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Interpolated potential energy surfaces and dynamics for atom exchange between H and H_3^+, and D and H_3^+

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Two *ab initio* interpolated potential energy surfaces have been constructed to study the dynamics of atomic hydrogen/deuterium exchange in collisions of H_3^+ with H (D). One of the surfaces is based on energy calculations using quadratic configuration interaction with single and double excitations. The second includes a perturbative treatment of the triple excitations and an additive correction for basis set deficiency. Results from classical dynamics simulation of the exchange reaction on these surfaces are presented and discussed.
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I. INTRODUCTION

Reactions of the form

$$H_3^+ + X \rightarrow XH_2^+ + H \tag{1.1}$$

and

$$H_3^+ + X \rightarrow XH^+ + H_2, \tag{1.2}$$

where X denotes an element, have been proposed as the initial steps in complex processes of molecular synthesis in interstellar chemistry.[1] The particular case of Eq. (1.1) in which H_3^+ reacts with a deuterium atom has been suggested by Dalgarno and Lepp[2] as an important contributor to deuterium fractionation in the interstellar medium. The product H_2D^+ should play an important role in the deuteration of many interstellar molecules. The experimental measurement of the corresponding rate for Eq. (1.1) has been impeded by parallel processes, and only an estimated value is available in the literature.[3] This estimated rate is close to the Langevin value[3] at about 20 K. For these reasons, a theoretical evaluation of the reaction dynamics would be useful. An accurate, fully quantum, calculation of the cross section and thermal rate coefficient of this reaction might be feasible if an accurate potential energy surface (PES) were available. Such a surface is the subject of this paper.

The interaction between H_3^+ and H has also been studied in order to solve the questions of whether the H_4^+ cluster and its relatives H_{2n}^+ with an even number of hydrogen atoms $(n>2)$ exist, what their structures are, and why these clusters are more difficult to obtain experimentally than the odd numbered ionic clusters of hydrogen.[4–7] The H_4^+ ion and other even numbered members of the family H_n^+ were observed for the first time in experiments on collision-induced dissociation of the odd H_n^+ clusters.[4,5] Other methods successfully used in the production of the odd H_n^+ clusters yield no amount of H_4^+ or other even H_n^+ clusters.

The theoretical study of this system has produced detailed, accurate, *ab initio* calculations of stationary points on the potential energy surface (PES) of H_4^+, with special attention to the Jahn–Teller distortions, which preclude stability in H_4^+ configurations with symmetries D_{4h} and T_d.[6–10] These calculations have been based on configuration interaction with all single and double substitutions,[6,8] and quadratic configuration interaction with all single and double substitutions (QCISD).[10] A local PES fitted to multiple reference single and double excitations configuration interaction (MRD-CI) calculations, has been reported for a vibrational analysis of H_4^+.[9]

The most stable structure for the H_4^+ cluster, from these calculations, is a triangular $H_3^{\delta+}$ bound to a partially charged hydrogen atom $H^{\delta+}$, in a planar (C_{2v}) configuration, as illustrated in Fig. 1. The energy of this structure depends only weakly on the H to H_3^+ distance.[7] The minimum energy from these calculations is just 10.5 kJ/mol below that of $H_3^+ + H$.[8,9] A significantly deeper minimum is reported here for a similar structure.

The reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H, \tag{1.3}$$

which proceeds on the H_4^+ surface, is known as an important source of H_3^+ ions. This reaction seems to occur by a direct mechanism in which the formation of a H_4^+ complex plays little role.[4,11] Here, we do not consider the higher energy region of the PES associated with $H_2^+ + H_2$.

In this paper, we report an *ab initio* interpolated PES for the ground electronic state of H_4^+, and classical dynamics simulations of low energy collisions between $H_3^+ + H$ and the isotopic analog $H_3^+ + D$. We analyze the reactions at different relative kinetic energies of the colliding fragments, and discuss aspects of the dynamics in common with other processes of the form (1.1), for which interpolated PES have been constructed in the past. However, due to the character of the PES revealed here, the prediction of accurate rate coefficients for the reactions between H_3^+ and H, in the typical conditions of interstellar chemistry, is likely to require a quantum dynamics treatment. The accurate PES reported here should provide the basis for such calculations.

This paper is set out as follows: Section II contains a description of the methods used to construct the PES and

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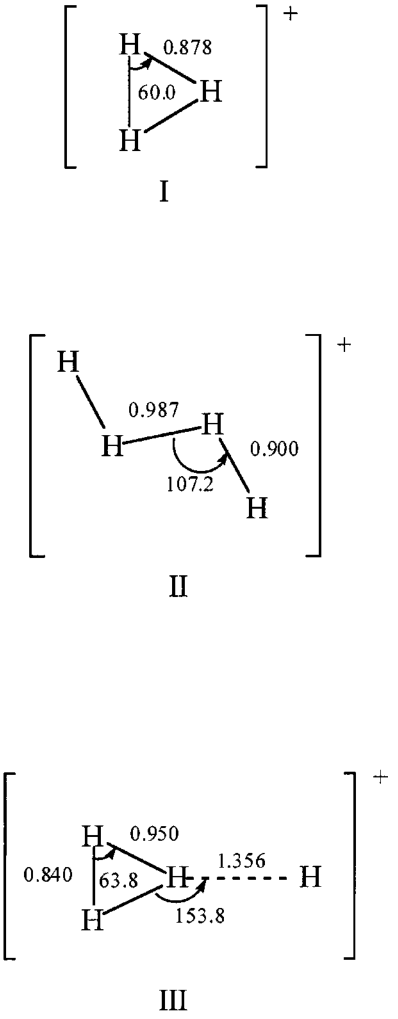

FIG. 1. Optimized molecular geometries at the QCISD/6-311G** level for H_3^+ (I), the H_4^+ transition state (II), and the H_4^+ complex (III).

evaluate the dynamics. Section III presents the interpolated PES and the results of the classical simulations of the reactions. The conclusions and additional comments regarding this work are presented in Sec. IV.

II. METHODS

A. Construction of the potential energy surface

The PES was constructed by a modified Sheppard interpolation method,[12] over a *data set* of *ab initio* points. The current method has been described in detail elsewhere,[13–16] so only a brief presentation in given here.

The interpolated PES has the form

$$E(\mathbf{Z})=\sum_{g\in G}\sum_{i=1}^{N_{data}} w_{goi}(\mathbf{Z})T_{goi}(\mathbf{Z}). \tag{2.1}$$

In Eq. (2.1), N_{data} is the number of *data points* or molecular configurations around which the energy is approximated by local second order Taylor expansions T_i. The Taylor expansions are constructed by calculating the *ab initio* energies and up to energy second derivatives at each of the data points. Those expansions are combined in a weighted average, according to Eq. (2.1), where the sum over index $g\in G$ is made in order to include all possible equivalents of a data point configuration by permutation of identical nuclei.

The variables upon which the sum (2.1) depends are the inverse interatomic distances $\mathbf{Z}=\{Z_l,\ldots,Z_k,\ldots,Z_{N(N-l)/2}\}$, where $Z_k=\mathrm{I}/R_k$ and N is the number of atoms in the system. The weights w_i depend on the distances from the data points as well as on the "confidence lengths" which are estimated for each data point from a Bayesian statistical analysis of the errors.[14] In this work the confidence lengths were evaluated using an energy tolerance, $E_{tol}=1.31$ kJ/mol, and energy gradients at $M=100$ data points (see Ref. 14 for definitions of E_{tol} and M).

An initial set of data points is usually constructed with the stable molecular configurations and a few geometries along the minimum energy paths for the reactions studied. Further data points are sampled from a set of molecular configurations encountered along classical trajectories in simulations of the reaction. These simulations and the sampling of new data points for the PES are performed in an iterative fashion according to an automated procedure, which is described in detail elsewhere.[15–17] The construction of the PES and the classical trajectory simulations were performed with the program suite GROW.[16]

B. *Ab initio* methods and initial data points for the PES

The critical points on the H_4^+ PES, corresponding to the stable species $H+H_3^+$, the complex H_4^+, and the transition state for the exchange reaction (1.1) (with $X=$H or D) were determined by geometry optimization at the Möller-Plesset perturbation theory (MP2) and QCISD levels of theory with a 6-311G(d,p) basis set. The energy of the QCISD/6-311G(d,p) optimized configurations (see Fig. 1) was calculated using MP2, QCISD, QCISD(T), and coupled cluster treatment with single and double excitations and perturbative treatment of triple excitations CCSD(T), with various size basis sets. The numerical results are shown in Table I. All the electronic structure calculations in this work were performed with the GAUSSIAN98 suite of programs.[18] The values for the bond lengths and angles at the stationary points are consistent with those found in the literature for the H_4^+ complex at the QCISD/6-31G(d,p) level,[10] and for the H_3^+ ion, at the most accurate levels of approximation currently available.[19]

As Fig. 2 indicates, structure II in Fig. 1 is a saddle point for the isomerization between equivalent minima (structure III). Separation of the H and H_3^+ moieties, following isomerization, is the mechanism for exchange. According to Table I, the variation of the well depth and barrier height with different basis sets is very similar for different levels of *ab initio* approximation. Moreover, it seems evident that the well depth and barrier height are converged with respect to basis set size for the largest basis sets considered. In addition, the variation in the well depth and barrier height between MP2, QCISD, and QCISD(T) calculations is relatively small, which suggests that these values are converged with respect to the treatment of electron correlation. The most reliable results give a well depth of about 23.1 kJ/mol and a barrier

TABLE I. The energy of the two stationary points on the path for reaction (1.1) with $X=\mathrm{H}$, relative to the energy of $\mathrm{H}_3^+ + \mathrm{H}$, for various *ab initio* methods and basis sets. The well depth corresponds to the minimum structure III and the barrier height to structure II of Fig. 1.

Method	Well depth (kJ/mol)	Energy barrier (kJ/mol)
MP2/6-311G**	−15.7	33.2
MP2/6-311++G(3*df*,2*pd*)	−19.1	29.5
MP2/cc-pVTZ	−19.4	29.2
MP2/aug-cc-pVTZ	−20.1	28.3
MP2/cc-pVQZ	−20.2	28.0
MP2/cc-pV5Z	−20.4	27.8
QCISD/6-311G**	−17.8	21.1
QCISD/6-311++G(3*df*,2*pd*)	−21.6	16.7
QCISD/cc-pVTZ	−21.8	16.6
QCISD/aug-cc-pVTZ	−22.5	15.6
QCISD/cc-pVQZ	−22.5	15.5
QCISD(T)/6-311G**	−18.2	20.3
QCISD(T)/cc-pVTZ	−22.4	15.5
QCISD(T)/cc-pVQZ	−23.1	14.4
QCISD(T)/aug-cc-pVTZ	−23.1	14.6
CCSD/6-311G**	−17.8	21.2
CCSD(T)/6-311G**	−18.2	20.4
Equation (2.2)	−22.6	15.4

height of about 14.4 kJ/mol. This well depth is significantly larger than 10.5 kJ/mol reported from MRD-CI calculations.[9]

The construction of a global PES requires calculation of the energy, energy gradient, and second derivative matrix at many hundreds of molecular configurations. Hence, the choice of *ab initio* level for the PES is constrained to be below the most reliable level shown in Table I. Two different *ab initio* approaches were chosen to calculate the PES: First, the QCISD/6-311G(d,p) method was used with evaluation of the second energy derivatives by numerical finite differences. Second, an approximation based on the QCISD(T) method was used with an additive correction for the basis set deficiency in the treatment of electronic correlation. This correction is calculated according to the expression

$$E[\mathrm{QCISD(T)/aug\text{-}cc\text{-}pVTZ}] \approx E[\mathrm{QCISD(T)/6\text{-}311G}(d,p)] + \Delta_{basis}, \tag{2.2a}$$

where

$$\Delta_{basis} = E[\mathrm{MP2/aug\text{-}cc\text{-}pVTZ}] - E[\mathrm{MP2/6\text{-}311G}(d,p)]. \tag{2.2b}$$

This sort of additive correction is similar to that employed for G2(MP2) calculations.[20] Table I shows that Eq. (2.2) provides an accurate estimate of the well depth and barrier height in comparison with the most reliable QCISD(T)/cc-pVQZ calculations. Moreover, this approach is computationally feasible for the construction of a global PES. For the method of Eq. (2.2), the first and second derivatives of the energy at the data points were calculated by a combination of analytic derivatives and numerical finite differences. The set of initial data points used for both PES contained 27 geometries, including the stationary geometries for the complex and transition state, the H_3^+ ion at a long distance (20 Å) from a H atom, and 24 geometries along the reaction path for exchange (1.1) with $X=\mathrm{H}$.

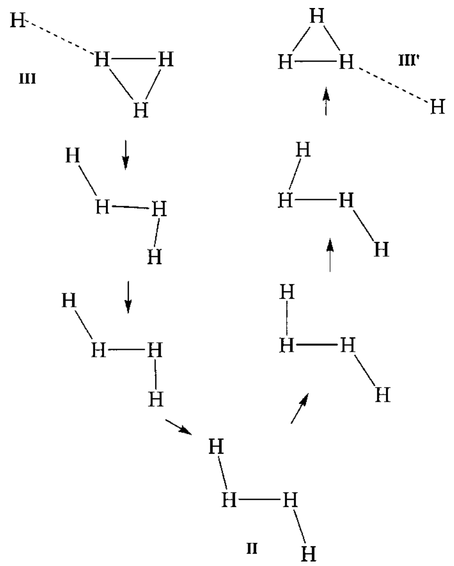

FIG. 2. Some molecular configurations found along the intrinsic reaction coordinate for the interconversion of two equivalent (permuted) versions of the H_4^+ complex (III in Fig. 1).

C. Classical trajectories

Classical trajectory calculations for the collisions between the species H_3^+ and H, and H_3^+ and D, were performed to sample the relevant configuration space during the construction of the PES and to evaluate the scattering cross sections. A velocity-Verlet integration algorithm[21] was used with a time step size of 1.0×10^{-17} s. The trajectories were initialized at the $\mathrm{H}_3^+ + \mathrm{H/D}$ asymptote with a center of mass separation between the fragments of 11.6 Å (22.0 bohr). The calculation of all trajectories was terminated when the fragments, moving apart, reached the same distance. For all the trajectory calculations, H_3^+ was given an initial vibrational energy corresponding to the zero point vibrational energy (ZPVE≃55.39 kJ/mol). The initial rotational angular momentum of the fragments was set to zero. The initial atomic velocities and geometric configurations for the reactants were obtained using the efficient microcanonical sampling method of Schranz *et al.*[22]

During the PES construction, the relative kinetic energy between the fragments was set to 7.88 kJ/mol and the impact parameter was set to zero. For calculation of the exchange cross sections, the relative kinetic energy of the fragments was taken in the range between 1.31 and 19.69 kJ/mol. Batches of 2500 trajectories were run at each kinetic energy. The impact parameter b was selected at random from a distribution of values limited by a maximum exceeding the largest value at which reaction was obtained for a particular relative kinetic energy between the fragments. The distribution of b values was such that the probability of a trajectory having an impact parameter between b and $b+db$ was proportional to b.

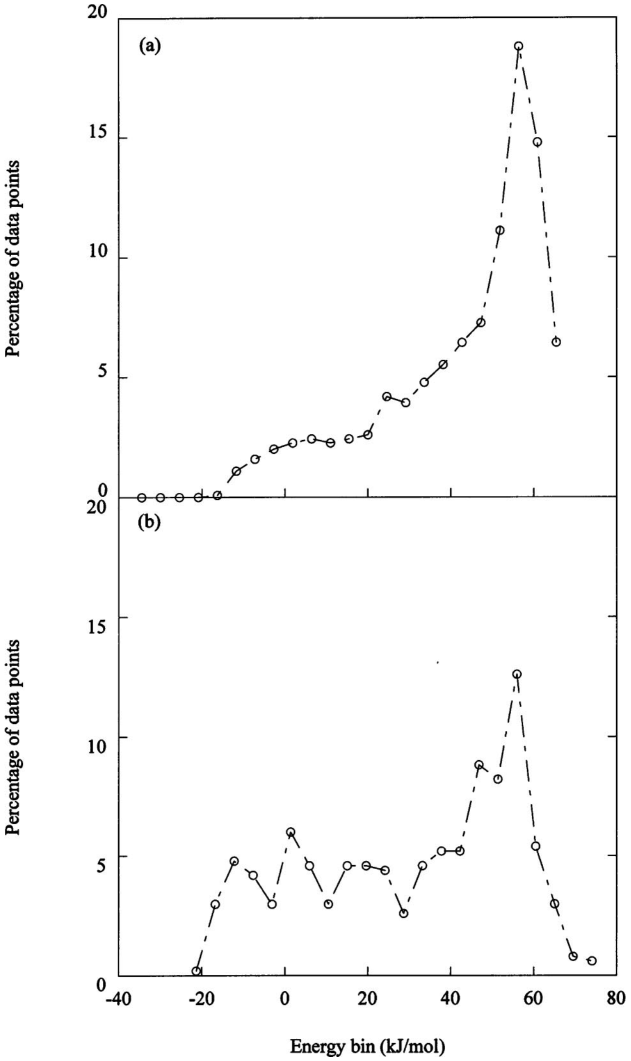

FIG. 3. Histograms of (a) the PES-*A* data point energies and (b) the PES-*B* data point energies. For both histograms, the reference energy corresponds to that of the separated fragments $\mathrm{H}_3^+ + \mathrm{H}$. A bin size of 4.54 kJ/mol was used.

III. RESULTS AND DISCUSSION

A. Interpolated potential energy surfaces

A QCISD/6-311G(d,p) interpolated PES with 1196 data points (denoted as PES-*A*), and a second 500 data point PES (denoted as PES-*B*), based on Eq. (2.2), were calculated for the H_4^+ system. Figures 3(a) and 3(b) present histograms which show the distribution of energy values for each of the two interpolation data sets. The maxima in these distributions occur at about 56.38 kJ/mol and 55.93 kJ/mol above the energy of $\mathrm{H}_3^+ + \mathrm{H}$, for PES-*A* and PES-*B*, respectively.

The convergence of the surfaces was demonstrated by calculating the cross section for reaction (1.1) (with $X = \mathrm{D}$ and H) at different data set sizes (see Figs. 4 and 5). At the final data set sizes, both surfaces can be considered converged for the hydrogen exchange cross sections.

The accuracy of the interpolation was estimated by calculating the interpolation error (the difference between the *ab initio* and the interpolated energy) at a random sample of molecular configurations encountered along classical trajectories. Using a set of 4739 configurations, the maximum interpolation errors found were 1.39 kJ/mol for PES-*A* and 1.08 kJ/mol for PES-*B*. The average interpolation errors found, with respect to the same reference set of geometries, were equal to 0.15 kJ/mol (0.18% of the range of energy values for the trajectory points) for both surfaces.

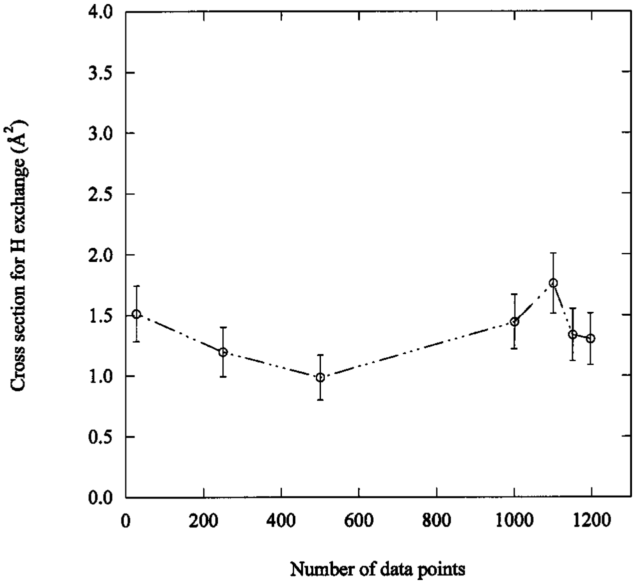

FIG. 4. The cross section for reaction (1.1) with $X = \mathrm{H}$ as a function of the PES data set size (at a relative kinetic energy of the reactants of 13.13 kJ/mol) for dynamics on PES-*A*. The error bars denote one standard deviation for 2500 trajectories.

B. Classical simulations of $\mathbf{H}_3^+ + \mathbf{H}$ and $\mathbf{H}_3^+ + \mathbf{D}$ collisions

In order to determine the classical cross section for the hydrogen (deuterium) exchange as a function of energy, batches of 2500 trajectories were run at seven relative translational energies of the fragments using the interpolated

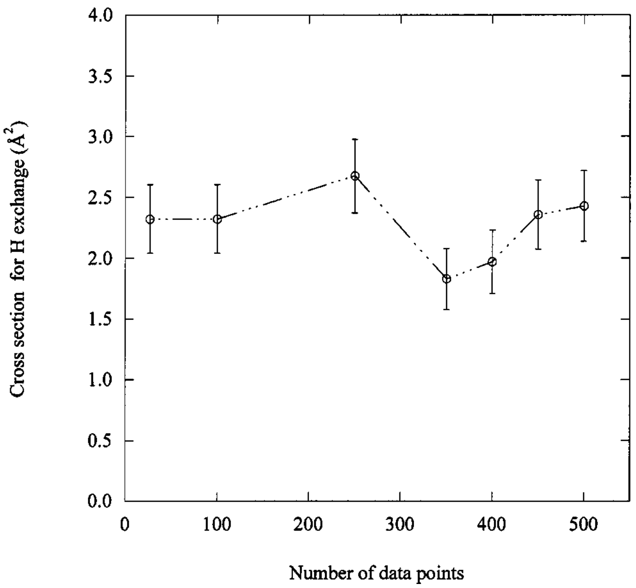

FIG. 5. As in Fig. 4, for dynamics on PES-*B*.

TABLE II. Cross sections (Å^2) for reaction (1.1) with $X=\text{H}$ and $X=\text{D}$, as a function of the relative kinetic energy of the reactants. The classical dynamics were evaluated on PES-*B*.

Energy (kJ/mol)	$\sigma\{\text{H}_3^+ + \text{H}\}$	$\sigma\{\text{H}_3^+ + \text{D}\}$
1.31	10.8±0.7	11.4±0.8
1.97	8.2±0.7	9.7±0.8
2.63	7.1±0.6	8.1±0.6
3.94	4.9±0.4	5.2±0.4
6.56	3.8±0.3	⋯
7.88	⋯	3.5±0.2
13.13	2.4±0.2	2.7±0.2
19.69	2.4±0.2	2.1±0.2

PES-*B*. The reaction cross sections are shown in Table II. Logarithmic plots of these cross sections along with the Langevin cross section (see Sec. 8.3.4 in Ref. 23, and references cited therein) are shown in Fig. 6. It can be seen that the values of the cross section for the exchange of hydrogen are coincident with those for the exchange of deuterium within the statistical uncertainty. The corresponding Langevin values are between 10–15 times higher than those obtained from the classical dynamics on PES-*B*. It is important to note that the literature on interstellar chemistry considers the Langevin value as a reference for the rate of these hydrogen/deuterium exchange reactions.[3]

It is useful to discuss these results for the exchange cross section in comparison with the cross sections for exchange in the $\text{H}_2/\text{D}_2+\text{H}_3^+$ reaction. The PESs of H_4^+ and H_5^+ have ion-molecule wells of comparable depth; about 22.6 kJ/mol for PES-*B* and about 33.3 kJ/mol for the PES on which D_2+H_3^+ has been studied.[24] The polarizabilities of H and H_2 are comparable, so that the Langevin capture cross sections for $\text{H}+\text{H}_3^+$ and H_2+H_3^+ reaction are very similar (to with about 8%). It is clear from Fig. 6 that the exchange cross section displays (approximately) the Langevin dependence on the relative collision energy, $E^{-1/2}$. The same is true for exchange in $\text{H}_2/\text{D}_2+\text{H}_3^+$. Hence, we might infer that ion-molecule capture occurs in both these systems, more or less according to the Langevin model. In that case, the exchange reaction would require rearrangement in the ion-molecule complex following capture.

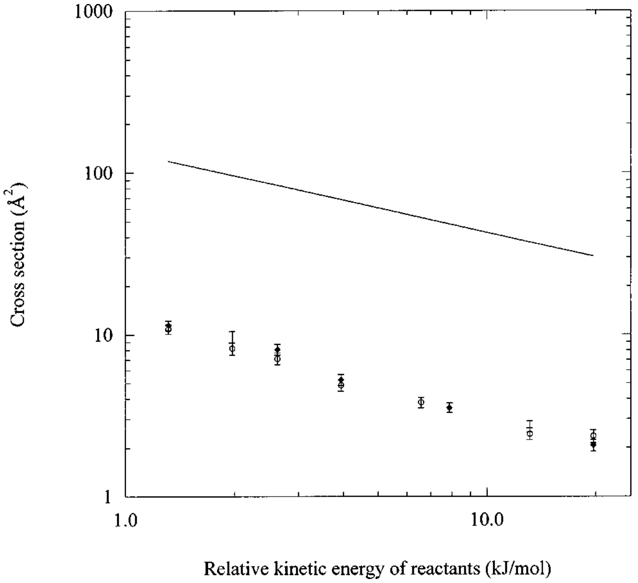

FIG. 6. The classical cross section for atom exchange (open circles correspond to H exchange and solid diamonds to D exchange) as a function of the relative kinetic energy of the reactants, evaluated on PES-*B*. The error bars denote one standard deviation for 2500 trajectories. The solid line represents the Langevin cross section.

The PES for H_5^+ shows many different stationary point structures in the ion-molecule well, all of comparable, low energy. This implies that there are no significant barriers to complicated rearrangement of the H atoms in the H_5^+ well. The cross sections for exchange in the $\text{H}_2/\text{D}_2+\text{H}_3^+$ reactions are below the Langevin limit (by almost 50%), but are a factor of about 8 larger than those for $\text{H/D}+\text{H}_3^+$. For the later system, PES-*B* shows just one type of stable structure for the ion-molecule complex and a substantial barrier (about 38 kJ/mol, relative to the minimum) to rearrangement in the complex. We recall that the ZPVE for H_3^+ is about 55.4 kJ/mol and that the ion-molecule minimum is about 22.6 kJ/mol for PES-*B*. Hence, even at zero translational energy, the ion-molecule complex has about 78 kJ/mol available energy, relative to the minimum. Nevertheless, although the total energy available may be well above any barrier to rearrangement, this barrier appears to reduce the reaction cross section by about an order of magnitude compared to $\text{H}_2/\text{D}_2+\text{H}_3^+$. This conclusion is consistent with the observation that PES-*A*, which has a higher barrier to rearrangement, produces smaller cross section for exchange than does PES-*B* (for example, 1.3±0.2 Å^2 compared to 2.4±0.2 Å^2 at a relative translational energy of 13.13 kJ/mol).

Unfortunately, the classical cross sections reported here for the exchange reaction cannot be reliably used to predict rate coefficients for the interstellar medium, because quantum effects are likely to be very significant. Given the low masses of H and D atoms, and the high ZPVE of H_3^+ relative to the barrier for rearrangement in the H_4^+ well, it is likely that the quantum wave function for H_4^+ would delocalize over all equivalent H_4^+ structures. Hence, the quantum cross section for exchange in $\text{D}+\text{H}_3^+$ might be larger than the classical simulation suggests.

IV. CONCLUDING REMARKS

Two *ab initio* interpolated energy surfaces have been constructed for the dynamics of atomic hydrogen/deuterium exchange with H_3^+. PES-*A* is based on QCISD/6-311G(d,p) calculations, whereas the more accurate PES-*B* is based on the composite level of approximation of Eq. (2.2). Classical dynamics for the hydrogen exchange run at the same initial conditions on the two PESs give cross sections which differ by about 50%.

There are no experimental results for the rate of exchange to test the predictions from the classical collisions. However, given that the harmonic ZPVE of the H_3^+ ion is about twice as high as the classical energy barrier for the atom exchange reaction, quantum dynamic behavior should be expected under the conditions of the interstellar medium. PES-*B* provides the basis for accurate quantum calculations of the exchange rate coefficient. The software and data for PES-*A* and PES-*B* are available as EPAPS documents.[25] This data and the GROW software are available from the authors on request.

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[25] See EPAPS Document No. E-JCPSA6-121-003445 for the data file and software to evaluate the PES. A direct link to this document may be found in the online article's HTML reference section. The document may also be reached via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.