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# FINAL PERFORMANCE REPORT

Infrared activity of atom-doped solid hydrogen

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## 1. Project objectives and summary of accomplishments

Specific impulse ( $I_{sp}$ ) is a standard performance metric for rocket propulsion systems, a metric that measures the momentum transferred to the rocket per unit weight of propellant consumed. For the current state-of-the-art liquid oxygen-liquid hydrogen propellant system,  $I_{sp} = 389$  s [Sut86]. However, if the hydrogen propellant contains Al atoms at a mole fraction of 5%, the theoretical  $I_{sp}$  of this propellant system increases by 9% to 425 s; if the hydrogen propellant contains 5% B atoms, the theoretical  $I_{sp}$  jumps to 470 s, for an improvement of 21% [Car93]. These potentially dramatic increases in performance sparked considerable interest, within both the Air Force Research Laboratory and the Air Force's contractor community, in the development of techniques for synthesizing gram-scale quantities of atom-doped solid  $H_2$  with dopant mole fractions near 5%.

To guide and evaluate these synthetic techniques, it is imperative that researchers have a method for measuring accurately the concentration of atomic dopants in solid  $H_2$  matrices with thicknesses on the order of one to several millimeters. For atomic dopants with allowed electronic transitions in the visible and ultraviolet spectral regions, such as Al and B atoms, electronic spectroscopy can quickly disclose the presence or absence of a dopant. However, these allowed electronic transitions become optically thick in millimeter-thick  $H_2$  solids with atomic dopant concentrations above roughly 0.5% [Faj93]; consequently, electronic spectroscopy cannot provide quantitative concentration information in the concentration range of interest.

Atom-doped solid  $H_2$  matrices also absorb weakly in the infrared (IR) spectral region [Faj98]. These dopant-induced IR absorption features arise from nominally IR inactive  $Q_1(0)$  pure vibrational transitions of individual  $H_2$  molecules in the matrix, transitions that become IR active in the presence of dopants [Hin03]. Because these dopant-induced

features are inherently weak [Faj98], 1-mm thick samples of doped solid  $H_2$  will remain optically thin (with transmittance values of 0.1 or higher) even at dopant concentrations approaching 5%. This makes these features attractive prospects for measuring dopant concentrations in thick  $H_2$  solids.

The objective of the research documented in this final performance report was the development of methods for computing, from first principles, the integrated intensity of these dopant-induced  $Q_1(0)$  vibrational transitions in solid  $H_2$  matrices containing atomic substitutional impurities. Progress toward this goal was made on several fronts for the case in which the impurity is an S-state atom such as an alkali metal atom or a rare gas atom: (1) The mechanism by which S-state atomic impurities generate IR activity in the vibrational coordinate of nearby  $H_2$  molecules was elucidated. (2) A theoretical framework was established for computing the line shapes and integrated intensities of dopant-induced  $Q_1(0)$  features in solid  $H_2$  matrices. (3) Path integral Monte Carlo simulations of rare-gas-doped solid  $H_2$  were performed. Based on these simulations, testable quantitative predictions were made for the dopant-induced  $Q_1(0)$  line shapes in solid  $H_2$  matrices containing Ar, Kr, or Xe atoms. (4) Ab initio calculations for Ar- $H_2$  dimers were performed to provide input for future calculations of the intensity of Ar-induced  $Q_1(0)$  features in Ar-doped solid  $H_2$ .

## 2. Atom-induced infrared absorption features in solid hydrogen

The central accomplishment during the performance period covered by this final report is the development of a theoretical framework for understanding and interpreting the pure vibrational  $H_2$   $Q_1(0)$  features induced by S-state atomic substitutional impurities in the infrared (IR) absorption spectra of solid hydrogen matrices. This theoretical framework includes: (1) an explanation of the mechanism by which atomic impurities generate  $Q_1(0)$  IR activity in neighboring  $H_2$  molecules, and (2) a method for relating the line shape of the dopant-induced  $Q_1(0)$  feature to the vibrational dependence of the dopant- $H_2$  potential energy surface.

Before describing this theoretical framework, we first review some of the relevant properties of pure solid  $H_2$  [Sil80, Van83]. In solid  $H_2$ , the rotational and vibrational motions of individual  $H_2$  molecules are essentially unperturbed by the interactions between adjacent molecules; hence the rotational and vibrational quantum numbers  $j$  and  $v$  of each molecule remain good quantum numbers in solid  $H_2$  [Sil80, Van83]. The theoretical framework summarized in this final performance report assumes that these quantum numbers also remain good in solid  $H_2$  matrices that have been doped with atomic substitutional

impurities. This will be the case if the dopant- $\text{H}_2$  interaction is only weakly anisotropic and only weakly dependent on the  $\text{H}_2$  vibrational quantum number.

The ground state of the solid hydrogen crystal is solid parahydrogen ( $\text{pH}_2$ ), a hexagonal close packed lattice [Van62] with nearest-neighbor spacing of 3.79 Å [Sil80] in which each  $\text{H}_2$  molecule has the rotational quantum number  $j = 0$ . The rotational degrees of freedom of these  $j = 0$   $\text{H}_2$  molecules are described by the isotropic spherical harmonic  $Y_{00}(\theta, \phi)$ ; the  $\text{pH}_2$  crystal is thus composed of spherically symmetric objects with multipole moments that are identically zero, and is held together by dispersion forces. The  $\text{H}_2$  molecules in the  $\text{pH}_2$  crystal can therefore be treated as point particles, each with an embedded vibrational degree of freedom. The translational zero point motion of individual molecules in the solid  $\text{H}_2$  matrix is rather large, so that the width of the first peak in the radial distribution function for solid  $\text{H}_2$  is approximately 18% of the nearest-neighbor distance, even in the  $T = 0$  K limit [Sil80].

#### A. The induction mechanism

Consider the  $Q_1(0)$  vibrational excitation  $(v, j) = (1, 0) \leftarrow (0, 0)$  of a single  $\text{H}_2$  molecule in solid  $\text{pH}_2$ . Upon excitation, this molecule induces pairwise transition dipole moments with each of its neighbors, as indicated schematically in Fig. 1(a); these transition moments arise from short-range overlap interactions between  $\text{pH}_2$  molecules [McK74, McK89, Mey89]. The high symmetry of the  $\text{pH}_2$  crystal causes these pairwise transition moment vectors to sum to zero, as is clear from Fig. 1(a). The  $Q_1(0)$  transition is therefore IR inactive in the pure solid.

However, if one of the  $\text{pH}_2$  molecules in the solid is replaced with an atomic substitutional impurity, the lattice symmetry is broken in the vicinity of the dopant. This symmetry breaking may arise both from physical restructuring of the  $\text{pH}_2$  crystal lattice in the vicinity of the impurity (structural symmetry breaking) and from the fact that the dopant- $\text{pH}_2$  interactions generate a  $Q_1(0)$  transition moment that differs from the one associated with  $\text{pH}_2$ - $\text{pH}_2$  pairs (electrical symmetry breaking). In either case, the net transition moment for  $Q_1(0)$  excitations localized on molecules neighboring the impurity is nonzero, as shown in Fig. 1(b), and the vibrational coordinates of these molecules are therefore IR active. Atomic impurities thus induce IR absorption activity in  $\text{pH}_2$  molecules in the host matrix as a direct consequence of the intermolecular interactions between the impurities and the  $\text{pH}_2$  molecules.

Because the overlap interactions that give rise to the  $Q_1(0)$  transition moment are short-ranged, the  $\text{pH}_2$  molecules that are in direct contact with the atomic impurity are the only ones that contribute directly to the intensity of the  $Q_1(0)$  transition. This observation plays a key role in our analysis of the dopant-induced  $Q_1(0)$  feature below.

### B. The vibrational Hamiltonian of atom-doped solid parahydrogen

Here we consider dopant-induced  $Q_1(0)$  absorption features in a crystal that contains  $N$   $\text{pH}_2$  molecules and an S-state atomic impurity. The position vector  $\mathbf{R}_0$  denotes the impurity's position and the vectors  $\{\mathbf{R}_n : n = 1, 2, 3, \dots, N\}$  denote the centers of mass of the  $\text{H}_2$  molecules in the crystal.

Because the vibrational motion of the  $\text{pH}_2$  molecules occurs on a much faster time scale than any of the system's other motions, we make the simplifying assumption that the  $\text{H}_2$  vibrations can be adiabatically separated from the other coordinates; we will use  $v_k$  to denote the vibrational quantum number of the  $\text{H}_2$  molecule at  $\mathbf{R}_k$ . The crystal is therefore described completely by the position vectors  $\{\mathbf{R}_0, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N\}$  and the list of vibrational quantum numbers  $\{v_1, v_2, \dots, v_N\}$ .

If the  $\text{H}_2$ - $\text{H}_2$  and dopant- $\text{H}_2$  potentials do not depend on the  $\text{H}_2$  vibrational coordinates, then the translational degrees of freedom  $\{\mathbf{R}_0, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N\}$  decouple from the  $\text{H}_2$  vibrational coordinates. In this limiting case, the wavefunction of the doped  $\text{pH}_2$  solid can be written as the product of a translational wavefunction  $\Psi(\mathbf{Q})$ , where  $\mathbf{Q} = \{\mathbf{R}_0, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N\}$ , and a wavefunction  $\Phi$  that describes the vibrational degrees of freedom of the  $N$   $\text{H}_2$  molecules. When the  $\text{H}_2$ - $\text{H}_2$  and dopant- $\text{H}_2$  potentials depend only weakly on the  $\text{H}_2$  vibrational coordinates, this separation of translational and vibrational degrees of freedom remains a good approximation to the doped solid's true wavefunction. Henceforth, this approximation is assumed to be valid, and the translational wavefunction  $\Psi(\mathbf{Q})$  is assumed to be independent of the list of vibrational quantum numbers  $\{v_1, v_2, \dots, v_N\}$ .

The initial state  $|i\rangle$  of the doped  $\text{pH}_2$  crystal, before the IR absorption event occurs, is one in which each  $\text{H}_2$  molecule in the system is in its vibrational ground state. After IR excitation, the crystal is in a final state  $|f\rangle$  whose vibrational wavefunction  $\Phi$  can be described within an excitonic formalism [Fre31] as a linear combination of localized excitations residing on individual  $\text{H}_2$  molecules. These localized excitations are denoted  $|n, v\rangle$ , which represents a localized state in which the vibrational quantum number of  $\text{pH}_2$  molecule  $n$  is  $v_n = v$ , while the vibrational quantum number of all other  $\text{pH}_2$  molecules is zero.

For the dopant-induced  $Q_1(0)$  excitation, the crystal's final vibrational wavefunction  $\Phi$  can be written as a linear combination of the  $v = 1$  manifold of localized excitations. Hence the final state  $|f\rangle$  is

$$|f\rangle = \Psi(\mathbf{Q}) \times \sum_n C_n |n, v = 1\rangle. \quad (1)$$

The coefficients  $\{C_n\}$  that define the crystal's final state following IR excitation can be obtained by diagonalizing the excitonic Hamiltonian matrix  $\mathbf{H}$  describing the vibrational degrees of freedom of the collection of  $N$   $\text{pH}_2$  molecules.

The Hamiltonian operator  $\hat{H}$  of the doped  $\text{pH}_2$  crystal depends on the translational variables  $\mathbf{Q}$  and the  $\text{H}_2$  vibrational quantum numbers  $\{v_1, v_2, \dots, v_N\}$  through the vibrationally averaged potential energy surface  $V(\mathbf{Q}; v_1, v_2, \dots, v_N)$  for the solid. The matrix elements of this operator in the basis of localized vibrational excitations can be written

$$H_{n',n} = \left\langle n', v = 1 \left| \left[ \int \hat{H}(\mathbf{Q}; v_1, v_2, \dots, v_N) |\Psi(\mathbf{Q})|^2 d\mathbf{Q} \right] \right| n, v = 1 \right\rangle \quad (2)$$

and are seen to contain integrals over the probability density function  $|\Psi(\mathbf{Q})|^2$  for the translational zero point motion of the doped solid.

The diagonal Hamiltonian matrix element  $H_{n,n}$  is simply the energy of the localized excited state  $|n, v = 1\rangle$  in which the  $\text{H}_2$  vibrational excitation resides on molecule  $n$ . The off-diagonal elements  $H_{n',n}$  are averages over  $|\Psi(\mathbf{Q})|^2$  of the terms in the potential energy surface  $V(\mathbf{Q}; v_1, v_2, \dots, v_N)$  which couple the vibrational coordinates of  $\text{pH}_2$  molecules  $n$  and  $n'$ .

The eigenvectors of  $\mathbf{H}$  describe the final states accessed in the IR absorption event, as indicated in Eq. (1). The coefficients  $\{C_n\}$  that describe a particular final state  $|f\rangle$  are the elements of a column eigenvector of  $\mathbf{H}$ . The absorption intensity for this final state is proportional to the square of the corresponding transition dipole moment integral, which for dopant-induced  $\text{Q}_1(0)$  excitations is

$$\langle i | \mathbf{M} | f \rangle = \sum_n C_n \int \mathbf{M}_n(\mathbf{Q}) |\Psi(\mathbf{Q})|^2 d\mathbf{Q}. \quad (3)$$

In Eq. (3),  $\mathbf{M}_n(\mathbf{Q})$  is the  $\text{Q}_1(0)$  transition moment associated with excitation from the initial state  $|i\rangle$  to the localized final state  $|n, v = 1\rangle$ . This transition moment depends, through  $\mathbf{Q}$ , on the structure of the doped  $\text{pH}_2$  crystal in the neighborhood of the dopant. Finally, the dopant-induced  $\text{Q}_1(0)$  IR absorption line shape for a doped  $\text{pH}_2$  solid can be obtained by weighting each final state  $|f\rangle$  by its absorption intensity  $\langle i | \mathbf{M} | f \rangle^2$ .

The integrals in Eqs. (2) and (3) can be evaluated using quantum many-body techniques such as diffusion quantum Monte Carlo (DQMC) and path integral Monte Carlo (PIMC) simulations [And75, And99, Cep96, Cha81, Suh91]. These techniques provide computationally efficient methods for treating the large-amplitude correlated motion of neighboring molecules in the doped  $\text{pH}_2$  solid. An accurate treatment of this large-amplitude motion is important for a number of reasons. First, the transition dipole moments  $\mathbf{M}$  in Eq. (3) are dominated by overlap interactions between the dopant and its  $\text{pH}_2$

neighbors. These transition moments depend strongly on the dopant-pH<sub>2</sub> distance [Mey89] and become substantially more important when they are averaged over the underlying zero point motion [Hin00]. Second, as Fig. 1 indicates, the transition dipole that controls the intensity of the dopant-induced IR absorption features is a *vector* quantity that depends simultaneously on the positions of the pH<sub>2</sub> molecule undergoing excitation, its impurity neighbor, and its eleven pH<sub>2</sub> neighbors. A faithful accounting of the correlated motions of these thirteen molecules is thus critical for computation of the transition moment.

### C. A tight-binding model for the vibrational Hamiltonian

A simplified model for the vibrational Hamiltonian matrix  $\mathbf{H}$  of doped pH<sub>2</sub> solids can be developed by extending the tight-binding vibron Hamiltonian introduced to explain the IR and Raman line shapes of pH<sub>2</sub> solids containing  $j = 1$  H<sub>2</sub> molecules as dopants [Fel95, Sea64, Van59]. In this tight-binding vibron Hamiltonian, the vibrational coordinates of nearest-neighbor (nn) pH<sub>2</sub> molecules are assumed to be coupled through the H<sub>2</sub>-H<sub>2</sub> intermolecular potential; pH<sub>2</sub> molecules which are not nearest neighbors are assumed to remain decoupled. Under the assumption of only nearest-neighbor coupling, the tight-binding vibron Hamiltonian operator can be written as [Fel95]

$$\hat{H} = \sum_k E_k |k, v = 1\rangle \langle k, v = 1| + \lambda \sum_{k,n=\text{nn}} |k, v = 1\rangle \langle n, v = 1| \quad (4)$$

where  $|n, v = 1\rangle$  again represents the state of the crystal in which the vibrational excitation is localized on pH<sub>2</sub> molecule  $n$ . In this equation,  $E_k$  is the  $Q_1(0)$  transition energy for the localized vibrational excitation associated with pH<sub>2</sub> molecule  $k$ ; this transition energy can be obtained from Eq. (2) by setting  $n' = n = k$ . Intermolecular interactions in the solid reduce  $E_k$  from its gas phase value of  $E_k = 4161.1 \text{ cm}^{-1}$  to  $E_k = 4152.2 \text{ cm}^{-1}$  [Van68]. The parameter  $\lambda$  in Eq. (4) represents the vibrational coupling between nearest-neighbor molecules. Analysis of the IR absorption spectrum of pairs of  $j = 1$  H<sub>2</sub> molecules isolated in solid pH<sub>2</sub> [Zha98] indicates that the hopping parameter  $\lambda = -0.225 \text{ cm}^{-1}$  for a nearest-neighbor pair of H<sub>2</sub> molecules.

In a doped pH<sub>2</sub> crystal, the  $Q_1(0)$  transition energy  $E_k$  for pH<sub>2</sub> molecules next to an impurity will differ slightly from that for pH<sub>2</sub> molecules distant from the impurity because of differences between the H<sub>2</sub> vibrational dependence of the H<sub>2</sub>-H<sub>2</sub> and dopant-H<sub>2</sub> potentials. We account for this by introducing a parameter  $\Delta E$  that quantifies the shift in the  $Q_1(0)$  transition energy for pH<sub>2</sub> molecules adjacent to the dopant. For these molecules,  $E_k = 4152.2 \text{ cm}^{-1} - \Delta E$ ; for all other pH<sub>2</sub> molecules,  $E_k$  remains at  $4152.2 \text{ cm}^{-1}$ . This leads to a one-parameter family of vibron Hamiltonians defined by the parameter  $\Delta E$ .

The matrix elements expressed in Eq. (2) are then equivalent to matrix elements of Eq. (4) evaluated in a basis set consisting of the localized vibrational excitations  $|n, v = 1\rangle$ . Diagonalizing this matrix and then weighting the eigenvalues by their respective absorption intensities ultimately yields the dopant-induced  $Q_1(0)$  line shape as described in section B above.

Figure 2 shows the normalized line shapes for several values of  $\Delta E$ , ranging from  $0.25 \text{ cm}^{-1}$  to  $2 \text{ cm}^{-1}$ ; the calculations leading to the results shown in Fig. 2 are described in detail in [Hin03]. At low values of the detuning parameter  $\Delta E$ , the dopant-induced  $Q_1(0)$  absorption feature shows substantial IR intensity over the entire  $\text{pH}_2$  vibron band ranging from  $\tilde{\nu} = 4149.5 \text{ cm}^{-1}$  to  $\tilde{\nu} = 4153.1 \text{ cm}^{-1}$ . As  $\Delta E$  increases, the dopant-induced absorption feature shifts to the red and sharpens; for  $\Delta E = 2 \text{ cm}^{-1}$  the feature's full width at half maximum is only  $0.02 \text{ cm}^{-1}$ . This evolution in the shape of the dopant-induced feature as the detuning parameter increases reflects a transition from a delocalized IR-active vibron at small  $\Delta E$  to a strongly localized IR-active vibron at large  $\Delta E$ . When  $\Delta E$  is small, the IR-active  $\text{pH}_2$  molecules adjacent to the dopant can readily share their excitation with neighboring  $\text{pH}_2$  molecules; consequently, the vibrons that contribute to the IR absorption spectrum can be quite spatially delocalized. As  $\Delta E$  increases, however, it becomes more and more difficult for a vibrational excitation localized in the dopant's first "solvation shell" to hop away from the dopant, and the vibrational coordinates of  $\text{pH}_2$  molecules in this solvation shell, which are the only IR-active molecules in the solid, become effectively decoupled from the rest of the system.

### 3. Detuning parameters for rare-gas-doped solid hydrogen

If the detuning parameter  $\Delta E$  for a particular atomic dopant is known, the vibron Hamiltonian defined by Eq. (4) allows us to predict the line shape of the dopant-induced  $Q_1(0)$  absorption feature in  $\text{pH}_2$  solids containing this atomic dopant. We have used PIMC simulations to estimate the  $\Delta E$  values for Ar, Kr, and Xe dopants in order to provide line shape predictions for these dopants that can eventually be compared with experiment.

The  $\Delta E$  value for molecule  $k$  in a rare-gas-doped  $\text{pH}_2$  solid can be estimated as

$$\Delta E^{(k)} = \int \Delta V^{(k)}(\mathbf{Q}) |\Psi(\mathbf{Q})|^2 d\mathbf{Q} \quad (5)$$

where the quantity

$$\begin{aligned} \Delta V^{(k)}(\mathbf{Q}) = & V(\mathbf{Q}; v_1 = 0, v_2 = 0, \dots, v_{k-1} = 0, v_k = 0, v_{k+1} = 0, \dots, v_N = 0) \\ & - V(\mathbf{Q}; v_1 = 0, v_2 = 0, \dots, v_{k-1} = 0, v_k = 1, v_{k+1} = 0, \dots, v_N = 0) \end{aligned} \quad (6)$$



is the negative of the change in the potential energy of the doped pH<sub>2</sub> solid when molecule  $k$  makes a transition from its  $v = 0$  vibrational level to its  $v = 1$  vibrational level. (Recall that  $\Delta E$  is defined above to be a positive number if the  $Q_1(0)$  transition of a H<sub>2</sub> molecule red shifts under the influence of a neighboring dopant.) In principle this function can be decomposed into contributions from H<sub>2</sub>-H<sub>2</sub> and dopant-H<sub>2</sub> potentials; however, at the moment there are no accurate H<sub>2</sub>-H<sub>2</sub> potentials that explicitly incorporate vibrational dependence of the individual H<sub>2</sub> molecules. Consequently, we approximate  $\Delta V^{(k)}(\mathbf{Q})$  as follows. We first assume that the 8.9-cm<sup>-1</sup> red shift of the H<sub>2</sub>  $Q_1(0)$  transition in pure solid pH<sub>2</sub> can be partitioned among an individual molecule's 12 nearest neighbors in an additive fashion. If molecule  $k$  is in the first solvation shell of the rare gas dopant, it has 11 pH<sub>2</sub> neighbors and is therefore missing  $(1/12) \times 8.9 = 0.74$  cm<sup>-1</sup> of this red shift. Consequently we define

$$\Delta V^{(k)}(\mathbf{Q}) = V_{\text{dop-H}_2}(\mathbf{R}_0, \mathbf{R}_k; v = 0) - V_{\text{dop-H}_2}(\mathbf{R}_0, \mathbf{R}_k; v = 1) - 0.74 \text{ cm}^{-1} \quad (7)$$

where  $V_{\text{dop-H}_2}(\mathbf{R}_0, \mathbf{R}_k; v)$  is the rovibrationally averaged dopant-pH<sub>2</sub> potential for a pH<sub>2</sub> molecule in vibrational level  $v$ . Recall that the vectors  $\mathbf{R}_0$  and  $\mathbf{R}_k$  specify the locations of the dopant and pH<sub>2</sub> molecule  $k$ , respectively.

The integral in Eq. (5) is computed for doped pH<sub>2</sub> solids at  $T = 4$  K using discrete-time PIMC simulations [Cha81] that employ the primitive Trotter factorization of the Boltzmann factor  $\exp(-\hat{H}/kT)$ . We model the rare-gas-doped pH<sub>2</sub> solid as a collection of 179 pH<sub>2</sub> molecules and one dopant atom at a number density equal to that of pure solid pH<sub>2</sub> at  $T = 4$  K; the particles are initially placed on a hexagonal close packed lattice containing six layers of 30 particles each [Che96]. We use periodic boundary conditions to eliminate surface effects. The potential energy of the doped solid is taken to be a pairwise additive sum of H<sub>2</sub>-H<sub>2</sub> potentials [Sil78] and dopant-H<sub>2</sub> potentials [LeR87]. We assume that the pH<sub>2</sub> molecules obey Boltzmann statistics.

Figure 3 shows how the  $\Delta E$  value for pH<sub>2</sub> molecules surrounding an Ar dopant atom depends on the Trotter number  $N_T$ . We see that  $\Delta E$  converges to the value  $\Delta E = 0.20$  cm<sup>-1</sup> for Trotter numbers  $N_T \geq 48$ . For our production calculations, we use the Trotter number  $N_T = 64$ . Our final estimates of the  $\Delta E$  values for Ar-, Kr-, and Xe-doped pH<sub>2</sub> are:  $\Delta E = 0.20$  cm<sup>-1</sup> for Ar dopants,  $\Delta E = 0.85$  cm<sup>-1</sup> for Kr dopants, and  $\Delta E = 1.68$  cm<sup>-1</sup> for Xe dopants. The statistical uncertainties in these estimates are roughly  $\pm 0.02$  cm<sup>-1</sup>.

These detuning parameters, when interpreted in light of the results summarized in Fig. 2, indicate that Ar-doped solid pH<sub>2</sub> should exhibit a broad, symmetric, featureless dopant-induced  $Q_1(0)$  spectrum spanning the entire pH<sub>2</sub> vibron band; this is in good

agreement with experimental observations [Hin02]. Kr-doped solid  $\text{pH}_2$  should exhibit an asymmetrical dopant-induced  $Q_1(0)$  feature with peak intensity near  $\tilde{\nu} = 4150.5 \text{ cm}^{-1}$ , while Xe-doped solid  $\text{pH}_2$  should exhibit a fairly narrow dopant-induced  $Q_1(0)$  feature near  $\tilde{\nu} = 4149.75 \text{ cm}^{-1}$ , with a low-intensity tail to the blue.

From our PIMC simulations, we can extract probability distribution functions for the distance between the dopant atom and its nearest-neighbor  $\text{pH}_2$  molecules. These are shown in Figure 4. Each panel in Fig. 4 also includes, for reference purposes, the nearest-neighbor distance distribution for pure solid  $\text{pH}_2$  at  $T = 4 \text{ K}$ ; this is computed using PIMC methods as well.

#### 4. Ab initio calculations of the Ar- $\text{H}_2$ dipole moment

The integrated intensities of dopant-induced  $Q_1(0)$  IR absorption features in atom-doped solid  $\text{pH}_2$  are determined by the transition dipole moment integral defined in Eq. (3). This integral in turn depends on the  $Q_1(0)$  transition moment  $\mathbf{M}_n(\mathbf{Q})$  associated with excitation from the initial state  $|i\rangle$  to the localized final state  $|n, v = 1\rangle$ . If the dipole moment operator for the doped  $\text{pH}_2$  solid can be written as a pairwise sum of interaction-induced dipoles (see Fig. 1), then

$$\mathbf{M}_n(\mathbf{Q}) = \sum_k \mathbf{m}^{(k,n)}(\mathbf{R}_k, \mathbf{R}_n) \quad (8)$$

where  $\mathbf{m}^{(k,n)}$  is the dipole moment generated by interactions between particles  $k$  and  $n$ , and the sum in Eq. (8) is over only the twelve nearest neighbors of  $\text{pH}_2$  molecule  $n$ .

If  $n$  is a  $\text{pH}_2$  molecule and  $k$  is either another  $\text{pH}_2$  molecule or an S-state atomic dopant, then  $k$  and  $n$  are both spherically symmetric particles. The dipole moment function  $\mathbf{m}^{(k,n)}$  then depends only on the interparticle vector  $\mathbf{R}_{k,n} = \mathbf{R}_n - \mathbf{R}_k$ . Furthermore, in this case  $\mathbf{m}^{(k,n)}$  must point along the interparticle vector  $\mathbf{R}_{k,n}$ , so that we have

$$\mathbf{m}^{(k,n)} = \hat{\mathbf{R}}_{k,n} m^{(k,n)}(R_{k,n}) \quad (9)$$

where  $m^{(k,n)}(R_{k,n})$  is now a scalar function of the interparticle distance  $R_{k,n}$ . The dependence of this function on the vibrational coordinate of  $\text{pH}_2$  molecule  $n$  contains the essential information needed to predict the integrated intensities of dopant-induced  $Q_1(0)$  features in doped  $\text{pH}_2$  solids.

In the case that  $k$  and  $n$  are both  $\text{pH}_2$  molecules, the vibrational dependence of this function has been computed using ab initio quantum chemical methods [Mey89]. Similar calculations are needed for dopant- $\text{pH}_2$  dimers to enable evaluation of the transition dipole

moment matrix elements defined by Eq. (3). We have used ab initio quantum chemical techniques to compute the interaction-induced dipole moment  $M$  for the Ar-H<sub>2</sub> dimer. This dipole moment is the derivative<sup>(1)</sup> of the Ar-H<sub>2</sub> interaction potential  $V$  with respect to the magnitude of an externally applied homogeneous electric field  $F$ :  $M = (\partial V / \partial F)_{F=0}$ . The interaction potential  $V$  is computed using Gaussian [Gau03] at the CCSD(T) level of theory employing the standard counterpoise correction [Boy70].

Our frozen-core calculations employ standard aug-cc-pVTZ atom-centered basis sets that have been extended with an additional set of diffuse functions. These additional functions consist of one primitive Gaussian of each symmetry with an exponent one-third as large as the smallest exponent of that symmetry in the standard aug-cc-pVTZ basis sets. Midway between the Ar nucleus and the H<sub>2</sub> center of mass, we place a (3s3p2d) set of bond functions [Tao92] to improve the description of dispersion interactions. Only valence electrons are correlated in our ab initio calculations. Extensive tests show that core-valence correlation makes an insignificant contribution to the interaction-induced dipole moment of the Ar-H<sub>2</sub> dimer.

We describe the configuration of the Ar-H<sub>2</sub> dimer using Jacobi coordinates, in which  $R$  is the Ar-H<sub>2</sub> distance,  $r$  is the H-H bond length, and  $\gamma$  is the angle between the Ar-H<sub>2</sub> vector and the H-H bond. For specificity, we place the dimer in the  $(x, z)$  plane with the Ar atom at the origin and the H<sub>2</sub> center of mass on the positive  $z$  axis; when  $0 < \gamma < \pi/2$ , the H atom which is closer to Ar has a positive  $x$  coordinate.

The derivative  $(\partial V / \partial F)_{F=0}$  is estimated from a finite-difference analysis of the interaction energies obtained when the dimer is perturbed by external fields of strength  $F = \pm 0.001$  au. Such an analysis gives accurate dipole moments if the interaction energy can be expressed as a quadratic function of the external field strength for small values of  $F$ ; tests show that this is indeed the case for field strengths less than or equal to 0.003 au. Hence the finite-difference analysis employed here should give reliable dipole moments.

For the configuration ( $R = 6.856 a_0, r = 1.401 a_0, \gamma = 0$ ), we obtain a field-free frozen-core Ar-H<sub>2</sub> interaction energy of  $V = -52.50 \text{ cm}^{-1}$ ; this is in excellent agreement with the value of  $-52.56 \text{ cm}^{-1}$  obtained from a frozen-core CCSD(T) calculation [Woo98] employing the aug-cc-pV5Z basis set for H and the d-aug-cc-pV5Z basis set for Ar. This demonstrates that bond functions can effectively compensate for inadequacies of atom-centered Gaussian basis sets in computing the binding energy of weakly bound dimers.

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<sup>(1)</sup> In Gaussian 03 revision B.05, the orientation of an externally applied field  $\mathbf{F}$  is defined so that when a molecule's permanent dipole moment vector  $\mathbf{M}$  points in the same direction as  $\mathbf{F}$ , the field-dipole interaction *raises* the molecule's energy.

Furthermore, we find that the interaction-induced dipole moment  $M$  changes by less than 1% when our extended triple-zeta basis sets are replaced by either larger aug-cc-pVQZ basis sets or smaller aug-cc-pVTZ basis sets. This indicates that the basis sets used here are large enough to yield converged interaction-induced dipole moments at the CCSD(T) level of theory.

At a fixed Ar-H<sub>2</sub> distance  $R$ , the Cartesian components of the interaction-induced dipole moment can be written as [Mey86a]

$$M_x = \sum_{k=0}^{\infty} \sum_{j=1}^{\infty} C_{2j,k} P_{2j}^1(\cos \gamma) (r - r_0)^k \quad (10)$$

and

$$M_z = \sum_{k=0}^{\infty} \sum_{j=0}^{\infty} D_{2j,k} P_{2j}(\cos \gamma) (r - r_0)^k \quad (11)$$

where  $P_n$  is a Legendre polynomial,  $P_n^m$  is an associated Legendre polynomial, and  $r_0$  is a reference H-H bond length which we choose to be  $1.4 a_0$  here. Figure 5 shows the angular dependence of  $M_x$  and  $M_z$  for Ar-H<sub>2</sub> at  $R = 5 a_0$  and  $r = 1.4 a_0$ . The ab initio results are accurately reproduced by a fit that includes the  $j = 1$  term in Eq. (10) and the  $j = 0$  through  $j = 2$  terms in Eq. (11). To determine the number of powers of  $(r - r_0)$  that must be retained in Eqs. (10) and (11), we calculate  $M_x$  and  $M_z$  for Ar-H<sub>2</sub> as functions of  $r$  at  $R = 5 a_0$  and three values of  $\gamma$ ; our results are shown in Fig. 6. We see that for  $r$  values between  $r = 0.9 a_0$  and  $2.1 a_0$ , truncating these power series expansions at  $(r - r_0)^2$  is adequate.

Figures 5 and 6 show that we can determine the coefficients of the leading terms in Eqs. (10) and (11) for a given  $R$  value by computing the Ar-H<sub>2</sub> dipole moment at nine configurations, specified by three choices for  $r$  and three choices for  $\gamma$ . Here we choose  $r = 1.1, 1.4$ , and  $1.7 a_0$  and  $\gamma = 0, \pi/4$ , and  $\pi/2$ . We calculate the interaction-induced Ar-H<sub>2</sub> dipole moment at these nine configurations for several  $R$  values between  $5 a_0$  and  $10 a_0$ . At a fixed value of  $R$ , we then integrate Eqs. (10) and (11) over specific H<sub>2</sub> rovibrational wavefunctions to obtain rovibrationally averaged dipole moments and rotationally averaged transition dipole moments. In Fig. 7, we present the rovibrationally averaged Ar-H<sub>2</sub> dipole moment

$$\langle M \rangle_{00} = \langle v = 0, j = 0 | M_z | v = 0, j = 0 \rangle \quad (12)$$

and the Ar-H<sub>2</sub> Q<sub>1</sub>(0)  $v = 1 \leftarrow 0$  transition dipole moment

$$\langle M \rangle_{01} = \langle v = 0, j = 0 | M_z | v = 1, j = 0 \rangle . \quad (13)$$

In Eq. (13), the relative phases of the  $\text{H}_2$   $v = 0$  and  $v = 1$  vibrational wavefunctions are chosen so that the integral  $\langle v = 0, j = 0 | r | v = 1, j = 0 \rangle > 0$ .

The  $\langle M \rangle_{00}$  and  $\langle M \rangle_{01}$  functions can be fit reasonably well by an expression of the form

$$\langle M \rangle = D_7/R^7 - c_0 \exp(c_1 R + c_2 R^2)$$

using these parameters (all in atomic units):

$$\begin{aligned} \langle M \rangle_{00} : \quad D_7 &= 278, \quad c_0 = 29.815, \quad c_1 = -1.1693, \quad c_2 = -0.0543 \\ \langle M \rangle_{01} : \quad D_7 &= 166, \quad c_0 = 4.450, \quad c_1 = -0.9479, \quad c_2 = -0.0496 \end{aligned} \tag{14}$$

Our  $\langle M \rangle_{00}$  curve for  $\text{Ar-H}_2$  is in qualitative agreement with that presented in [Mey86b], where the vibrationally averaged  $\text{Ar-H}_2$  dipole moment  $\langle M \rangle_{00}$  was estimated by performing ab initio calculations for  $\text{Ar-H}_2$  dimers with the  $\text{H}_2$  fragment frozen at its  $v = 0$  vibrationally averaged bond length. If we evaluate the rotationally averaged ( $j = 0$ )  $\text{Ar-H}_2$  dipole moment at this H-H bond length using Eqs. (10) and (11) and our computed  $C$  and  $D$  coefficients, our results are roughly 10% larger than those presented in [Mey86b] for  $\text{Ar-H}_2$  distances  $R$  between 5 and 6  $a_0$ .

## 5. Publications

The following publications report work supported in part or in full by AFOSR grant F49620-01-1-0068:

- “High-resolution spectroscopy of  $\text{HCl}$  and  $\text{DCl}$  isolated in solid parahydrogen: direct, induced, and cooperative infrared transitions in a molecular quantum solid”, D. T. Anderson, R. J. Hinde, S. Tam, and M. E. Fajardo, *J. Chem. Phys.* **116**, 594–607 (2002).
- “Probing quantum solvation with infrared spectroscopy: infrared activity induced in solid parahydrogen by  $\text{N}_2$  and  $\text{Ar}$  dopants”, R. J. Hinde, D. T. Anderson, S. Tam, and M. E. Fajardo, *Chem. Phys. Lett.* **356**, 355–360 (2002).
- “Infrared-active vibron bands associated with substitutional impurities in solid parahydrogen”, R. J. Hinde, *J. Chem. Phys.* **119**, 6–9 (2003).
- “ $\text{Mg-He}$  and  $\text{Ca-He}$  van der Waals interactions: approaching the Born-Oppenheimer limit”, R. J. Hinde, *J. Phys. B* **36**, 3119–3128 (2003).

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Figure 1. Symmetry breaking induces IR activity in solid  $\text{pH}_2$  matrices containing atomic substitutional impurities. Open single circles represent  $v = 0$   $\text{pH}_2$  molecules; double circles represent  $\text{pH}_2$  molecules undergoing a  $v = 1 \leftarrow 0$  excitation. (a) In a close packed pure  $\text{pH}_2$  solid, excitation of a single  $\text{pH}_2$  molecule generates twelve transition dipole moment vectors, six of which are shown here. The twelve vectors sum to zero because of the underlying symmetry of the close packed lattice. (b) In a  $\text{pH}_2$  solid containing an atomic substitutional impurity (shaded circle), excitation of a  $\text{pH}_2$  molecule next to the impurity yields a nonzero net transition dipole moment because the transition moment for dopant- $\text{pH}_2$  dimers differs from that for  $\text{pH}_2$ - $\text{pH}_2$  dimers.

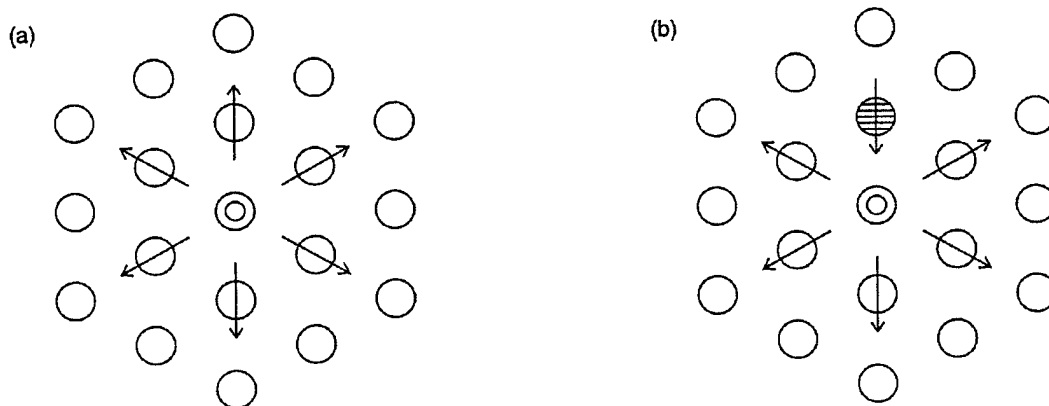




Figure 2. Theoretical dopant-induced  $\text{pH}_2$   $Q_1(0)$  absorption spectra for several values of the detuning parameter  $\Delta E$ . From bottom to top,  $\Delta E = 0.25 \text{ cm}^{-1}$ ,  $0.5 \text{ cm}^{-1}$ ,  $0.75 \text{ cm}^{-1}$ ,  $1 \text{ cm}^{-1}$ ,  $1.5 \text{ cm}^{-1}$ , and  $2 \text{ cm}^{-1}$ . The spectra are offset vertically for clarity. Note that the spectra for  $\Delta E \geq 1 \text{ cm}^{-1}$  have been reduced in intensity for ease of presentation.

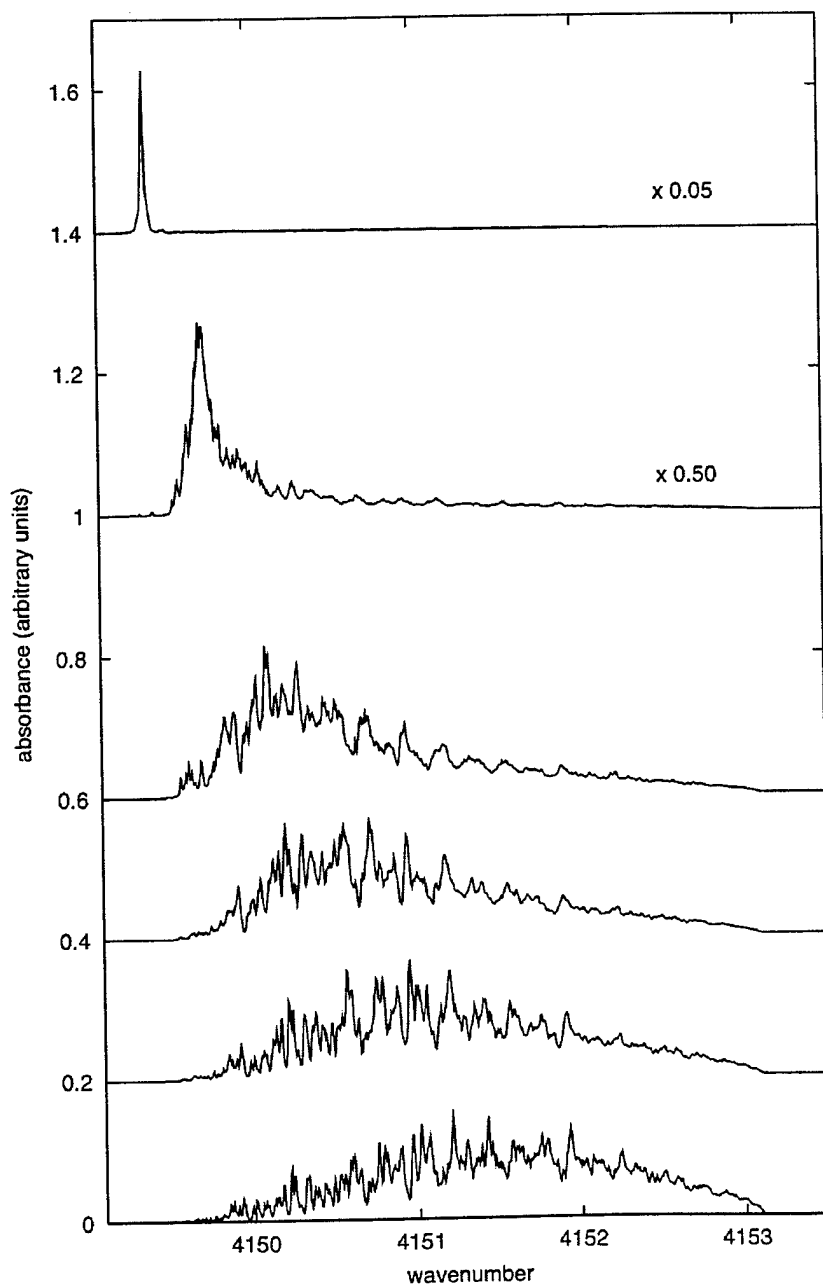


Figure 3. Convergence of  $\Delta E$  for Ar-doped solid  $\text{pH}_2$  with Trotter number  $N_T$ . For  $N_T \geq 48$ ,  $\Delta E$  converges to its asymptotic value of  $0.20 \text{ cm}^{-1}$ .

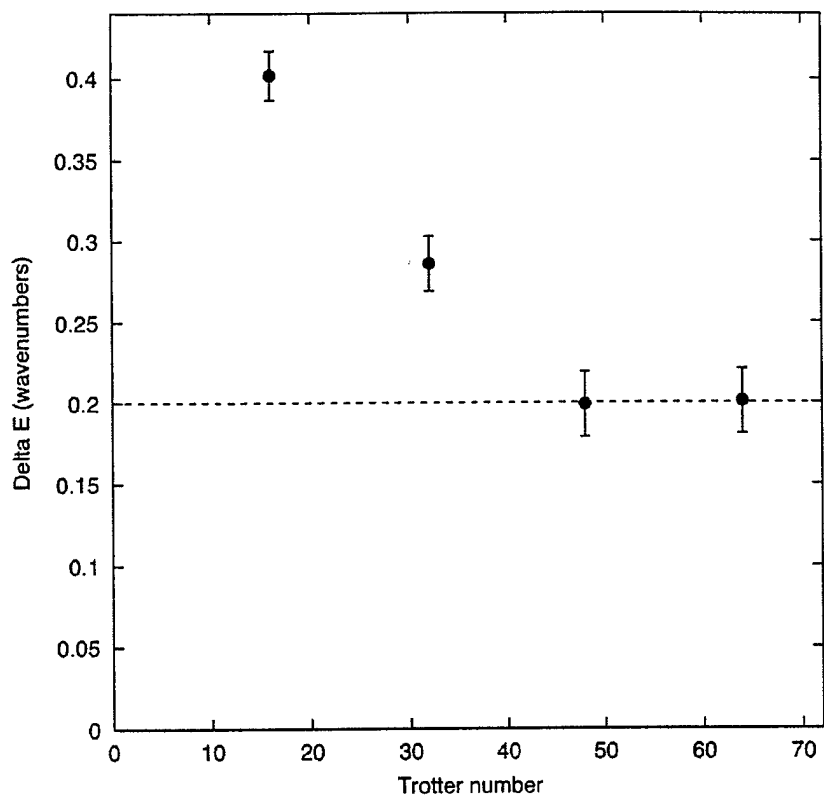


Figure 4. Distribution of dopant-H<sub>2</sub> nearest-neighbor distances in (a) Ar-doped, (b) Kr-doped, and (c) Xe-doped solid pH<sub>2</sub> at  $T = 4$  K. The dashed line in each panel represents the distribution of nearest-neighbor H<sub>2</sub>-H<sub>2</sub> distances in pure solid pH<sub>2</sub> at  $T = 4$  K.

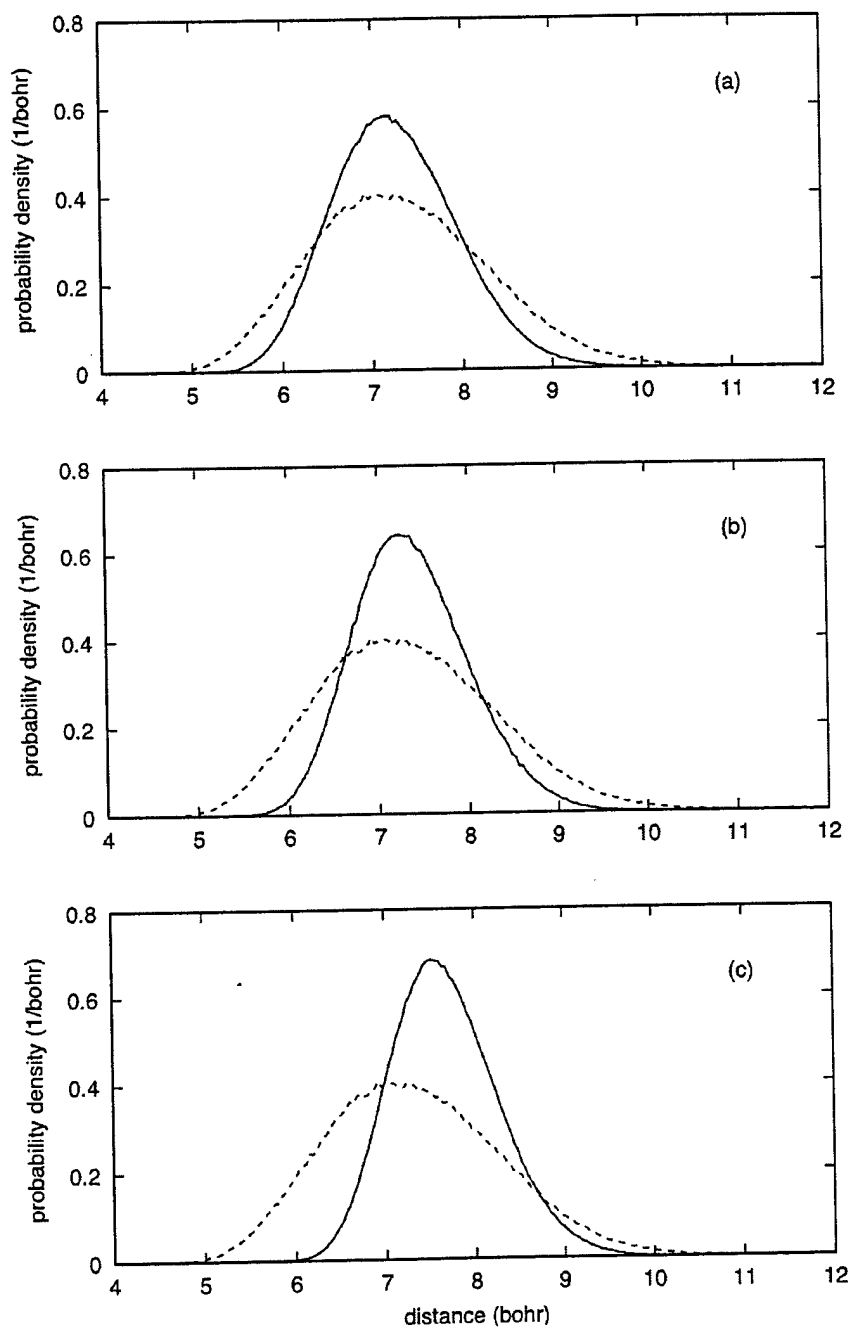


Figure 5. Dependence of the Ar-H<sub>2</sub> dipole moment on  $\gamma$  at  $R = 5 a_0$  and  $r = 1.4 a_0$ . Open circles indicate values of  $M_x$ ; open squares indicate values of  $M_z$ . The lines are fits to truncated Legendre polynomial expansions as described in the body of the report.

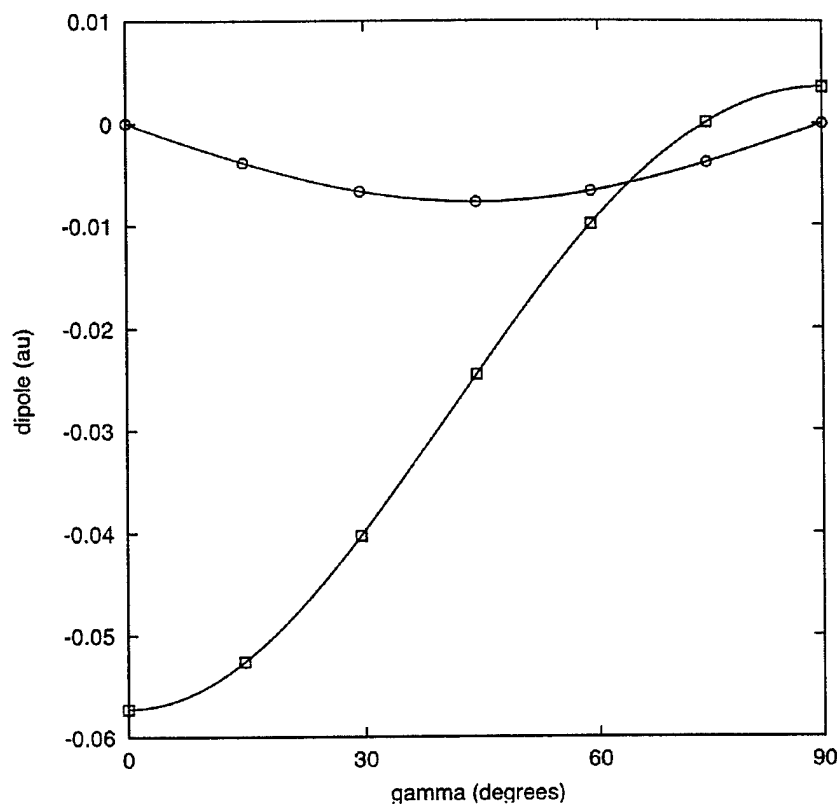


Figure 6. Dependence of the Ar-H<sub>2</sub> dipole moment on  $r$  at  $R = 5 a_0$ . Panel (a) shows  $M_x$  as a function of  $r$  at  $\gamma = \pi/4$ ; panel (b) shows  $M_z$  as a function of  $r$  at three  $\gamma$  values. The solid lines are quadratic fits to the ab initio calculations.

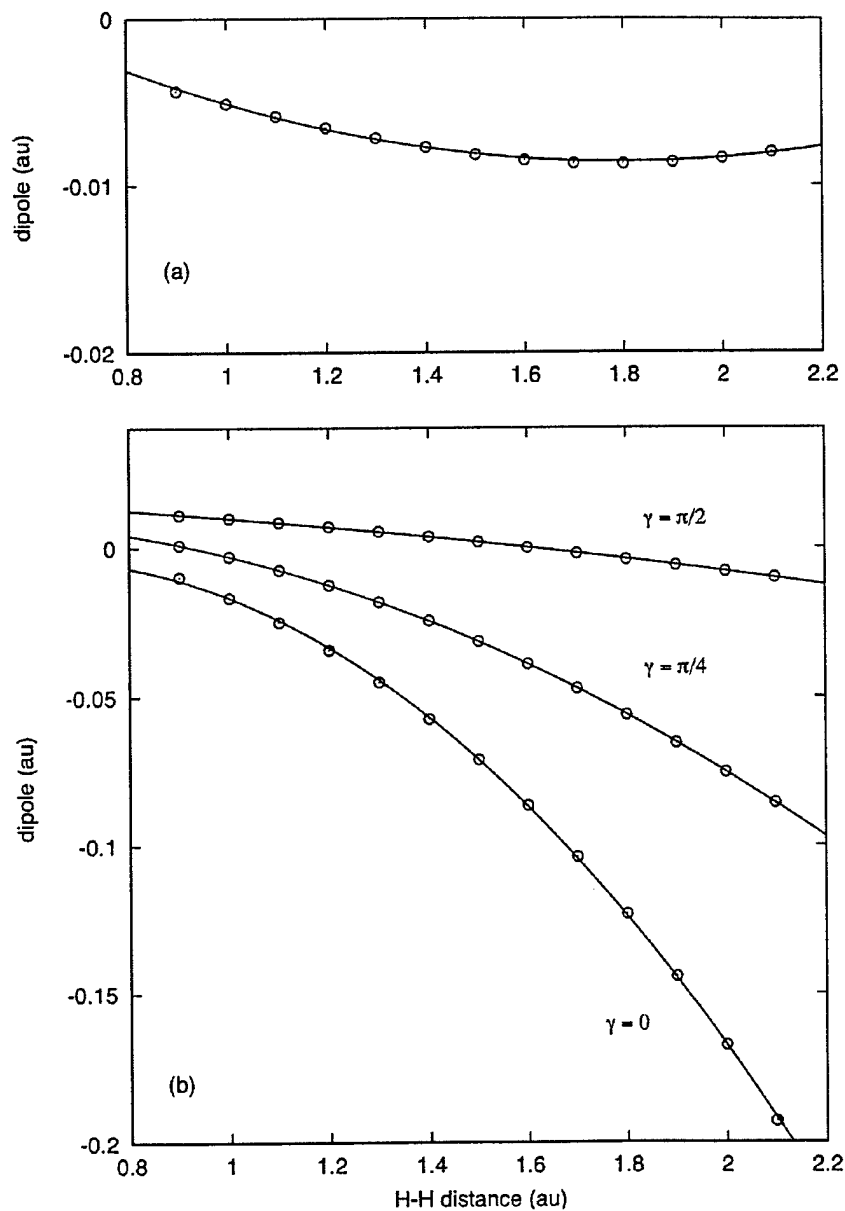


Figure 7. Dependence on  $R$  of (a) the rovibrationally averaged Ar-H<sub>2</sub> dipole moment  $\langle M \rangle_{00}$  and (b) the Ar-H<sub>2</sub> Q<sub>1</sub>(0) transition dipole moment  $\langle M \rangle_{01}$ . The solid lines are cubic spline fits to the data. Note the change from linear to logarithmic scale in each plot at  $\langle M \rangle = -2 \times 10^{-5}$  au.

