

# Intermolecular potentials and isotope effects for molecular hydrogen-inert gas complexes\*

Holger Kreek<sup>†</sup> and Robert J. Le Roy<sup>‡</sup>

Guelph Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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An exact power series expansion is derived which interrelates the coefficients of the Legendre expansions for an atom-diatomic molecule potential function expanded about the centers of mass of two different isotopes of the diatomic. Its application to the anisotropic potential recently obtained for H<sub>2</sub>- and D<sub>2</sub>-Ar yields a potential for HD-Ar, which is then used to predict the transition frequencies in the infrared absorption spectrum of the latter. The relatively large discrepancies between these predictions and the recent measurements of McKellar [J. Chem. Phys. **61**, 4636 (1974)] are attributed to the unusual sensitivity of such predictions to the shape of the isotropic potential in the region between its minimum at  $R_e^{(0)}$  and its zero energy turning point,  $\sigma^{(0)}$ .

## I. INTRODUCTION

A recent paper<sup>1</sup> has reported a detailed analysis of McKellar and Welsh's<sup>2,3</sup> spectroscopic data for the weakly bound van der Waals molecules formed between H<sub>2</sub> or D<sub>2</sub>, and Xe, Kr, Ar and Ne. For the complexes formed by the three heavier inert gas partners,<sup>4</sup> this work yielded three-dimensional intermolecular potentials which accurately account for the frequencies of all the uniquely-assigned and nonoverlapping transitions of both the H<sub>2</sub> and D<sub>2</sub> isotopes.<sup>5</sup> This analysis<sup>1</sup> was based on the Born-Oppenheimer approximation assumption that all isotopes of a given species have the same intramolecular potential function, and the consistency of the H<sub>2</sub> and D<sub>2</sub> isotope results confirmed its accuracy for these complexes. Thus, when McKellar reported his subsequent measurements of the spectrum of HD-Ar,<sup>6</sup> it appeared that a straightforward application of the techniques and potential functions reported in Ref. 1 should have yielded predictions in good agreement with his observations. The purpose of the present paper is to report on these calculations, and on the reason for the remaining discrepancies between the predicted and experimental transition frequencies.

A calculation of the spectrum of these complexes requires a determination of the eigenvalues of the internal motion Hamiltonian in which the positions of all the particles are expressed relative to the center of mass. The coordinates in which this Hamiltonian is usually defined are the diatomic bond length, the distance between the atom and the diatomic center of mass, and the angle between these two axes. However, the centers of mass of two diatomic molecule isotopes which are not both homonuclear have different positions on the internuclear axis. Thus, a potential function obtained for a complex formed from one of these isotopes must undergo a change of variables before it is used to calculate the eigenvalues of the other isotope of the complex. The fact that the centers of mass of H<sub>2</sub> and D<sub>2</sub> both lie at the bond midpoint allows one to use the same intermolecular potential expansion for both H<sub>2</sub>-Ar and D<sub>2</sub>-Ar. However, the same expression is not suitable for a calculation of the eigenvalues of HD-Ar.

A derivation of the effect of a shift of the diatomic center of mass on the coefficients of the Legendre ex-

pansion for an atom-diatomic molecule potential function is presented in Sec. II. Its application to the existing interaction potential for H<sub>2</sub>- and D<sub>2</sub>-Ar is reported in Sec. III, together with a discussion of additional terms contributing to the HD-Ar potential. A comparison of the ensuing predicted HD-Ar transition frequencies with experiment is then presented in Sec. IV, together with a discussion of the source of the residual discrepancies. Throughout, this paper relies on the notation and computational methods used in Ref. 1.

## II. EFFECT OF SHIFTING THE DIATOMIC CENTER OF MASS ON THE LEGENDRE EXPANSION FOR AN ATOM-DIATOMIC MOLECULE INTERACTION POTENTIAL

This section presents a general derivation of the relation between the expressions for the interaction potential between an atom, A, and two different isotopes of a diatomic molecule, BC. The coordinates appearing in this problem are shown in Fig. 1; the centers of mass of two isotopes of the diatomic molecule are located at  $c_1$  and  $c_2$ , and are separated by the distance  $\delta$ . As in Ref. 1, it is convenient to replace the diatomic bond length  $r$  by the dimensionless stretching coordinate  $\xi$ , defined as

$$\xi \equiv (r - r_0)/r_0, \quad (1)$$

where the reference length  $r_0$  has the same value for *all* isotopes of a given species.

The transformation relating the interaction potential expressed in terms of the initial coordinates,  $V(R', \xi, \theta')$ , to the analogous function of the final coordinates,  $U(R, \xi, \theta)$ , is now derived. It is convenient to expand the interaction potential between an atom and a diatomic molecule in terms of Legendre polynomials of the angle between the diatomic axis and a line joining its center of mass to the atom. With this in mind, the interaction potential may be written as

$$\begin{aligned} V(R', \xi, \theta') &= \sum_{n=0}^{\infty} V_n(R', \xi) P_n(\cos \theta') = U(R, \xi, \theta) \\ &= \sum_{k=0}^{\infty} U_k(R, \xi) P_k(\cos \theta). \end{aligned}$$

The present problem is the derivation of expressions

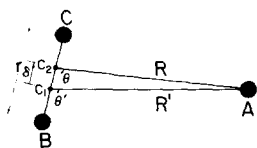


FIG. 1. Atom-diatom molecule internal coordinates for isotopes with diatomic center of mass at  $c_1$  and  $c_2$ , respectively.

for the functions  $U_k(R, \xi)$  in terms of the known functions  $V_n(R, \xi)$ .

The orthogonality property of Legendre polynomials gives

$$U_k(R, \xi) = (k + \frac{1}{2}) \int_0^\pi V(R', \xi, \theta') P_k(\cos \theta) d(\cos \theta) \\ = (k + \frac{1}{2}) \sum_{n=0}^{\infty} \int_0^\pi V_n(R', \xi) P_n(\cos \theta') P_k(\cos \theta) d(\cos \theta). \quad (2)$$

The two sets of coordinates appearing in this problem are related by the equations (see Fig. 1):

$$R' = R(1 + t^2 - 2t \cos \theta)^{1/2} \\ \cos \theta' = (\cos \theta - t) / (1 + t^2 - 2t \cos \theta)^{1/2}, \quad (3)$$

where  $t \equiv \delta/R$ . The power series expansion for a Legendre polynomial is<sup>7</sup>

$$P_m(z) = 2^{-m} \sum_{l=0}^{[m/2]} (-1)^l \binom{m}{l} \binom{2m-2l}{m} z^{m-2l}, \quad (4)$$

where  $\binom{u}{v}$  represents the usual binomial expansion coefficient

$$\binom{u}{v} \equiv \frac{u!}{v!(u-v)!}.$$

Combining Eq. (4) with the binomial expansion formula

$$(a+b)^s = \sum_{p=0}^s \binom{s}{p} a^{s-p} b^p \quad (5)$$

yields

$$P_n(\cos \theta') = 2^{-n} \sum_{l=0}^{[n/2]} (-1)^l \binom{n}{l} \binom{2n-2l}{n} \\ \times (1 + t^2 - 2t \cos \theta)^{-(n-2l)/2} \\ \times \sum_{i=0}^{n-2l} \binom{n-2l}{i} (-t)^i (\cos \theta)^{n-2l-i} \quad (6)$$

Defining  $x = \cos \theta$ , and using Eq. (4) [for  $P_k(x)$ ] and Eq. (6) in Eq. (2) then yields

$$U_k(R, \xi) = (2k+1) 2^{-(k+1)} \sum_{n=0}^{\infty} 2^{-n} \sum_{l=0}^{[n/2]} (-1)^l \binom{n}{l} \binom{2n-2l}{n} \\ \times \sum_{m=0}^{[k/2]} (-1)^m \binom{k}{m} \binom{2k-2m}{k} \sum_{i=0}^{n-2l} \binom{n-2l}{i} (-t)^i \int_{-1}^1 V_n(R', \xi) (1+t^2-2tx)^{-(n-2l)/2} x^{n+k-2m-2l-i} dx. \quad (7)$$

The next step is the expansion of  $V_n(R', \xi) = V_n[R(1+t^2-2tx)^{1/2}, \xi]$  as a Taylor series about  $t=0$ ,

$$V_n(R', \xi) = \sum_{j=0}^{\infty} \frac{t^j}{j!} \sum_{w=0}^j x^w V_n^{(j;w)} \quad (8)$$

Here,  $V_n^{(j;w)}$  is defined as the coefficient of  $x^w$  appearing in the  $j$ th derivative of  $V_n(R', \xi)$  with respect to  $t$ , evaluated at  $t=0$ . For example, the first derivative of  $V_n(R', \xi)$  with respect to  $t$

$$\frac{\partial V_n(R', \xi)}{\partial t} = R(t-x)(1+t^2-2tx)^{-1/2} \frac{\partial V_n(R', \xi)}{\partial R'}$$

yields  $V_n^{(1;0)} = 0$  and  $V_n^{(1;1)} = -R \partial V_n(R, \xi) / \partial R \equiv -R V_n^{(1)}$ . Analogous expressions for  $V_n^{(j;w)}$  for  $j=0-4$  are given in Table I; as indicated there, this quantity is always zero unless  $(j+w)$  is even. The results in Table I suggest that certain of these quantities are interrelated. For instance, it appears that  $\sum_{w=0}^j V_n^{(j;w)} = (-R)^j V_n^{(j)}$ , where  $V_n^{(j)} \equiv \partial^j V_n(R, \xi) / \partial R^j$ . However, we were unable to find a general expression for the functions  $V_n^{(j;w)}$  in terms of the more basic quantities  $R^m V_n^{(m)}$  ( $m=0-j$ ).

When Eq. (8) is substituted into Eq. (7), the integral in the latter becomes

$$\sum_{j=0}^{\infty} \frac{t^j}{j!} \sum_{w=0}^j V_n^{(j;w)} I(\alpha, \beta; t),$$

where  $\alpha = (w+n+k-2l-2m-i)$ ,  $\beta = (n-2l)/2$ , and

$$I(\alpha, \beta; t) = \int_{-1}^1 x^\alpha (1+t^2-2tx)^{-\beta} dx.$$

For  $\beta = (n-2l)/2 = 0$ ,

$$I(\alpha, 0; t) = [2/(\alpha+1)] \delta_{\alpha, \text{even}}.$$

For  $\beta \neq 0$ , the factor  $[1 - (2tx - t^2)]^{-\beta}$  is expanded as a power series in  $(2tx - t^2)$ , which powers are in turn expanded using Eq. (5). Performance of the integration gives

$$I(\alpha, \beta; t) = \sum_{p=0}^{\infty} \binom{\beta-1+p}{p} \sum_{q=0}^p (-1)^{p-q} 2^q \binom{p}{q} t^{2p-q} \\ \times \frac{2}{(\alpha+q+1)} \delta_{\alpha+q+1, \text{odd}}$$

TABLE I. Definition of the functions  $V_n^{(j;w)}$  in terms of the derivatives of the potential,  $V_n^{(m)} \equiv \partial^m V_n(R, \xi) / \partial R^m$ . Note that  $V_n^{(j;w)} = 0$  whenever  $(j+w)$  is (odd).

$V_n^{(0;0)} = V_n^{(0)} = V_n$
$V_n^{(1;1)} = -R V_n^{(1)}$
$V_n^{(2;0)} = R V_n^{(1)}$
$V_n^{(2;2)} = R^2 V_n^{(2)} - R V_n^{(1)}$
$V_n^{(3;1)} = -3R^2 V_n^{(2)} + 3R V_n^{(1)}$
$V_n^{(3;3)} = -R^3 V_n^{(3)} + 3R^2 V_n^{(2)} - 3R V_n^{(1)}$
$V_n^{(4;0)} = 3R^2 V_n^{(2)} - 3R V_n^{(1)}$
$V_n^{(4;2)} = 6R^3 V_n^{(3)} - 18R^2 V_n^{(2)} + 18R V_n^{(1)}$
$V_n^{(4;4)} = R^4 V_n^{(4)} - 6R^3 V_n^{(3)} + 15R^2 V_n^{(2)} - 15R V_n^{(1)}$

Substituting these results into Eq. (7) then yields the desired general expression for the Legendre expansion

$$\begin{aligned}
 U_k(R, \xi) = & (2k+1)2^{-k} \sum_{j=0}^{\infty} t^j \sum_{q=0}^j \frac{1}{(j-q)!} \sum_{n=0}^{\infty} \sum_{w=0}^{j-q} V_n^{(j-q, w)} \sum_{i=0}^{\min(q, n)} \sum_{p=\lfloor \frac{q-i}{2} \rfloor}^{q-i} (-1)^{p-q} 2^{2p+i-q-n} \binom{p}{2p-q+i} \sum_{l=0}^{\lfloor \frac{n-i}{2} \rfloor} (-1)^l \binom{n}{l} \binom{2n-2l}{n} \binom{n-2l}{i} \\
 & \times \binom{\frac{1}{2}n-l+p-1}{p} \sum_{m=0}^{\lfloor \frac{k/2 \rfloor} } (-1)^m \binom{k}{m} \binom{2k-2m}{k} \frac{\delta_{(n+k+w-q), \text{even}}}{n+k+w-2l-2m+2p-q+1} + (2k+1)2^{-k} \sum_{j=0}^{\infty} \left(\frac{t}{j!}\right) \sum_{n=0}^{\infty} 2^{-2n} (-1)^n \binom{2n}{n} \\
 & \times \sum_{w=0}^j V_n^{(j, w)} \sum_{m=0}^{\lfloor \frac{k/2 \rfloor} } (-1)^m \binom{k}{m} \binom{2k-2m}{k} (k+w-2m+1)^{-1} \delta_{(k+w), \text{even}} . \quad (9)
 \end{aligned}$$

In spite of the complexity of Eq. (9), values of the coefficients of  $t^j V_n^{(j)}$  may be readily evaluated on a computer. In general, the magnitudes of contributions to this expansion die off rapidly with increasing powers of  $t$ . For a case in which the initial Legendre expansion for  $V(R', \xi, \theta')$  includes terms from  $n=0-4$ , explicit expressions for  $U_k(R, \xi)$  which include all contributions of order less than  $t^5$ , are given in the Appendix.

The expansion in powers of  $t$  is a natural parameterization if the diatomic molecule is treated as a rigid rotor, since this approximation makes the displacement  $\delta$  a constant. However, for a formulation which also takes account of the vibration of the diatomic,  $t = \delta/R$  should be replaced by the expression

$$t = [\gamma_0(\delta/\gamma)](1 + \xi)/R. \quad (10)$$

Here, the factor  $[\gamma_0(\delta/\gamma)]$  is truly a constant, since the displacement  $\delta$  is a fixed fraction of the diatomic bond length  $\gamma$ .

Most previous discussions of effects associated with this type of coordinate transformation focussed attention on the leading contribution to  $U_1(R, \xi)$ . If  $V_n(R, \xi) = 0$  for all  $n > 0$ , the leading  $k=1$  contribution to Eq. (9) yields the familiar result

$$U_1(R, \xi) \approx -\delta \partial V_0(R, \xi) / \partial R.$$

An exception to this restricted treatment is the work of van Montfort, Heukels and van de Ree.<sup>8</sup> For cases in which the initial isotropic potential  $V_0(R')$  is a linear combination of inverse power, Gaussian, or exponential terms, they have presented exact closed form expressions for its contribution to each term  $U_k(R)$  in the transformed potential. Unfortunately, their neglect of the effect of contributions from  $V_n(R')$  terms for  $n > 0$  makes their final expressions no more accurate than the result obtained on adding the leading correction terms to  $V_0(R)$  and  $V_1(R) (=0)$ . The present Eq. (9) avoids both this difficulty and any restrictions to particular analytic forms for the potential. Moreover, by including terms corresponding to sufficiently high powers of  $t$ , it can yield any desired accuracy.

### III. INTERACTION POTENTIAL OF HD WITH Ar

#### A. Effect of the center of mass displacement

The interaction potential for H<sub>2</sub>- and D<sub>2</sub>-Ar obtained in Ref. 1 has the form:

coefficients  $U_k(R, \xi)$ , in terms of the known functions  $V_n(R, \xi)$ :

$$V(R', \xi, \theta') = V_0(R', \xi) + V_2(R', \xi) P_2(\cos \theta'), \quad (11)$$

where the two radial strength functions are generalized Lennard-Jones (12, 6) functions,

$$V_0(R', \xi) = \epsilon^{(0)} \left[ \left( \frac{R_e^{(0)}}{R'} \right)^{12} (1 + s_1 \xi) - 2 \left( \frac{R_e^{(0)}}{R'} \right)^6 (1 + s_2 \xi) \right] \quad (12)$$

$$V_2(R', \xi) = \epsilon^{(2)} \left[ \left( \frac{R_e^{(2)}}{R'} \right)^{12} (1 + s_3 \xi) - 2 \left( \frac{R_e^{(2)}}{R'} \right)^6 (1 + s_4 \xi) \right], \quad (13)$$

whose parameters are  $\epsilon^{(0)} = 52.21 \text{ cm}^{-1}$ ,  $R_e^{(0)} = 3.5573 \text{ \AA}$ ,  $\epsilon^{(2)} = 6.78 \text{ cm}^{-1}$ ,  $R_e^{(2)} = 3.814 \text{ \AA}$ ,  $s_1 = s_3 = 1.445$  and  $s_2 = s_4 = 0.919$ . For this case, Eq. (9) shows that contributions to  $U(R, \xi, \theta)$  of order less than  $t^3$  yield:

$$U_0(R, \xi) = V_0 + t^2 \left( \frac{1}{3} R V_0^{(1)} + \frac{1}{8} R^2 V_0^{(2)} + \frac{1}{5} V_2 + \frac{1}{3} R V_2^{(1)} + \frac{1}{15} R^2 V_2^{(2)} \right) + O(t^4). \quad (14)$$

$$U_1(R, \xi) = t \left( -R V_0^{(1)} - \frac{6}{5} V_2 - \frac{2}{5} R V_2^{(1)} \right) + O(t^3). \quad (15)$$

$$U_2(R, \xi) = V_2 + t^2 \left( -\frac{1}{3} R V_0^{(1)} + \frac{1}{3} R^2 V_0^{(2)} - \frac{11}{7} V_2 + \frac{11}{21} R V_2^{(1)} + \frac{11}{42} R^2 V_2^{(2)} \right) + O(t^4). \quad (16)$$

$$U_3(R, \xi) = t \left( \frac{6}{5} V_2 - \frac{3}{5} R V_2^{(1)} \right) + O(t^3). \quad (17)$$

$$U_4(R, \xi) = t^2 \left( \frac{46}{35} V_2 - \frac{6}{7} R V_2^{(1)} + \frac{6}{35} R^2 V_2^{(2)} \right) + O(t^2). \quad (18)$$

As in Ref. 1, the (arbitrary) scaling length  $\gamma_0$  appearing in Eqs. (1) and (10) is chosen to be the known<sup>9</sup> expectation value of  $\gamma$  for the ground rotation-vibration level of an isolated H<sub>2</sub> molecule,  $\gamma_0 = 0.76662 \text{ \AA}$ . In HD-Ar, the displacement of the HD center of mass from its center of interaction yields  $(\delta/\gamma) = 0.16650$ . At  $\xi = 0$  this corresponds to  $\delta = 0.1276 \text{ \AA}$ , while for the initial and final states of the S<sub>1</sub>(0) transitions of HD-Ar it yields  $\delta = 0.1271$  and  $0.1348 \text{ \AA}$ , respectively. Using the above value of  $(\delta/\gamma)$  in Eq. (10), and substituting it and the potential  $V(R', \xi, \theta')$  of Eqs. (11-13) into Eq. (9) then yields the desired HD-Ar potential. Its components  $U_k(R, \xi_{00})$  are pictured in the bottom segment of Fig. 2<sup>10</sup>; since the differences  $(U_0 - V_0)$  and  $(U_2 - V_2)$  would not show up on this scale, they are plotted separately in the upper half of this figure. The  $P_1(\cos \theta)$  anisotropy function arising from this transformation has roughly the same strength as the  $P_2(\cos \theta)$  anisotropy. However, it turns out that the odd anisotropies have very little effect on the eigenvalues of these complexes.

Figures 3-5 illustrate the relative magnitudes of the various contributions to each term in the transformed potential. The quantity  $U_k^{(j, n)}$  is the sum of all contribu-

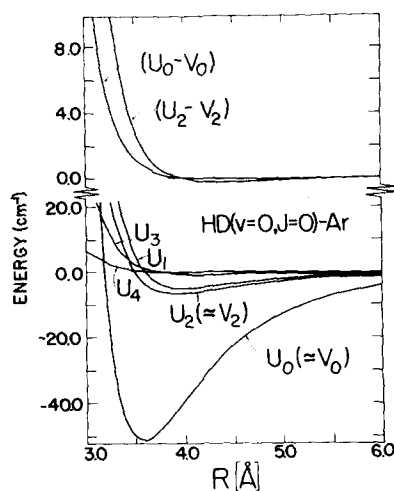


FIG. 2. Lower: components of the HD( $v=0, J=0$ )-Ar potential derived from Eqs. (11)–(13) and Eq. (9). Upper: differences  $[U_k(R, \bar{\xi}_{00}) - V_k(R, \bar{\xi}_{00})]$  for  $k=0$  and 2 (for  $k \neq 0$  or 2,  $V_k(R, \xi) \equiv 0$ ).

tions to  $U_k(R, \xi)$ , which are of order  $t^j$ , and arise from  $V_n(R', \xi)$ . For example [see Eq. (16)],

$$U_2^{(2,0)} = -\frac{1}{3}RV_0^{(1)} + \frac{1}{3}R^2V_0^{(2)}$$

In order to facilitate comparisons, the vertical scale in these figures is linear in  $(U_k^{(j,n)})^{1/3}$ . These results clearly illustrate the rapid convergence of the expansion in powers of  $t$  which appears in Eq. (9).

### B. Other contributions to the HD-Ar potential

The small dipole moment of HD gives rise to additional terms in the HD-Ar potential function which do not occur for  $H_2$ -Ar or  $D_2$ -Ar. The first of these is the interaction between the HD dipole moment and the dipole it induces in the Ar atom. Hirschfelder, Curtiss, and Bird<sup>11</sup> show that this term has the form

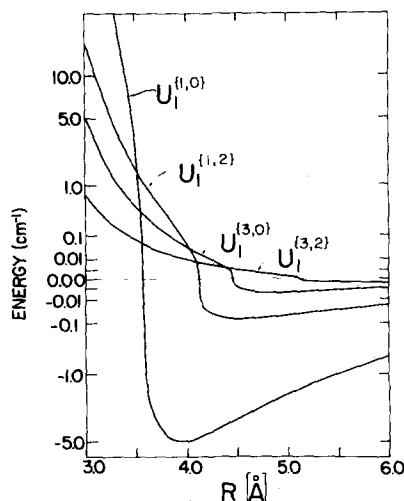


FIG. 4. Terms contributing to  $U_1(R, \bar{\xi}_{00})$ ; as in Fig. 3.

$$-\frac{1}{2}M^2\alpha(1+3\cos^2\theta)/R^6, \quad (19)$$

where  $M$  is the HD dipole moment and  $\alpha$  the polarizability of the Ar atom. The next term is the quadrupole-induced dipole interaction given by<sup>11</sup>

$$-3MQ\alpha\cos^3\theta/R^7, \quad (20)$$

where  $Q$  is the HD quadrupole moment relative to the bond midpoint.

Teachout and Pack<sup>12</sup> gave the dipole polarizability of Ar as  $1.642 \text{ \AA}^3$ ; Trefler and Gush<sup>13</sup> found the dipole moment of ground-state HD to be  $5.85 \times 10^{-4} \text{ D}$ , and Birnbaum and Poll<sup>14</sup> reported the quadrupole moment of HD to be  $0.646 \times 10^{-26} \text{ esu} \cdot \text{cm}^2$ . Substitution of these values into Eqs. (19) and (20) shows that at the HD-Ar potential minimum of  $R \approx 3.6 \text{ \AA}$ , the dipole-induced dipole and quadrupole-induced dipole terms, respectively, contribute less than  $3 \times 10^{-6}$  and  $2 \times 10^{-3} \text{ cm}^{-1}$  to the interaction energy. Since these terms yield virtually negligible contributions to the HD-Ar interaction in the region of interest, they may be ignored.

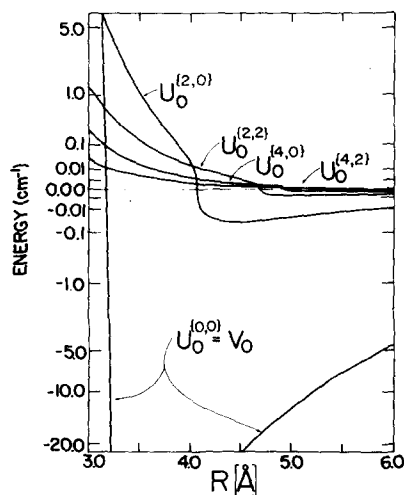


FIG. 3. Terms contributing to  $U_0(R, \bar{\xi}_{00})$ ;  $U_k^{(j,n)}$  is the total contribution to  $U_k(R, \bar{\xi}_{00})$  of order  $t^j$  arising from  $V_n(R, \bar{\xi}_{00})$ .

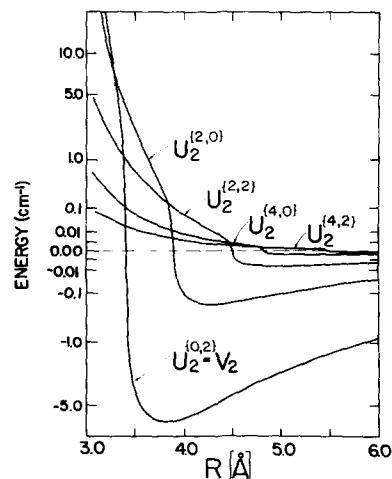


FIG. 5. Terms contributing to  $U_2(R, \bar{\xi}_{00})$ ; as in Fig. 3.

## IV. RESULTS AND DISCUSSION

## A. Comparing the calculated HD-Ar spectrum with experiment

Predicted frequencies for the transitions comprising the  $S_1(0)$  spectrum of HD-Ar are obtained from a straight forward application of the techniques presented in Ref. 1 to the transformed interaction potential described above. The only change from the computations of Ref. 1 arises from the presence of odd anisotropies in the transformed potential. They allow  $\Delta L$ ,  $\Delta J = \pm 1, \pm 3, \dots$ ,  $\pm k$  ( $k$  odd) coupling of the zeroth order eigenstates, in addition to the  $\Delta L$ ,  $\Delta J = 0, \pm 2$  coupling which occurred for  $H_2$ - and  $D_2$ -Ar. While this increases the size of the secular determinants whose diagonalization yields the desired eigenvalues, it raises no serious difficulties. In these secular determinants, the elements which arise from the additional anisotropies are calculated in the same way as those for the  $P_2(\cos\theta)$  anisotropy, as discussed in Ref. 1. The expectation values of the hydrogen stretching coordinate corresponding to the  $(\nu, J) = (0, 0)$  and  $(1, 2)$  levels of HD are<sup>9,10</sup>  $\bar{\xi}_{0,0} = -0.00449$  and  $\bar{\xi}_{1,2} = 0.05646$ . The calculation utilizes McKellar's value<sup>15</sup> of the  $S_1(0)$  transition frequency of an isolated HD molecule,  $3887.684(\pm 0.008)$   $\text{cm}^{-1}$ .

Table II compares McKellar's observed frequencies<sup>6</sup> for the N- and T-branch transitions of HD-Ar with two sets of calculated values. Those labeled  $(\delta/r) = 0$  resulted from a calculation which utilized the correct mass and  $\bar{\xi}_{\nu,J}$  values for HD, but which ignored the displacement of the HD center of mass away from its center of charge. Thus, the potential used for this case is precisely given by Eqs. (11)–(13). The second set of differences, those labeled  $(\delta/r) = 0.1665$ , were obtained from this potential after it was transformed to take account of the displacement of the HD center of mass, with terms through order  $t^4$  and anisotropies up to  $P_4(\cos\theta)$  being retained in the expansion. This second approach is of course the correct one, and it was expected to give

TABLE II. Comparison of observed<sup>a</sup> and predicted frequencies (in  $\text{cm}^{-1}$ ) of transitions in the  $S_1(0)$  spectrum of HD-Ar. RMSD is the root mean square value of the deviations for this case.

Assignment	$\nu(\text{obs})$	[ $\nu(\text{calc}) - \nu(\text{obs})$ ]	
		$(\delta/r) = 0$	$(\delta/r) = 0.1665$
N(9)	3869.33	-0.61	-0.17
N(8)	3871.07	-0.68	-0.27
N(7)	3873.06	-0.69	-0.30
N(6)	3875.24	-0.72	-0.35
N(5)	3877.51	-0.73	-0.38
N(3)	3881.8	-0.2 <sub>3</sub>	0.0 <sub>7</sub>
T(1)	3892.9	+0.0 <sub>4</sub>	0.2 <sub>9</sub>
T(2)	3895.82	-0.56	-0.38
T(3)	3898.00	-0.51	-0.40
T(4)	3900.04	-0.45	-0.39
T(5)	3901.87	-0.32	-0.32
T(6)	3903.54	-0.27	-0.34
T(7)	3904.70	-0.12	-0.26
RMSD		0.53	0.33

<sup>a</sup>Reference 6.

TABLE III. Changes in the predicted HD-Ar  $S_1(0)$  frequencies as each function  $V_k(R, \xi)$ , for  $k = 0-4$ , is in turn replaced by the corresponding transformed function,  $U_k(R, \xi)$ . The last column shows the changes associated with contributions to  $U(R, \xi, \theta)$  of order  $t^3$  and  $t^4$ . All quantities are in  $\text{cm}^{-1}$ .

Transition	Include terms of order up to $t^2$				Add terms of order $t^3, t^4$ 0-4
	$k = 0$	1	2	3, 4	
N(10)	0.279	0.016	0.128	0.006	0.009
N(9)	0.266	0.012	0.146	0.003	0.009
N(8)	0.229	0.009	0.160	0.004	0.009
N(7)	0.204	0.006	0.171	0.004	0.009
N(6)	0.180	0.003	0.179	0.003	0.010
N(5)	0.157	0.001	0.183	0.003	0.009
N(4)	0.133	0.001	0.183	0.002	0.010
N(3)	0.109	0.000	0.182	0.002	0.009
T(0)	0.001	0.000	0.303	0.021	0.015
T(1)	-0.016	0.000	0.234	0.012	0.012
T(2)	-0.038	-0.001	0.198	0.008	0.011
T(3)	-0.063	0.000	0.167	0.007	0.007
T(4)	-0.090	0.000	0.140	0.005	0.005
T(5)	-0.117	0.001	0.110	0.004	0.003
T(6)	-0.152	0.002	0.078	0.003	0.000
T(7)	-0.185	0.005	0.044	-0.001	-0.004

good agreement with experiment. However, while the agreement is significantly improved by inclusion of the center-of-mass displacement, the final discrepancies are still much larger than the reported experimental uncertainties of  $0.07$   $\text{cm}^{-1}$ .

In considering the significance of the differences in Table II, it must be remembered that the basic potential, Eq. (11)–(13), was able to account for 45 independent  $H_2$ -Ar and  $D_2$ -Ar transition frequencies (31 for the former and 14 for the latter), within a standard error equal to the experimental uncertainty<sup>2</sup> of  $0.03$   $\text{cm}^{-1}$ . Thus, with the change of variables performed properly, there is no obvious reason for expecting the accuracy of the HD-Ar predictions to be as bad as they are.

## B. Source of the discrepancies

Let us first examine how the changes in the different components of the potential caused by the change of variables affect the calculated transition frequencies. Starting from the  $(\delta/r) = 0$  predictions of Table II, the first four columns in Table III show the changes in the predicted frequencies as each of the functions  $V_k(R, \xi)$ , for  $k = 0-4$ , is in turn replaced by the corresponding transformed function  $U_k(R, \xi)$  calculated from Eq. (9) using terms of order up to  $t^2$ . The last column in Table III then shows the effect of adding correction terms of order  $t^3$  and  $t^4$  to the transformed potential. The sum of the quantities in any row of Table III equals the difference between the two corresponding discrepancies in Table II.

The results in the  $k = 1$  column of Table III show that the  $k = 1$  anisotropy has almost no effect on the eigenvalues of the complex, in spite of the fact that it is almost as strong as that for  $k = 2$  (see Fig. 2). This may seem surprising, since it is the  $k = 1$  term which is responsible for most of the anisotropy-induced inelasticity in this type of system.<sup>16,17</sup> However, an examination of Sec. III in Ref. 1. shows that the small influence of the

odd anisotropies on the eigenvalues of these complexes simply arises from parity considerations. In particular, Eqs. (30) and (31) in Ref. 1, show that for odd  $k$ , the  $P_k(\cos\theta)$  anisotropy can only influence eigenvalues via  $\Delta J$ ,  $\Delta L = \pm 1, \pm 3, \dots, \pm k$  coupling between the zeroth order eigenstates of the complex. Since the rotational spacings of the diatomic are much larger than those of the complex, even a relatively weak  $P_2$  anisotropy, which gives rise to  $\Delta J = 0$ ,  $\Delta L = 0, \pm 2$  coupling, will tend to affect the eigenvalues much more than the  $\Delta J = \pm 1$  coupling associated with a strong  $P_1$  term.

While the influence of the odd anisotropies is made small by the large rotational spacings of the diatomic hydrogen, the factor of  $l^2$  appearing in Eq. (18) also makes the influence of the  $P_4$  term quite weak. Thus, the center of mass displacement affects the spectrum almost solely via the modifications in the  $P_0$  and  $P_2$  anisotropy terms. The upper segment of Fig. 2 shows that these changes are virtually negligible for  $R$  larger than  $R_e^{(0)}$ , the equilibrium distance of the isotropic potential,  $V_0(R, \xi)$ . Equations (14) and (16) show that these correction functions depend on the derivatives with respect to  $R$  of the potentials  $V_0(R, \xi)$  and  $V_2(R, \xi)$ . The results in Figs. 3 and 5 show that (at least in the present problem) the derivatives of the isotropic part of the potential dominate these correction functions. In addition, the bound state eigenvalues are quite insensitive to the intermolecular potential at distances smaller than the zero energy classical turning point,  $\sigma^{(0)}$ . Thus, in addition to the usual mass-dependent isotope effects, replacing  $H_2$  or  $D_2$  by HD modifies the spectrum of the complexes in a manner which is strongly dependent on the precise shape of the isotropic potential in the narrow interval

$$\sigma^{(0)} \lesssim R \lesssim R_e^{(0)}.$$

The discrepancies in the last column of Table II therefore arise from the fact that in this region, the potential function obtained in Ref. 1 does not satisfy the rather severe restrictions on its shape provided by the HD-Ar data.

In some ways this conclusion is rather gratifying. The discussion in Ref. 1 implied that in spite of the rather good agreement between the calculated and experimental frequencies for both  $H_2$ - and  $D_2$ -M ( $M = Xe, Kr, Ar, Ne$ ), the data were not very sensitive to the shape of the potential function. This point is emphasized by Dunker's report<sup>5</sup> that he obtained good fits to the same data using a quite different potential form. However, we now see that the existence of data for complexes formed from both homonuclear and heteronuclear isotopes of molecular hydrogen provides much more severe constraints on the form of the potential than had been expected.

## V. CONCLUSIONS

The present paper shows that a concurrent analysis of spectroscopic data for inert-gas complexes formed

by both homonuclear and heteronuclear isotopes of molecular hydrogen should yield a more accurate intermolecular potential than can be obtained from data for complexes formed from one or more homonuclear isotopes. In other words, requiring consistency between the data for complexes formed from diatomic isotopes with different mass asymmetries introduces greater sensitivity to the shape of the short-range intermolecular potential than would normally be expected on the basis of the quality of the data, or the magnitudes of the de Broglie wavelengths associated with the observed eigenstates. This special sensitivity to the shape of the isotropic potential in the region  $\sigma^{(0)} \lesssim R \lesssim R_e^{(0)}$  is the isotope effect referred to in the title. It points out the importance of obtaining data for the complexes formed between HD and other inert gas atoms. As in the case of HD-Ar, the data reanalysis which will almost certainly be required should yield improved intermolecular potentials for these species.

The "unusual" isotope effect described here will also occur for the dimers of molecular hydrogen, for which the small number of bound levels<sup>18</sup> should enhance its importance in accurately determining the interaction potential. Moreover, it will also arise in complexes not formed from molecular hydrogen, such as the species  $(HF)_2$ , HCl-Ar, and HF-Ar studied by Klemperer and his colleagues,<sup>19-21</sup> or the molecules  $(O_2)_2$ ,  $O_2$ -Ar,  $N_2$ -Ar and  $(N_2)_2$  studied by Ewing and his co-workers.<sup>22-25</sup> However, the quantity  $(\delta/r)$  which governs the magnitude of these effects will be much smaller for these other cases. While replacing an H with a D in  $H_2$  corresponds to  $(\delta/r) = 0.1665$ , in HF and HCl it yields only 0.045 and 0.025, respectively, while isotopic substitution in  $N_2$  or  $O_2$  would yield relative center-of-mass shifts of only  $(\delta/r) = 0.017$  and 0.030. On the other hand, the magnitude of these correction terms also depends on the strength of the contributions to the original interaction potential. Since both isotropic and anisotropic parts of the potential are relatively stronger for the nonhydrogen species, this "unusual" isotope effect may also play an important role in determining their interaction potentials.

Another significant conclusion concerns the relatively small effect of odd-anisotropy contributions to the potential, upon the eigenvalues of one of these weakly bound van der Waals molecules. This should also apply to complexes formed from polar diatomic molecules such as HCl-Ar or HF-Ar, for which the  $P_1$  anisotropy is expected to be much stronger than the  $P_2$  term. As a result, their energy level spectra may turn out to be more like those for the hydrogen-inert gas complexes than might have been expected.

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APPENDIX: EXPLICIT EXPRESSIONS FOR  $U_k(R, \xi)$ 

Explicit expressions are presented for all contributions to the transformed potential  $U(R, \xi, \theta)$  of order less than  $t^5$ , which are obtained from Eq. (9) when the initial potential  $V(R', \xi, \theta')$  has nonzero Legendre components  $V_n(R', \xi)$  for  $n=0-4$ . As before,  $V_n^{(m)} \equiv \partial^m V_n(R, \xi)/\partial R^m$ .

$$U_0(R, \xi) = V_0 + t[-\frac{2}{3}V_1 - \frac{1}{3}RV_1^{(1)}] + t^2[\frac{2}{3}RV_0^{(1)} + \frac{1}{6}R^2V_0^{(2)} + \frac{1}{5}V_2 + \frac{1}{3}RV_2^{(1)} + \frac{1}{15}R^2V_2^{(2)}] + t^3[-\frac{2}{15}R^2V_1^{(2)} - \frac{1}{30}R^3V_1^{(3)} - \frac{1}{7}RV_3^{(1)} - \frac{3}{35}R^2V_3^{(2)} - \frac{1}{105}R^3V_3^{(3)}] + t^4[\frac{1}{30}R^3V_0^{(3)} + \frac{1}{120}R^4V_0^{(4)} + \frac{2}{70}V_2 - \frac{2}{70}RV_2^{(1)} + \frac{1}{70}R^2V_2^{(2)} + \frac{1}{30}R^3V_2^{(3)} + \frac{1}{210}R^4V_2^{(4)} - \frac{1}{63}V_4 + \frac{1}{63}RV_4^{(1)} + \frac{1}{21}R^2V_4^{(2)} + \frac{2}{135}R^3V_4^{(3)} + \frac{1}{945}R^4V_4^{(4)}] + O(t^5) \quad (A1)$$

$$U_1(R, \xi) = V_1 + t[-RV_0^{(1)} - \frac{6}{5}V_2 - \frac{2}{5}RV_2^{(1)}] + t^2[-\frac{3}{5}V_1 + \frac{3}{5}RV_1^{(1)} + \frac{3}{10}R^2V_1^{(2)} + \frac{24}{35}V_3 + \frac{3}{5}RV_3^{(1)} + \frac{3}{35}R^2V_3^{(2)}] + t^3[\frac{1}{5}RV_0^{(1)} - \frac{1}{5}R^2V_0^{(2)} - \frac{1}{10}R^3V_0^{(3)} + \frac{12}{35}V_2 + \frac{4}{35}RV_2^{(1)} - \frac{2}{7}R^2V_2^{(2)} - \frac{2}{35}R^3V_2^{(3)} - \frac{4}{21}V_4 - \frac{44}{105}RV_4^{(1)} - \frac{16}{105}R^2V_4^{(2)} - \frac{4}{315}R^3V_4^{(3)}] + t^4[-\frac{1}{14}R^2V_1^{(2)} + \frac{1}{14}R^3V_1^{(3)} + \frac{1}{56}R^4V_1^{(4)} - \frac{5}{21}RV_3^{(1)} + \frac{1}{21}R^2V_3^{(2)} + \frac{1}{14}R^3V_3^{(3)} + \frac{1}{126}R^4V_3^{(4)}] + O(t^5) \quad (A2)$$

$$U_2(R, \xi) = V_2 + t[\frac{2}{3}V_1 - \frac{2}{3}RV_1^{(1)} - \frac{12}{7}V_3 - \frac{3}{7}RV_3^{(1)}] + t^2[-\frac{1}{3}RV_0^{(1)} + \frac{1}{3}R^2V_0^{(2)} - \frac{11}{7}V_2 + \frac{11}{21}RV_2^{(1)} + \frac{11}{42}R^2V_2^{(2)} + \frac{10}{7}V_4 + \frac{6}{7}RV_4^{(1)} + \frac{2}{21}R^2V_4^{(2)}] + t^3[-\frac{4}{7}V_1 + \frac{4}{7}RV_1^{(1)} - \frac{2}{21}R^2V_1^{(2)} - \frac{2}{21}R^3V_1^{(3)} + \frac{4}{3}V_3 + \frac{1}{3}RV_3^{(1)} - \frac{1}{3}R^2V_3^{(2)} - \frac{1}{18}R^3V_3^{(3)}] + t^4[\frac{1}{7}RV_0^{(1)} - \frac{1}{7}R^2V_0^{(2)} + \frac{1}{42}R^3V_0^{(3)} + \frac{1}{42}R^4V_0^{(4)} + \frac{3}{7}V_2 - \frac{3}{14}R^2V_2^{(2)} + \frac{1}{14}R^3V_2^{(3)} + \frac{1}{56}R^4V_2^{(4)} - \frac{340}{693}V_4 - \frac{68}{99}RV_4^{(1)} + \frac{17}{231}R^2V_4^{(2)} + \frac{17}{189}R^3V_4^{(3)} + \frac{17}{2079}R^4V_4^{(4)}] + O(t^5) \quad (A3)$$

$$U_3(R, \xi) = V_3 + t[\frac{6}{5}V_2 - \frac{3}{5}RV_2^{(1)} - \frac{20}{9}V_4 - \frac{4}{9}RV_4^{(1)}] + t^2[\frac{3}{5}V_1 - \frac{3}{5}RV_1^{(1)} + \frac{1}{5}R^2V_1^{(2)} - \frac{46}{15}V_3 + \frac{23}{45}RV_3^{(1)} + \frac{23}{90}R^2V_3^{(2)}] + t^3[-\frac{1}{5}RV_0^{(1)} + \frac{1}{5}R^2V_0^{(2)} - \frac{1}{15}R^3V_0^{(3)} - \frac{28}{15}V_2 + \frac{14}{15}RV_2^{(1)} - \frac{7}{90}R^2V_2^{(2)} + \frac{112}{33}V_4 + \frac{112}{165}RV_4^{(1)} - \frac{196}{495}R^2V_4^{(2)} - \frac{28}{495}R^3V_4^{(3)}] + t^4[-\frac{5}{9}V_1 + \frac{5}{9}RV_1^{(1)} - \frac{1}{6}R^2V_1^{(2)} - \frac{1}{54}R^3V_1^{(3)} + \frac{1}{54}R^4V_1^{(4)} + \frac{65}{33}V_3 - \frac{13}{33}R^2V_3^{(2)} + \frac{13}{198}R^3V_3^{(3)} + \frac{13}{792}R^4V_3^{(4)}] + O(t^5) \quad (A4)$$

$$U_4(R, \xi) = V_4 + t[\frac{12}{7}V_3 - \frac{4}{7}RV_3^{(1)}] + t^2[\frac{46}{35}V_2 - \frac{6}{7}RV_2^{(1)} + \frac{6}{35}R^2V_2^{(2)} - \frac{390}{77}V_4 + \frac{39}{77}RV_4^{(1)} + \frac{39}{154}R^2V_4^{(2)}] + t^3[\frac{4}{7}V_1 - \frac{4}{7}RV_1^{(1)} + \frac{8}{35}R^2V_1^{(2)} - \frac{4}{105}R^3V_1^{(3)} - \frac{48}{11}V_3 + \frac{16}{11}RV_3^{(1)} + \frac{4}{55}R^2V_3^{(2)} - \frac{4}{55}R^3V_3^{(3)}] + t^4[-\frac{1}{7}RV_0^{(1)} + \frac{1}{7}R^2V_0^{(2)} - \frac{2}{35}R^3V_0^{(3)} + \frac{1}{105}R^4V_0^{(4)} - \frac{816}{385}V_2 + \frac{68}{55}RV_2^{(1)} - \frac{68}{385}R^2V_2^{(2)} - \frac{17}{385}R^3V_2^{(3)} + \frac{17}{1155}R^4V_2^{(4)} + \frac{5787}{1001}V_4 - \frac{843}{1001}R^2V_4^{(2)} + \frac{643}{10010}R^3V_4^{(3)} + \frac{643}{40040}R^4V_4^{(4)}] + O(t^5) \quad (A5)$$

$$U_5(R, \xi) = t[\frac{20}{9}V_4 - \frac{5}{9}RV_4^{(1)}] + t^2[\frac{30}{21}V_3 - \frac{10}{9}RV_3^{(1)} + \frac{10}{63}R^2V_3^{(2)}] + t^3[\frac{32}{21}V_2 - \frac{22}{21}RV_2^{(1)} + \frac{2}{7}R^2V_2^{(2)} - \frac{2}{63}R^3V_2^{(3)} - \frac{2300}{273}V_4 + \frac{575}{273}RV_4^{(1)} + \frac{115}{819}R^2V_4^{(2)} - \frac{115}{1638}R^3V_4^{(3)}] + t^4[\frac{5}{9}V_1 - \frac{5}{9}RV_1^{(1)} + \frac{5}{21}R^2V_1^{(2)} - \frac{10}{189}R^3V_1^{(3)} + \frac{1}{189}R^4V_1^{(4)} - \frac{1540}{273}V_3 + \frac{220}{91}RV_3^{(1)} - \frac{55}{273}R^2V_3^{(2)} - \frac{55}{819}R^3V_3^{(3)} + \frac{11}{819}R^4V_3^{(4)}] + O(t^5) \quad (A6)$$

$$U_6(R, \xi) = t^2[\frac{40}{11}V_4 - \frac{15}{11}RV_4^{(1)} + \frac{5}{35}R^2V_4^{(2)}] + t^3[\frac{100}{33}V_3 - \frac{380}{231}RV_3^{(1)} + \frac{80}{231}R^2V_3^{(2)} - \frac{20}{693}R^3V_3^{(3)}] + t^4[\frac{126}{77}V_2 - \frac{93}{77}RV_2^{(1)} + \frac{29}{77}R^2V_2^{(2)} - \frac{2}{33}R^3V_2^{(3)} + \frac{1}{231}R^4V_2^{(4)} - \frac{8480}{693}V_4 + \frac{265}{63}RV_4^{(1)} - \frac{53}{231}R^2V_4^{(2)} - \frac{53}{594}R^3V_4^{(3)} + \frac{53}{4158}R^4V_4^{(4)}] + O(t^5) \quad (A7)$$

$$U_7(R, \xi) = t^3[\frac{2240}{429}V_4 - \frac{1015}{429}RV_4^{(1)} + \frac{175}{429}R^2V_4^{(2)} - \frac{35}{1287}R^3V_4^{(3)}] + t^4[\frac{525}{143}V_3 - \frac{95}{35}RV_3^{(1)} + \frac{235}{429}R^2V_3^{(2)} - \frac{10}{143}R^3V_3^{(3)} + \frac{5}{1287}R^4V_3^{(4)}] + O(t^5) \quad (A8)$$

$$U_8(R, \xi) = t^4[\frac{8960}{1287}V_4 - \frac{350}{99}RV_4^{(1)} + \frac{323}{423}R^2V_4^{(2)} - \frac{28}{351}R^3V_4^{(3)} + \frac{14}{3861}R^4V_4^{(4)}] + O(t^5) \quad (A9)$$

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†Present address: Computer Center, University of Regina, Regina, Saskatchewan, Canada S4S 0A2.

‡Alfred P. Sloan Foundation Fellow.

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