$  K.

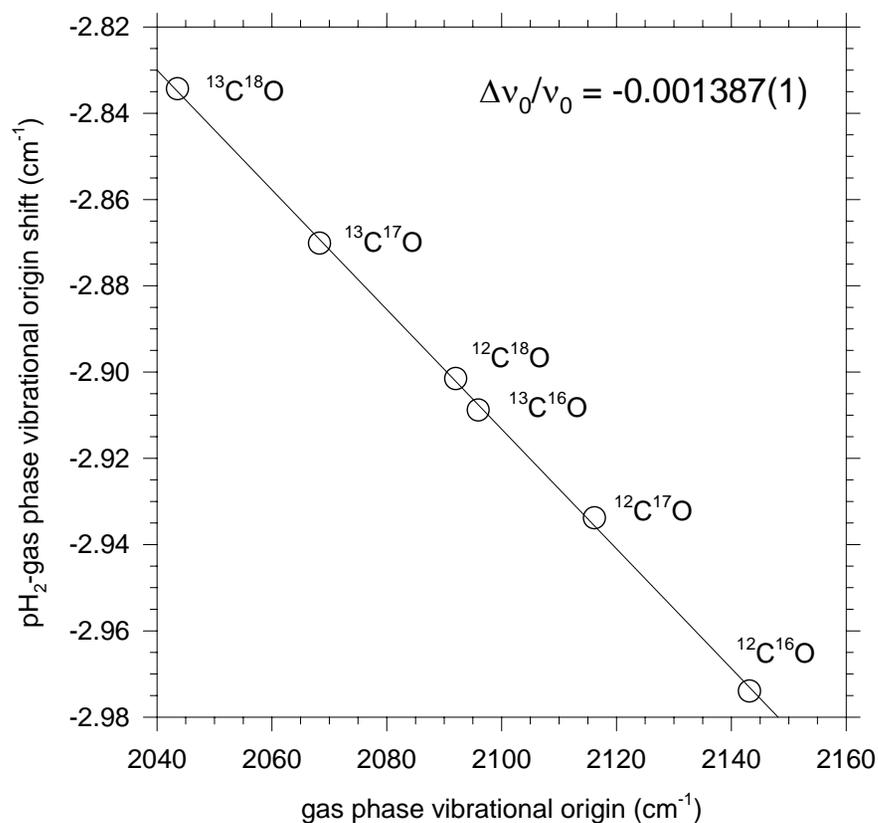
Spectra shifted by subtracting gas-phase R(0) line.

isotopomer	$B_{pH_2}$ (cm <sup>-1</sup> )	$B_{gas}$ (cm <sup>-1</sup> )	$B_{pH_2}/B_{gas}$
$^{12}\text{C}^{16}\text{O}$	1.577	1.9313	0.8165
$^{13}\text{C}^{16}\text{O}$	1.538	1.8462	0.8331
$^{12}\text{C}^{18}\text{O}$	1.469	1.8391	0.7988
$^{13}\text{C}^{18}\text{O}$	1.437	1.7540	0.8193

Matrix effect on rotational constant  $B$  depends on CO isotopic composition.



# CO/pH<sub>2</sub> vibrational origin shift

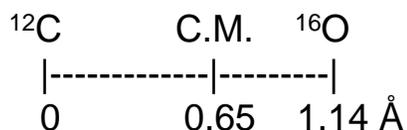
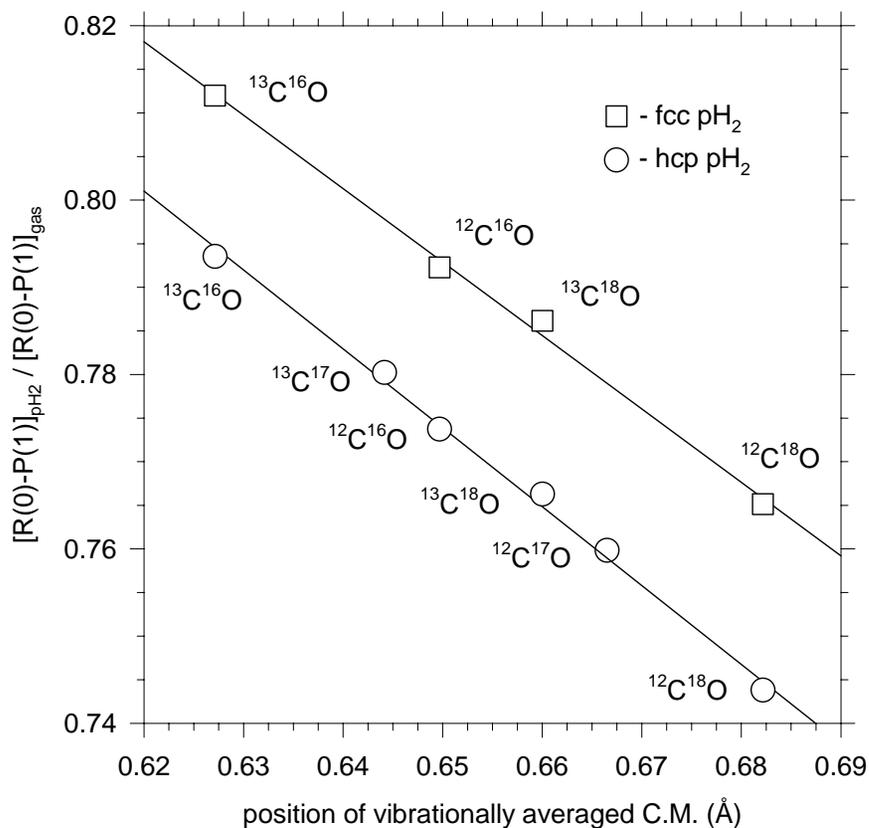


isotopomer	$v_0(\text{pH}_2)$ (cm <sup>-1</sup> )	$v_0(\text{gas})$ (cm <sup>-1</sup> )	$\Delta v_0/v_0$
<sup>12</sup> C <sup>16</sup> O	2140.280	2143.254	-0.001388
<sup>12</sup> C <sup>17</sup> O	2113.345	2116.279	-0.001386
<sup>13</sup> C <sup>16</sup> O	2093.142	2096.051	-0.001388
<sup>12</sup> C <sup>18</sup> O	2089.204	2092.106	-0.001387
<sup>13</sup> C <sup>17</sup> O	2065.567	2068.437	-0.001388
<sup>13</sup> C <sup>18</sup> O	2040.843	2043.677	-0.001387

Normalized matrix shift:  
 $\Delta v_0/v_0 = -0.001387(1)$   
does not depend on CO  
isotopic composition.



# $B_{\text{eff}}(\text{pH}_2) / B_{\text{avg}}(\text{gas})$ vs. C.M.



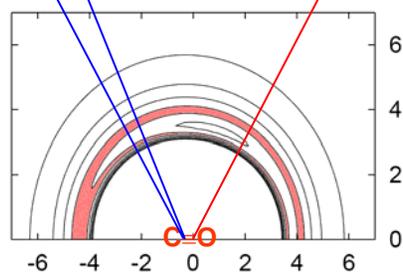
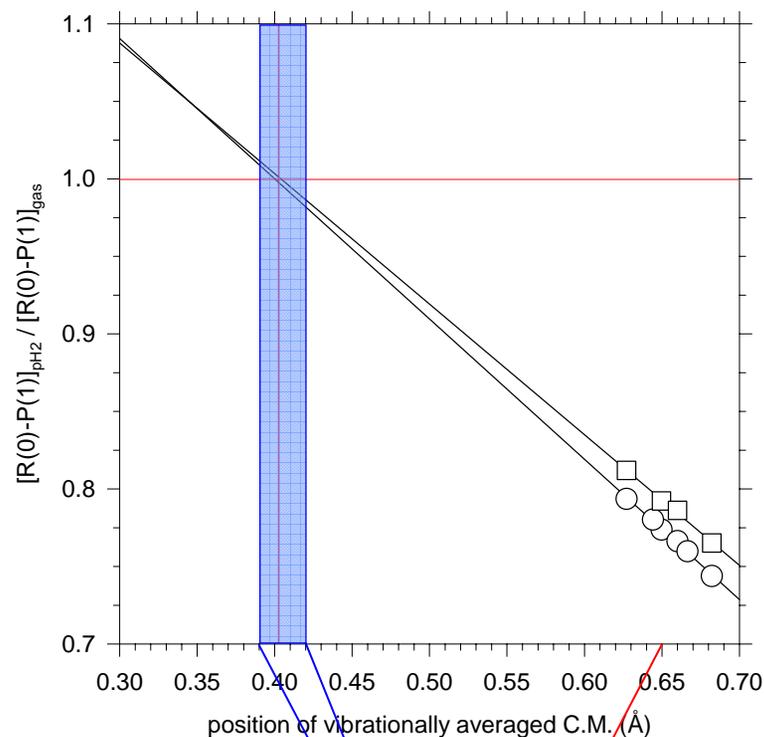
gas phase isotopomer	$B_{\text{avg}}$ ( $\text{cm}^{-1}$ )	$R_{\text{avg}}$ (Å)	C - C.M.  (Å)
$^{12}\text{C}^{16}\text{O}$	1.9313	1.1371	0.6497
$^{13}\text{C}^{16}\text{O}$	1.8462	1.1370	0.6271
$^{12}\text{C}^{18}\text{O}$	1.8391	1.1370	0.6822
$^{13}\text{C}^{18}\text{O}$	1.7540	1.1368	0.6600

Excellent linear correlation between matrix effect and location of C.M. (plotted relative to C atom);  
 $r^2 = 0.9963$  for fcc,  $0.9959$  for hcp.

But, Rotation-Translation Coupling and Pseudorotating Cage models predict curvature in  $B_{\text{eff}}/B$  vs. C.M.!



# Center of Interaction for CO/pH<sub>2</sub>



\* Extrapolation of linear correlations back to  $B_{\text{eff}}/B_{\text{avg}} = 1$  (*i.e.* vanishing matrix effect on rotations) yields "experimentally determined" C.I. located 0.402 Å from C atom, or 0.248 Å from C.M. of <sup>12</sup>C<sup>16</sup>O.

\* Excellent (fortuitous?) agreement with 0.24-0.27 Å C.I. - C.M separation calculated by energy minimization in linear pH<sub>2</sub>-CO-pH<sub>2</sub> construct for  $R_{\text{nn}} = 3.8\text{-}4.1$  Å.

\* Caveat! For N<sub>2</sub>/pH<sub>2</sub>: C.I.  $\equiv$  C.M. and  $B_{\text{eff}}/B_{\text{avg}} = 0.90(\pm 0.02)$ , not unity.

S. Moroni, M. Botti, S. DePalo, and A.R.W. McKellar, *J. Chem. Phys.* **122**, 094314 (2005).

P. Jankowski and K. Szalwicz, *J. Chem. Phys.* **108**, 3554 (1998).

P. Jankowski, potH2CO\_V04.f, private communication (2004).



# Relevance to rotations in IHe?

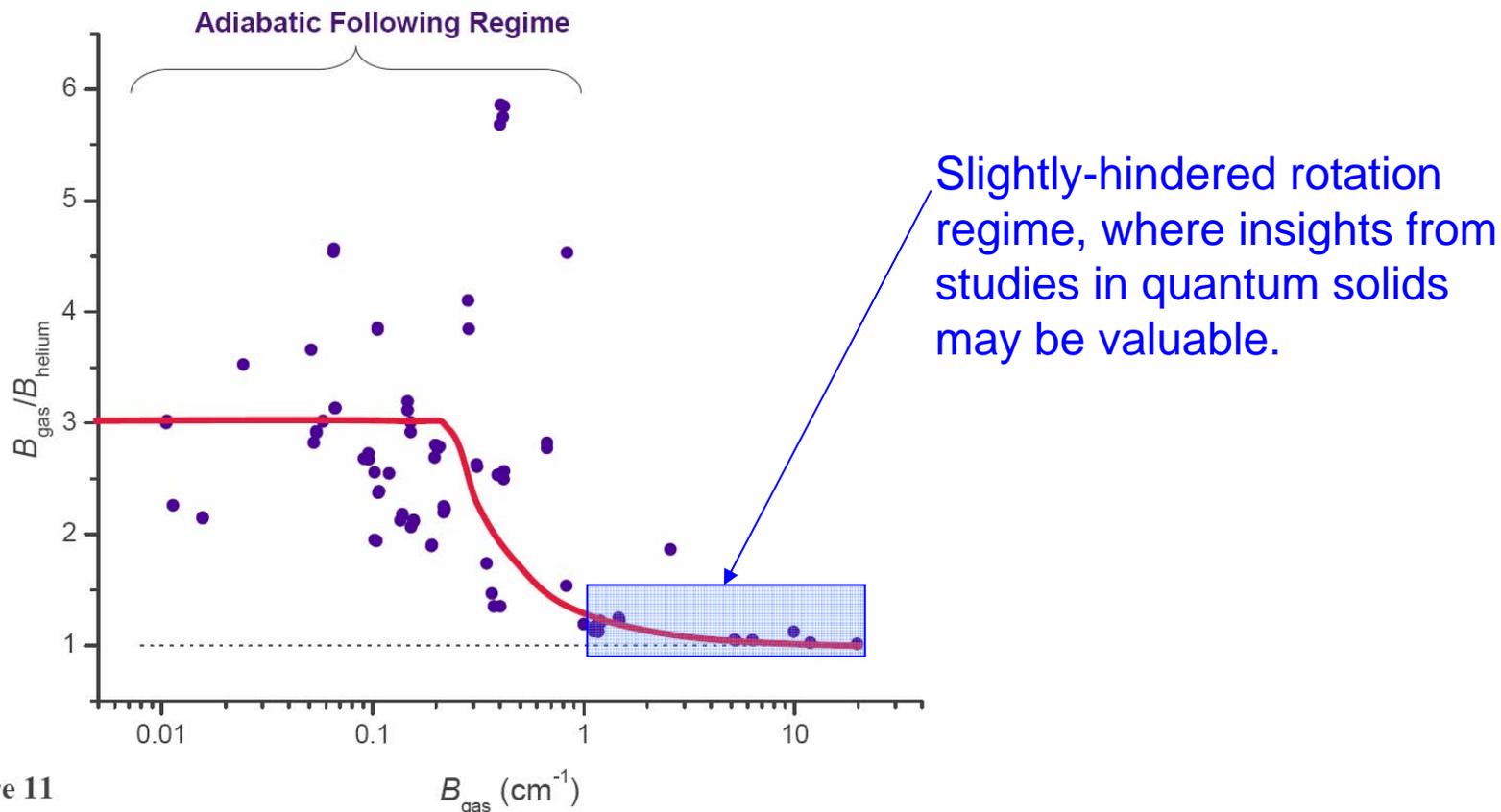


Figure 11

M. Y. Choi, G. E. Douberly, T. M. Falconer, W. K. Lewis, C. M. Lindsay, J. M. Merritt, P. L. Stiles, and R. E. Miller, *International Reviews in Physical Chemistry* **25**, 15 (2006).



# CO / IHe alternative analysis

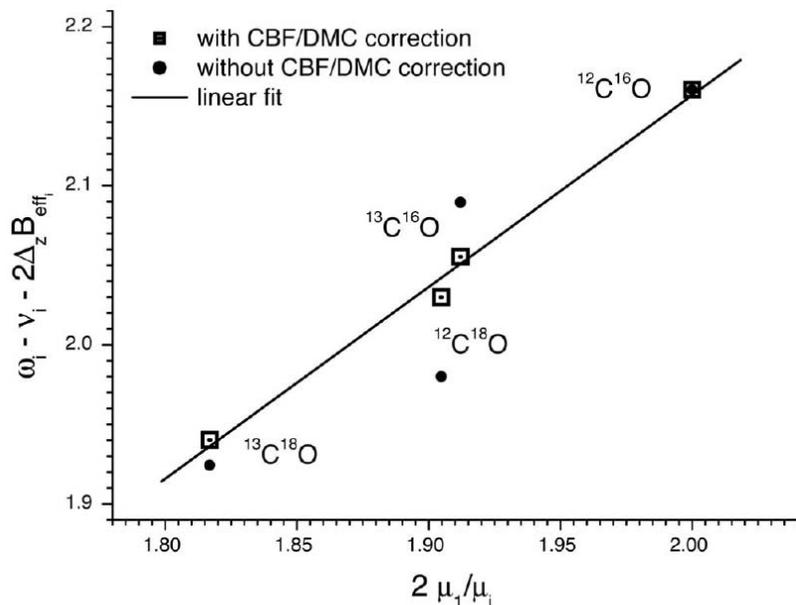
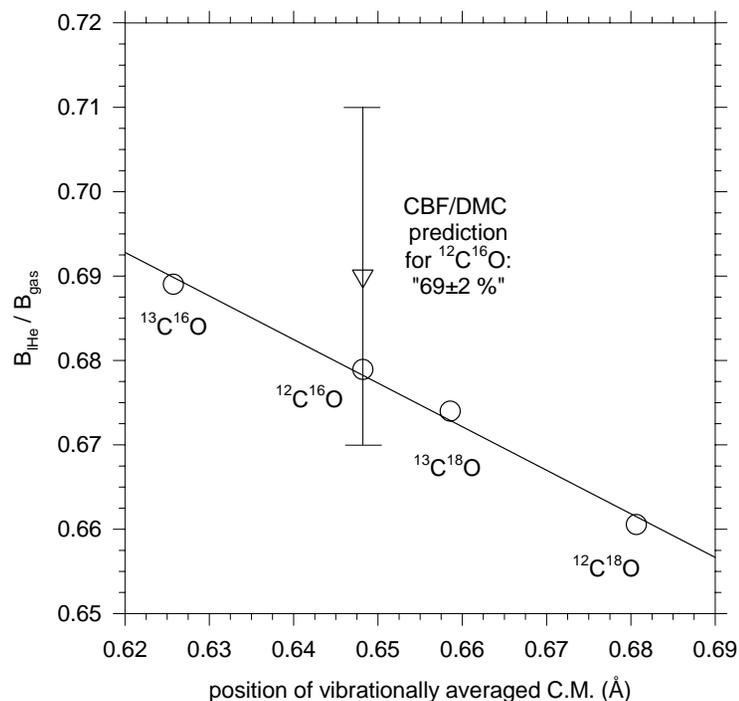


FIG. 7. Rotational energies of CO isotopomers plotted versus the ratios of the reduced masses (squares).  $\mu_i$  is the reduced mass of the isotopomer  $i$ , with  $i=1$  denoting the reference  $^{12}\text{C}^{16}\text{O}$  species.

Assumes:  $B_{\text{IHe}}/B_{\text{gas}} = \text{constant} = 0.63$   
 $\Rightarrow \Delta\nu_0 = -0.214 \text{ to } -0.317 \text{ cm}^{-1}$

K. von Haeften, S. Rudolph, I. Simanovski,  
 M. Havenith, R.E. Zillich, and K.B. Whaley,  
 Phys. Rev. B **73**, 054502 (2006).

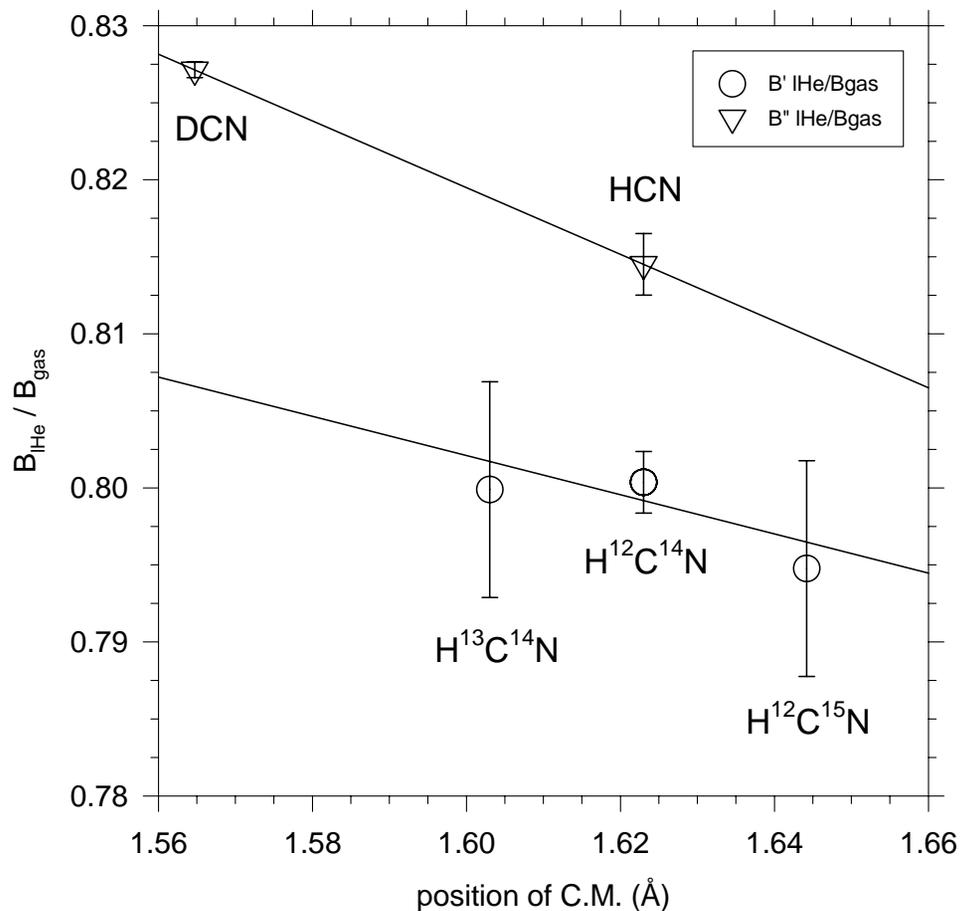


Assumes  $\Delta\nu_0/\nu_0 = -0.0002$   
 $(\Delta\nu_0 = -0.429 \text{ cm}^{-1} \text{ for } ^{12}\text{C}^{16}\text{O})$

Chosen to give best straight line  
 correlation  $B_{\text{IHe}}/B_{\text{gas}}$  vs. C.M.

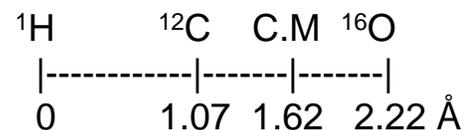


# General applicability ?



Analysis of HCN / IHe rotational and ro-vibrational spectra via our approach is inconclusive.

Need more/better experimental data to test for linear correlation between  $B_{IHe} / B_{gas}$  and position of C.M.

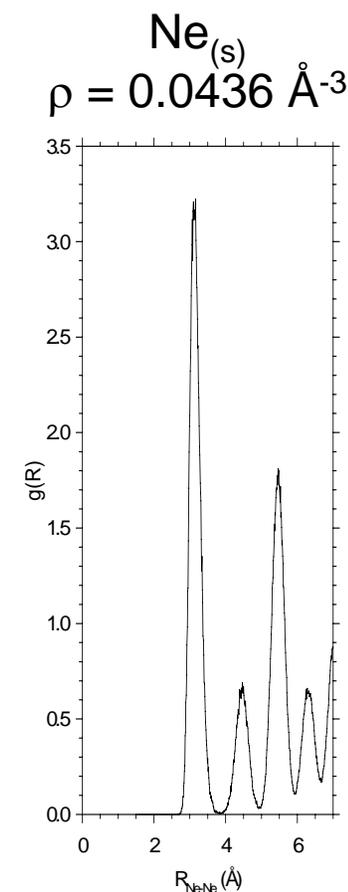
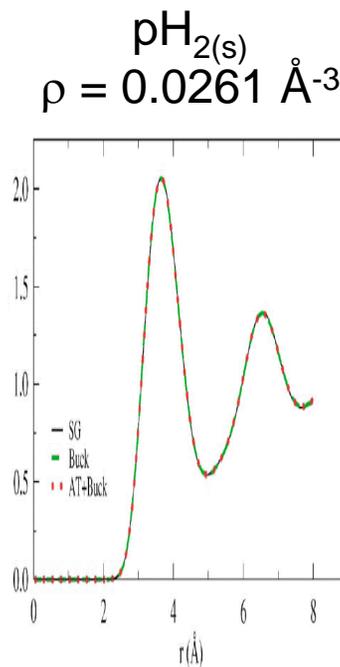
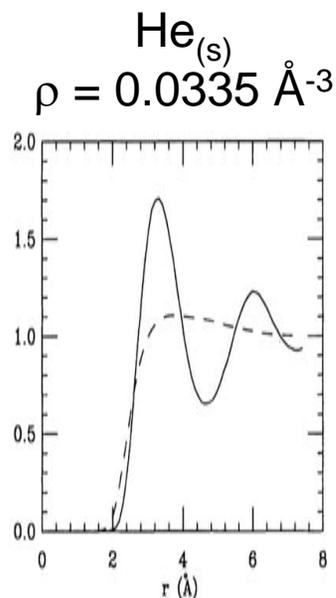
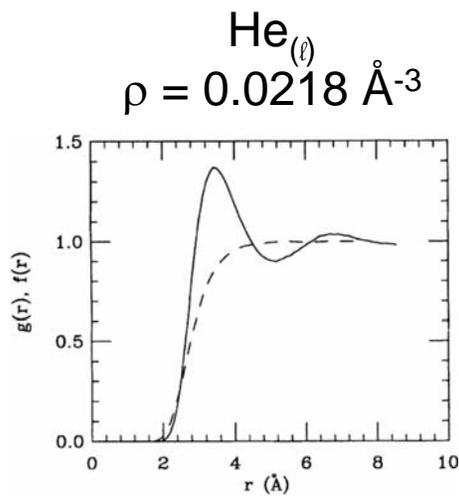


K. Nauta, Ph.D. Dissertation, U. North Carolina, Chapel Hill (2000).

A. Conjusteau, C. Callegari, I. Reinhard, K.K. Lehmann, and G. Scoles, J. Chem. Phys. **113**, 4840 (2000).



# Quantum Solids vs. Liquids



Radial pair distribution functions in quantum solids appear quite "liquid-like" due to large amplitude ZPM.

He: S.A. Vitiello and K.E. Schmidt, Phys. Rev. B **46**, 5442 (1992).

H<sub>2</sub>: F. Operetto and F. Pederiva, Phys. Rev. B **73**, 184124 (2006).

Ne: M.E. Fajardo, J. Chem. Phys. **88**, 119 (1993).



# Summary



- \* High resolution IR absorption spectra of diatomic dopants in solid  $p\text{H}_2$  provide rigorous tests of theories describing molecular rotations in solids.
- \* Leading candidate theories cannot explain strong linear correlation of  $B_{\text{eff}}/B$  vs.  $|\text{C.M.} - \text{C.I.}|$ .
- \* Physical significance and general applicability of these correlations still under investigation.
- \* Are the similarities between  $\text{CO}/p\text{H}_2$  and  $\text{CO}/\text{He}$  just due to large amplitude ZPM of nearest neighbors?