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Potential energy and dipole moment surfaces of $H_3^-$ molecule

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A new potential energy surface for the electronic ground state of the simplest triatomic anion $H_3^-$ is determined for a large number of geometries. Its accuracy is improved at short and large distances compared to previous studies. The permanent dipole moment surface of the state is also computed for the first time. Nine vibrational levels of $H_3^-$ and 14 levels of $D_3^-$ are obtained, bound by at most $\sim 70$ and $\sim 126$ cm$^{-1}$, respectively. These results should guide the spectroscopic search of the $H_3^-$ ion in cold gases (below 100K) of molecular hydrogen in the presence of $H^-$ ions. © 2010 American Institute of Physics. [doi:10.1063/1.3424847]

I. INTRODUCTION

Collisions involving hydrogen atoms, molecules, and their positive ($H^+$, $H_2^+$) and negative ($H^-$) ions play an important role in chemistry and evolution of neutral or negatively charged hydrogen plasma such as laboratory hydrogen plasma, the interstellar medium (ISM), atmospheres of the Sun and other stars, as well as the Earth atmosphere. Binary collisions of these species are simple enough to be treated using first principle methods without any adjustable parameter. Therefore, such processes are often used as benchmarks for testing theoretical methods.

The existence of bound states of the $H_3^-$ ion in a linear configuration for the three nuclei has been suggested in 1937, but has been questioned since then. Different ab initio calculations have been giving contradictory results for the depth of the potential well. The estimated error bar in the calculations was comparable or larger than obtained binding energies, so the calculations could not predict for sure if the $H_3^-$ ion is stable. Although first observations of $H_3^-$ ions have been reported in low resolution experiments as early as in 1974, they could not warrant either the stability of $H_3^-$. It is only in the 1990s (Refs. 10 and 18) that theory became precise enough to confirm the stability of the $H_3^-$ anion.

At present, there are three available accurate potential energy surfaces (PES) of $H_3^-$: the PES by Stüric and Meyer, by Belyaev and Tiukanov, and by Panda and Sathyamurthy. In the following, these three PES will be referred to as PES-SM, PES-BT, and PES-PS, respectively. In addition, Belyaev et al. have obtained PES of excited electronic states of $H_3^-$ and their non-Born–Oppenheimer couplings with the ground state. The excited electronic states are unstable with respect to electron autodetachment. Bound state calculation based on the PES-SM have been performed for $H_3^-$, $H_2D^-$, and $D_3H^-$ in Ref. 10 and using the PES-BT for $H_3^-$ in Ref. 16. It is worth to mention a stand alone study by Robicheaux confirming the stability of $H_3^-$ (and similar ions), where the PES was derived from the scattering length for the electron-H$^-$ collisions, and from the polarizability of $H_2$.

While never observed in the ISM, the collisions between $H_2$ and $H^-$, and of their isotopologues, have been studied in a number of laboratory experiments back to the 1950s. Such collisions should also play a role in processes in tokamaks, especially if the negative ion source is used for the tokamak neutral beam injectors. Many studies have been devoted to the calculation of elastic and inelastic cross sections for $H_2^+H^-^+$ collisions and for all isotopologues, most of them for energies significantly larger than 1 eV above the lowest dissociation limit of $H_2^+H^-$. However, at such energies the theoretical cross sections may not be reliable. The dissociation energy of the $H_3$ ground state lies only 0.75 eV above the $H_3^-$ dissociation energy, and the non-Born–Oppenheimer interaction between the ground states of $H_3$ and $H_3^-$ could be significant. The non-Born–Oppenheimer interactions have been taken into account only in Ref. 47 within a reduced-dimensionality approach, where only linear geometries of $H_3^-$ have been taken into account. Finally, the photodissociation of $H_3D^-$ has been studied in a simplified approach based on the Franck–Condon overlap between a bound level and a scattering state of $H_3D^-$, since the ab initio dipole moments of $H_3^-$ were not available at that time.

The present study is mainly motivated by the formation of $H_3^-$ bound states in low-energy collisions between $H_2$ and $H^-$. In such collisions $H_3^-$ can be formed only if a third body (other than $H_2$ or $H^-$) participates (three-body recombination) or if a photon is emitted [radiative association (RA)]. Both processes could be relevant for the chemistry of cold interstellar clouds, if $H^-$ is present. Note that the $H^-$ ion has not been detected so far in the ISM: it cannot be directly observed by usual photoabsorption spectroscopy because $H^-$ has only one bound electronic state.

The evaluation of the cross section for RA of $H_2$ and $H^-$ at low energy (10–30 K) requires an accurate PES with a precision around 1 cm$^{-1}$ or better, and permanent dipole moment surfaces (PDMS) for $H_3^-$. In the present study, we calculated a new ab initio PES for the $H_3^-$ electronic ground
state on a dense and large grid for internal coordinates, using a larger electronic basis set than those of PES-SM and PES-PS calculations. Special care is taken in order to account for the long-range behavior of the surface. We also obtain for the first time the PDMS of the H$_3$ electronic ground state. We constructed FORTRAN subroutines, yielded as supplementary material to the paper, that calculate PES and PDMS values for any arbitrary geometry using B-spline interpolation procedures, and we determine the bound states of H$_3$ and D$_3$. The RA reaction will be treated in a separate study.

The article is organized in the following way. In Sec. II, we discuss the calculation of the new PES and the interpolation procedure. In Sec. III, we compare the new PES with the PES from previous studies. Section IV is devoted to the calculation of bound levels of H$_3$ and D$_3$ and Sec. V presents our results on the dipole moment of H$_3$. Section VI is the conclusion. Atomic units (a.u.) for distances (1 a.u. =0.052 917 7 nm) and for energies (1 a.u. =219.474.631 37 cm$^{-1}$) will be used throughout the paper, except otherwise stated.

II. AB INITIO CALCULATION AND INTERPOLATION OF THE H$_3$ GROUND STATE POTENTIAL SURFACE

As in Ref. 10, we used the coupled-electron pair approximation (CEPA-2) method,$^{50}$ which is part of the MOLPRO package.$^{51}$ It is a nonvariational variant of the configuration interaction method for closed-shell molecules. Here we used a considerably larger basis set, AVSZ with spdfg basis functions from the MOLPRO basis library, and a much larger number of geometries, than in Refs 10 and 11. The reasons for choosing this method and a comparison with other $ab$ initio methods are presented in Appendix, Sec. I.

As explained below, the H$_3$ molecule is weakly bound by long-range electrostatic forces with no electron exchange. We defined a three-dimensional (3D)-grid in Jacobi coordinates: $r$—the distance between two protons, $R$—the distance from the center of mass of the two protons to the third proton, and $\gamma$—the angle between vectors $\vec{R}$ and $\vec{r}$. The grid in $r$ is uniform from $r=0.8$ a.u. to $r=2.4$ a.u. and changes by a step $\Delta r=0.2$ a.u. The grid in $\gamma$ changes from 0° to 90° by a constant step of $\Delta \gamma=15°$. The grid in $R$ was chosen denser for small $R$ than for large $R$: the grid points $R_i$ were calculated according to $R_i=1.5+0.452 \exp(i/10)$ (in a.u.) with $i=1,2,\ldots,48$, which makes $R$ changing from 1.9995 to 56.4227 a.u. Therefore, the calculations were performed for $9\times7\times48=3024$ geometries. Notice that the above grid starts at a smaller value of $r=0.8$ a.u. than in Refs. 10 and 11 ($r=1$ a.u.). Indeed, we found that a grid starting at $r=1$ a.u. cannot properly represent the repulsive part of the H$_2$ ground state potential curve (at fixed $R$ and $\gamma$) and gives an appreciable error in energies obtained of the lowest H$_2$ vibrational levels and, as a result, a comparable error in dissociation energies of H$_3^+\rightarrow$H$_2^+(\nu,j)+\text{H}^-$ when $R\rightarrow\infty$. We also used a denser grid in $\gamma$ and a longer and denser grid in $R$ than in Refs. 10 and 11.

For each geometry, we calculated the potential energy of the H$_3$ ground state, and the components of the PDM vector with respect to the principal axes of inertia. The obtained $ab$ initio PES and PDMS were used to prepare FORTRAN subroutines that calculate PES and PDMS for any arbitrary geometry. The FORTRAN subroutines are available in the supplementary material$^{72}$ and can be provided by the authors upon request. Inside the 3D box $r\in[0.8;2.4], R\in[1.9995;56.4227], \gamma\in[0;360°]$ (central region in Fig. 1) the procedures interpolate the surfaces using the 3D B-spline method. Outside of the box, the procedures rely on analytical formulas for the extrapolation of PES and PDMS. To simplify the description of this region, we divided the $r\times R$ configuration space in four different parts (I-IV) surrounding the $ab$ initio rectangle (Fig. 1). Regions “$ab$ initio” and II are the only ones relevant to bound and scattering states of the system with energies $\leq 2$ eV above the H$_2^+(\nu=0,j=0)+\text{H}^-$ dissociation. Therefore, the extrapolation procedure for the PES and PDMS in the two regions should be physically justified. In contrast, wave functions of bound and continuum states with such energies vanish in regions I, III, and IV, and empirical formulas will be used. As it will be discussed in Sec. IV, the extrapolation is needed to map the configuration space in Jacobi coordinates on the space of hyperspherical coordinates, which will be used for bound state and scattering calculations.

In region II, we represent the long-range (in $R$, at fixed $r$ and $\gamma$) potential $V_{LR}$ for the interaction between H$_2$ and H$^-$ as$^{52}$

$$V_{LR}(R; r, \gamma) = D_{ii}(r) + \frac{C_3}{R^3} + \frac{C_4}{R^4},$$

with
where the first term $D_{ab}(r)$ is the sum of $H^+$ and $H_2$ energies at a given internuclear distance $r$ of the $H_2$ molecule. The second term is the interaction between the electric charge of $H^+$ with the quadrupole moment $Q(r)$ of $H_2$ (taken from Ref. 53), and the third term is the interaction of the dipole moment of $H_2$ induced by $H^+$, involving the second order Legendre polynomial $P_2(\cos \gamma)$. The functions $\alpha_0(r)$ and $\alpha_2(r)$ are the isotropic and anisotropic polarizabilities of $H_2$, for which we used the analytical functions given in Ref. 11 that were obtained by fitting the numerical values from Ref. 54. The dispersion energy varying as $1/R^6$ and other smaller terms are neglected, which is a good approximation because the long-range expansion is only used for $R>56.4$ a.u. Notice that the leading term is attractive for $\gamma=0^\circ$ and repulsive for $\gamma=90^\circ$.

In region I we used the following extrapolation formula in $r$ for fixed $R$ and $\gamma$:

$$V_{SP}(r; R, \gamma) = a(R, \gamma)e^{-b(R, \gamma)r},$$

where $a(R, \gamma)$ and $b(R, \gamma)$ are functions of $R$ and $\gamma$ that are obtained considering the two $ab$ initio energies $V(r=0.8; R, \gamma)$ and $V(r=1; R, \gamma)$ calculated at the first two values of the coordinate $r$. In this way, we obtain the quantities $a$ and $b$ given on a two-dimensional (2D) grid of points in the $(R, \gamma)$ space. Then we used the 2D B-spline interpolation to obtain smooth 2D functions $a(R, \gamma)$ and $b(R, \gamma)$.

In region III, we extrapolate the PES in $r$ and at fixed $R$ and $\gamma$ using a dispersion-like expression

$$V_{LB}(r; R, \gamma) = D_0(R, \gamma) - \frac{C_0(R, \gamma)}{r^6},$$

where the $D_0(R, \gamma)$ and $C_0(R, \gamma)$ (always positive) coefficients are obtained in a way similar to the coefficients $a$ and $b$, considering the two last points $V(r=2.2$ a.u.$; R, \gamma)$ and $V(r=2.4$ a.u.$; R, \gamma)$. They are also interpolated using the 2D B-spline method for arbitrary values of $R$ and $\gamma$.

The behavior of the PES in region IV is described by the short-range (in $R$) repulsive expression at given values of $r$ and $\gamma$

$$V_{SP}(R; r, \gamma) = A(r, \gamma)e^{-B(r, \gamma)r}.$$  

The $A(r, \gamma)$ and $B(r, \gamma)$ coefficients are obtained in a way similar to the one described above, considering the first two values of the $ab$ initio potential energy $V(R=2$ a.u.$; r, \gamma)$ and $V(R=2.052$ a.u.$; r, \gamma)$, and are further interpolated for any $(r, \gamma)$ using the same 2D B-spline procedure.

We show in Fig. 2 the $H_3^+$ PES as a function of two internuclear distances, $r_1$ and $r_2$ for two values (180° and 90°) of the bonding angle $\delta$. These coordinates are convenient to describe main features of the PES. As expected, the figure is symmetric with respect to the $r_1 \leftrightarrow r_2$ exchange, and shows the shallow potential well in each coordinate (with the minimum labeled with $M$), separated by a potential barrier (with the maximum labeled with $B$) for the exchange of two identical nuclei. As in previous studies, the lowest energy is found for a linear configuration as expected from Eq. (1). The position and energy of $M$ and $B$ are reported in Table I, together with other characteristic parameters of the PES.

III. COMPARISON WITH PREVIOUS STUDIES

Figures 3–5 illustrate the comparison of the PES in Jacobi coordinates obtained in the present study with the results of Refs. 10 and 11 for three values of $\gamma=0^\circ$, 30°, and 90°, respectively. Each figure gives the PES for one value of $\gamma$ and eight values of $r$ versus the coordinate $R$. The origin of potential energy yielded by the $ab$ initio procedure corresponds to an infinite separation of all electrons and nuclei. Because the absolute energy of the PES-PS (Ref. 11) is unknown, the origin of this surface is chosen in such a way that the asymptotic energy of the infinite separation between $H_3^+(r_e=1.4$ a.u.$)$ and $H^+$ is the same as in the present study. We would like to stress that the present CEPA-2 method gives the energy of $H_3^+$ at $R \rightarrow \infty$ exactly equal to the sum of $H_2$ and $H^+$ energies calculated separately within the same approach (Table I). Moreover, the asymptotic energy is remarkably accurate: the hydrogen electronic affinity is obtained at 6019.97 cm$^{-1}$, in good agreement with experimental value 6082.96 cm$^{-1}$. Similarly, our electronic binding energy of $H_2$, $E_{b}(r_e)=-1.174 252$ at its equilibrium distance $r_e=1.4$ only differs by 49 cm$^{-1}$ from the almost exact Born–Oppenheimer energy computed by Wolniewicz and Dressler. These results confirm the good accuracy of the total energy obtained with the CEPA-2 method.

The insets of these figures, together with the data in Table I demonstrate that the present $ab$ initio energies are systematically lower that those of Ref. 10 for all geometries. For instance, the potential well depth has increased by 0.01% (around 160 cm$^{-1}$) at $r_e=1.4$ a.u.$\ d$. This was expected, as we use the same CEPA-2 method than in Ref. 10 with a larger basis set, leading then to a PES with an improved accuracy. The overall behavior of the present PES and PES-SM as a function of $R$ is similar at small and large distances. In contrast, a noticeable difference of PES-PS with the present re-
TABLE I. Different quantities characterizing the $H_3$ ground state PES obtained in the present study compared with previous calculations (Refs. 10, 11, and 19).

| Quantity | Present study | Ref. 10 | Ref. 11 | Ref. 19 |
|----------|---------------|---------|---------|---------|
| $D_{e1}^e$ (a.u.) | $-1.701683$ | $-1.70095$ | n/a | n/a |
| $r_0^a$ (a.u.) | 1.403 | 1.40 | n/a | n/a |
| $B^e$ (a.u.) | $-1.68509$ | $-1.68562$ | n/a | n/a |
| Position of $B$ | | | | |
| $r_1$, $r_2$ (a.u.), $\delta_0=0$ | 1.996, 1.996 | 1.997, 1.997 | 1.999, 1.999 | 1.74, 1.74 |
| $r$, $R$ (a.u.), $\gamma=0$ | 1.996, 2.994 | 1.997, 2.996 | 1.999, 2.999 | 1.74, 2.61 |
| $M^e$ (a.u.) | $-1.703511$ | $-1.70270$ | n/a | n/a |
| Position of $M$ | | | | |
| $r$, $R$ (a.u.), $\gamma=0$ | 1.421, 6.069 | 1.416, 6.183 | 1.419, 5.915 | n/a |
| $B-M$ (cm$^{-1}$) | 4042.9 | 3748.62 | 3786.42 | n/a |
| $D_{e1}-M$ (cm$^{-1}$) | 401.2 | 384.05 | 384.27 | 443.60 |

**Energies obtained separately for $H_2$ and $H^-$**

| Present study | Ref. 10 | Ref. 55 | Ref. 56 |
|---------------|---------|---------|---------|
| $E_{H_2,j=1.4}$ | $-1.174252$ | $-1.17368$ | $-1.1744757$ | n/a |
| $E_{H^-}$ | $-0.527429$ | $-0.52727$ | n/a | 0.527716$^{d}$ |

$^{a}$Asymptotic energy at infinite separation between $H_2(r_e)$ and $H^-$.  
$^{b}$Internuclear distance corresponding to the minimum of the $H_2$ dimer potential.  
$^{c}$Energy of the maximum of the barrier, $B$ in Fig. 2.  
$^{d}$Reference 19 gives the height of the barrier (0.624 eV) with respect to the $H_2(v=0,j=0)+H^-$ dissociation.  
$^{e}$Energy of the PES minimum, $M$ in Fig. 2.  
$^{f}$Energy is obtained by adding 0.5 a.u. to the experimental affinity (Ref. 56) of $H^-$.  

results and the PES-SM is the presence of a potential well at $\gamma=90^\circ$ near $R=7.6$ a.u. (see the inset in Fig. 5) with a significant depth ($\sim 90$ cm$^{-1}$ for $r=1.4$ a.u.). For $\gamma=90^\circ$ the $C_1/R^3$ long-range energy contribution is positive and $C_4/R^4$ is negative [see Eq. (1)]. Therefore, their sum combined with the short-range interaction produces a potential curve (for fixed $r$ and $\gamma$ near $90^\circ$) that has a pronounced minimum in PES-PS and just a shoulder-like feature in the present PES [see inset (c) in Fig. 5]. The curve is repulsive asymptotically. A possible reason for the above differences is the somewhat smaller basis set (d-aug-cc-PVTZ) used in calculation of PES-PS.$^{11}$

The numerical data available about PES-BT$^{19,23}$ is given in Table I. Since the calculation method (diatomics-in-molecule) explicitly uses the $ab$ $initio$ data (wave functions and energies) obtained for fragments ($H_2, H^-, H_2^+, H_3^-$) in separate $ab$ $initio$ calculations, it gives automatically the correct dissociation energy.

Since we have calculated PES at relatively large distances $R$, we can extract $ab$ $initio$ values (labeled with “ai”) of the corresponding long-range coefficients $C_{11}^{ai}$ and $C_{44}^{ai}$ and compare them with the theoretical values $C_{31}^{th}$ and $C_{44}^{th}$ of Eq. (1). We first make a fit of $C_{11}^{ai}$ to the $ab$ $initio$ data by fixing $C_{13}^{ai}$ to the theoretical value $C_{13}^{th}$. In this way the value of $C_{11}^{ai}$ agrees with the value of $C_{31}^{th}$ within 0.3% for $\gamma=0$, and 5% for $\gamma=90^\circ$ at $r=1.4$ a.u. Then, we did the opposite: we fitted $C_{31}^{ai}$ to the $ab$ $initio$ data by fixing $C_{44}^{ai}$ to $C_{44}^{th}$. In this case, we found that fitted and theoretical values of $C_{31}$ agree within 0.1% for $\gamma=0$ and 2% for $\gamma=90^\circ$ at $r=1.4$ a.u. The PES-PS differs significantly from the analytical long-range behavior of Eq. (1). Surprisingly, the long-range behavior of the PES-PS is quite different from ours and the one of PES-SM, and probably inaccurate due to the matching procedure between the long and short distances used by these authors.

**IV. VIBRATIONAL STATES OF $H_3$ AND $D_3^-$**

As mentioned in the introduction, one of the motivations of this study is to describe low-energy collisions between $H_2$...
and \( H^+ \), and to investigate the formation of \( H_2^+ \) in such collisions. Therefore, we need an approach which treats both bound and continuum states of the triatomic ion (including rearrangement of nuclei). We use the Smith–Whitten hyperspherical coordinates:

\[
\begin{align*}
 r_i & = 3^{-1/4} \rho_i (1 + \sin \theta \sin(\phi + \epsilon_i)), \\
 \end{align*}
\]

where \( \epsilon_1 = 2\pi/3 \), \( \epsilon_2 = -2\pi/3 \), and \( \epsilon_3 = 0 \). We also employ the adiabatic separation between hyper-radius and hyperangles, which are known to be well adapted to atom-molecule inelastic and reactive scattering involving identical particles. The dynamics is treated within the framework of the slow variable discretization (SVD) method\(^{58–60} \) that allows us to account easily for nonadiabatic couplings\(^{25} \) between hyperspherical adiabatic channels. We briefly recall below the main steps of our approach, which is discussed in greater details in Refs. \( 59 \) and \( 60 \).

The eigenstates \( \Psi \) of three particles interacting through a potential \( V \) depending only on the three internuclear distances are obtained by solving the Schrödinger equation with the following Hamiltonian expressed in hyperspherical coordinates \( \rho, \omega \) in the center-of-mass frame:\(^{37} \)

\[
 - \frac{1}{2\mu} \frac{\partial^2}{\partial \rho^2} \frac{\partial}{\partial \rho} + \frac{\Lambda^2}{2\mu \rho^2} + V,
\]

where \( \mu = m/\sqrt{3} \) is the three-body reduced mass and \( m \) is the mass of each of the three identical particles. The operator \( \Lambda \) above is the grand angular momentum.\(^{61,62} \) It depends only on the set \( \omega \) of five angles, which include the three Euler angles (for the orientation of the molecular frame in the laboratory frame) and the hyperangles \( \theta \) and \( \phi \). If the total angular momentum \( J = 0 \), \( \Lambda \) depends only on the two hyperangles. The explicit form of \( \Lambda^2 \) is given, for example, by Eq. (27) of Ref. \( 62 \).

![Fig. 4](image-url)

**FIG. 4.** Same as Fig. 3 except \( \gamma = 30^\circ \).

The eigenstates \( \Psi \) of three particles interacting through a potential \( V \) depending only on the set \( \omega \) of five angles, which include the three Euler angles (for the orientation of the molecular frame in the laboratory frame) and the hyperangles \( \theta \) and \( \phi \). If the total angular momentum \( J = 0 \), \( \Lambda \) depends only on the two hyperangles. The explicit form of \( \Lambda^2 \) is given, for example, by Eq. (27) of Ref. \( 62 \).

![Fig. 5](image-url)

**FIG. 5.** Same as Fig. 3 except \( \gamma = 90^\circ \). The two insets [(b) and (c)] show the behavior of the potentials for \( r = 1.4 \) a.u. on two different enlarged scales. Region (b) is the enlarged version of (a) and region (c) is enlarged (b).

\[
\Lambda^2 = - \frac{4}{\sin(2\theta)} \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} + \frac{4}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} + \frac{2J_Y^2}{1 - \sin \theta}
\]

\[
+ \frac{2J_Y^2}{1 + \sin \theta} + \frac{J_Y^2}{\sin^2 \theta} + \frac{4i \cos \theta J_Y}{\sin^2 \theta} \frac{\partial}{\partial \phi},
\]

where \( J_X, J_Y, \) and \( J_Z \) are the components of the angular momentum along the principal axes of inertia. The orientation of the axes is approximately indicated in Fig. 1. After rescaling the wave function \( \Psi \) as \( \Psi = \rho^{-5/2} \psi \), the Hamiltonian for the new function \( \psi \) is written as

\[
H = T_\rho + H_{ad},
\]

where

\[
T_\rho = - \frac{1}{2\mu} \frac{\partial^2}{\partial \rho^2},
\]

and

\[
H_{ad} = \frac{\Lambda^2 + 15/4}{2\mu \rho^2} + V.
\]

The eigenfunctions \( \psi(\rho, \omega) \) of the above Hamiltonian are sought as an expansion over the basis functions \( y_{a,j}(\rho, \omega) \) with unknown coefficients \( c_{a,j} \)

\[
\psi(\rho, \omega) = \sum_{a,j} y_{a,j}(\rho, \omega) c_{a,j}.
\]

The basis functions \( y_{a,j}(\rho, \omega) \) are constructed as products

\[
y_{a,j}(\rho, \omega) = \pi_j(\rho) \varphi_{a,j}(\omega),
\]

where the functions \( \pi_j(\rho) \) are discrete variable representation (DVR)-like functions localized at DVR grid points \( \rho_j \) along the hyper-radius. As in our earlier study,\(^{63,64} \) here we used the plane wave DVR functions. The functions \( \varphi_{a,j}(\omega) \) are the adiabatic hyperspherical states obtained by solving the three-body Schrödinger equation at fixed \( \rho = \rho_j \), i.e., they are eigenstates of \( H_{ad} \) at fixed \( \rho = \rho_j \) with eigenvalues \( U_j(\rho_j) \).
The functions $U_\alpha(\rho)$ are usually referred to as hyperspherical adiabatic potentials. Inserting the expansion of Eq. (11) into the Schrödinger equation $H\psi=E\psi$ reduces the equation to a generalized eigenvalue problem for coefficients $c_{a,j}$ with eigenvalues $E$

$$\sum_{a',j'} \left[ \langle \pi_{j'} | -\frac{1}{2\mu} \frac{\partial^2}{\partial \rho^2} | \pi_{j'} \rangle \rho O_{a',j',a}^{(j)} + \langle \pi_{j'} | U_\alpha(\rho) | \pi_{j'} \rangle \rho \delta_{a,a'} \right] c_{j'} = E \sum_{a',j'} \langle \pi_{j'} | \pi_{j'} \rangle \rho O_{a',j',a}^{(j)} c_{j'}$$

(14)

where $O_{a',j',a}^{(j)}$ are the overlap integrals (in the $\omega$ space) between adiabatic states $\varphi_{a',j'}$ and $\varphi_{a,j}$

$$O_{a',j',a}^{(j)} = \langle \varphi_{a',j'} | \varphi_{a,j} \rangle \omega.$$  

(15)

The subscripts $\rho$ and $\omega$ at kets in the above expressions refer to the integration coordinate of the bracket.

The system (14) of equations resembles to the system of coupled-channel equations, where nonadiabatic couplings

$$\langle \varphi_{a,j} | \frac{\partial}{\partial \rho} | \varphi_{a,j} \rangle d$$

and

$$\langle \varphi_{a,j} | \frac{\partial^2}{\partial \rho^2} | \varphi_{a,j} \rangle,$$

are replaced with the overlap matrix elements $O_{a',j',a}^{(j)}$. The use of overlap matrix elements instead of the derivatives of adiabatic states with respect to $\rho$ simplifies significantly the numerical solution of the equation, and is the main advantage of the SVD method.

We restricted the present computations to energies and wave functions of bound states for two $H_2^+$ and $D_2^+$, with total angular momentum $J=0$. The hyperangle $\theta$ varies in the interval $[0, \pi/2]$, while the full interval of variation for the second hyperangle, $\phi$, is $[0, 2\pi]$. However, for three identical particles, the interval along $\phi$ can be restricted to $[-\pi/2, -\pi/6]$ for wave functions of the $A_1'$ or $A_2'$ irreducible representations (irreps) in the following of the molecular symmetry group ($D_{3h}$), and to the interval $[-\pi/2, +\pi/2]$ for wave functions of the $E'$ irrep. Irreps with odd parities, $A_1''$, $A_2''$, and $E''$ are not allowed for $J=0$. This is because the inversion applied to the rotational part of the total wave function is reduced to the rotation of the system about the $Y$-axis by $\pi$. The $J=0$ rotational states are isotropic, so only the even parity is allowed. The hyper-radius $\rho$ can vary in the interval $[0, \infty)$. In this study, it varies from 1 to 120 a.u. for $H_3^+$ and from 1 to 80 a.u. for $D_3^+$. In the numerical calculation, we have used equal masses $m = 1837.3621$ a.u. for all three atoms in the $H_3^+$ molecule. This value is the sum of the hydrogen mass and one third of electron mass. Similarly, we took $m = 3670.8162$ a.u. (which is the sum of the deuterium mass and one third of electron mass) for $D_3^+$.

The resulting adiabatic potentials of $A_1'$ and $A_2'$ irreps are shown in Fig. 6 for $H_3^+$ and in Fig. 7 for $D_3^+$. The curves of $E'$ irrep are not shown in Figs. 6 and 7. The lowest $E'$ curves are almost identical to the $A_1'$ and $A_2'$ curves and would be indistinguishable from them in the figures because for low vibrational levels, the energies of levels are independent on the symmetry ($A_1', A_2'$, or $E'$) of wave functions with respect to the proton exchange between the dimer and the $H^-$ ion. (We assume here that the dimer is in a particular rovibrational state such that the proton exchange is made without changing the dimer state. The energy does depend on the $H_2$ rovibrational state.) At large $\rho$, all adiabatic curves dissociate into an atom+dimer system characterized by the rovibrational state $(v_d,j)$ of the dimer.

Some of the adiabatic curves in Figs. 6 and 7 exhibit avoided crossings at energies above $\sim 4000$ cm$^{-1}$. Dynamic
TABLE II. Comparison of energies (in cm⁻¹) of H₃⁺ bound levels obtained in the present study with those of Ref. 10. Energies in the second and third columns are given with respect to the dissociation limits \( D_{01} \) (for \( A' \) levels) and \( D_{00} \) (for \( A'' \) levels). The energies in parentheses are calculated with respect to \( D_{00} \), to compare with Ref. 10.

| \( J, \Omega, j, v, v_d, \Gamma \) | Energies above \( D_{ar} \) | Binding energies |
|---------------------------------|------------------|-----------------|
| Present study Calculations of Ref. 10 | Present study Calculations of Ref. 10 |
| 0,0,0,0,0,\( A' \) | 2103.3 | 2100.6 | –70.7 | –68.4 |
| 0,0,0,1,0,\( A' \) | 2148.4 | 2147.1 | –25.6 | –21.9 |
| 0,0,0,2,0,\( A' \) | 2168.7 | 2165.9 | –5.4 | –3.1 |
| 0,0,0,3,0,\( A' \) | 2174.1 | 2168.7 | –0.01 | –0.3 |
| \( D_{01} \) | 2174.1 | 2169.0 | |
| 0,0,1,0,0,\( A'' \) | 2140.3 | 2140.8 | –152.1 (–33.7) | n/a (–28.2) |
| 0,0,1,1,0,\( A'' \) | 2215.1 | | –77.4 | |
| 0,0,1,2,0,\( A'' \) | 2259.3 | | –33.2 | |
| 0,0,1,3,0,\( A'' \) | 2281.9 | | –10.6 | |
| 0,0,1,4,0,\( A'' \) | 2290.9 | | –1.6 | |
| \( D_{00} \) | 2292.5 | n/a | |

\( a \) Asymptotic energy of \( \text{H}^+ + \text{H}_2 \) (\( v_d = 0, j = 0 \)) dissociation.

\( b \) Asymptotic energy of \( \text{H}^+ + \text{H}_2 \) (\( v_d = 0, j = 1 \)) dissociation.

coupling between hyperspherical adiabatic states is mostly determined by the avoided crossings and responsible for nuclei exchange above the potential barrier identified in Fig. 2. Such transitions are much less probable at smaller energies as each adiabatic state is only weakly coupled to other adiabatic states of the same irrepr. As a consequence, only one component \( \varphi_n \) in the expansion of Eq. (11) is dominant. Each adiabatic state for a given irrepr \( \Gamma \) is correlated with a definite pair of quantum numbers \( (v_d, j) \), and can be approximately characterized by these two quantum numbers. The value \( \Omega \) of the projection of the \( \text{H}_2 \) angular momentum \( j \) on the axis connecting the dimer with the atom is also a relevant quantum number. For \( J = 0 \), \( \Omega \) is always zero and, therefore is not specified in Figs. 6 and 7.

To characterize completely a bound state of the trimer, an additional quantum number \( v \) is needed for the excitation within each adiabatic state (along the hyper-radius). Therefore, the bound states are characterized by four approximate quantum numbers \( \Omega, J, v, v_d \) and two exact quantum numbers \( J \) and \( \Gamma \). At high energies, the mixing between different \( \Omega, J, v, v_d \) for given \( J \) and \( \Gamma \) becomes important.

We summarized in Table II the present \( H_3^+ \) bound state energies and those of Ref. 10 labeled with the set of quantum numbers \( J, j, \Omega, v, v_d, \Gamma \). In agreement with Ref. 10, we found four vibrational energies levels of the \( A'_1 \) irrepp and one other level of the \( A''_2 \) irrepp. We also found four more vibrational levels of the \( A'_2 \) irrepp. Although their energies are located above the \( v_d = 0, j = 0 \) dissociation threshold, they are stable because they cannot dissociate due to the symmetry restriction. Their binding energies are given in the table with respect to their first allowed dissociation limit \( v_d = 0, j = 1 \). It is worth noticing that our binding energies for all levels but one are larger than the energies of Ref. 10, expressing that the well depth of our potential surface is found about 17 cm⁻¹ deeper than in Ref. 10. The last bound level of the \( A'_1 \) irrepp has a very small binding energy and may not be fully converged. The bound state energies of \( D_3^- \) are given in Table III. Since the \( D_3^- \) molecule is heavier than \( H_3^+ \), it has more vibrational levels. No data from previous calculation is available for \( D_3^- \).

In Appendix, Sec. 2, we estimate also the role of diagonal non-Born–Oppenheimer couplings, which is found to be smaller or comparable to the accuracy of the present calculations.

V. PERMANENT DIPOLE MOMENT SURFACE FOR THE \( H_3^+ \) GROUND STATE

For calculation of different observables (such as the RA cross section) involving matrix elements of the dipole moment, the components of the permanent dipole moment for each geometry should be evaluated. In contrast with neutral charge distributions, the magnitude of the dipole moment vector for charged species depends on the origin of the coordinates. The dipole moment approximation for electromagnetic transitions requires a vector computed with the origin at the center of mass of the system.

The MOLPRO package delivers also the components of the permanent dipole moment together with the PES. For a fixed geometry, the obtained components of the dipole moment correspond to the coordinate system with the \( X, Y, Z \) axes along the principal axes of inertia of the molecule with the origin at the center of mass of the system. In our notations, the \( Y \)-axis is orthogonal to the plane of \( H_3^+ \), therefore \( D_Y = 0 \). For \( \gamma = 0° \) or \( 90° \) there is only one non-zero component \( (D_Z \text{ in our notations}) \). \( D_Z \) becomes also zero at the origin at the center of mass of the system. For other geometries (\( \gamma \neq 0° \) or \( 90° \)) there are two nonzero components, \( D_Z \) and \( D_X \). We used the following convention to label the components: at large values of \( R \), the component \( D_Z \) is the largest of the two in

TABLE III. Energies (in cm⁻¹) of \( D_3^- \) bound levels obtained in the present study. Energies in the second column are given with respect to \( D_{ar} \) (see Table I, \( D_{ar} \) being the same for \( H_3^+ \) and \( D_3^- \)). The binding energies in the third column are given with respect to the dissociation limits \( D_{00} \) for the \( A'_1 \) levels and \( D_{00} \) for the \( A''_2 \) levels. The \( D_{ar} \) and \( D_{00} \) dissociation \( D_3^+ + D^- \) limits are calculated with respect to \( D_{ar} \) and also given in the table.

| \( J, \Omega, j, v, v_d, \Gamma \) | Energies above \( D_{ar} \) | Binding energies |
|-----------------|------------------|-----------------|
| Present study Calculations of Ref. 10 | Present study Calculations of Ref. 10 |
| 0,0,0,0,0,\( A'_1 \) | 1416.5 | | –126.2 |
| 0,0,0,1,0,\( A'_1 \) | 1474.1 | | –68.6 |
| 0,0,0,2,0,\( A'_1 \) | 1510.1 | | –32.6 |
| 0,0,0,3,0,\( A'_1 \) | 1530.2 | | –12.5 |
| 0,0,0,4,0,\( A'_1 \) | 1539.8 | | –2.9 |
| 0,0,0,5,0,\( A'_1 \) | 1542.7 | | –0.02 |
| \( D_{ar} \) | 1542.7 | | |
| 0,0,1,0,0,\( A''_2 \) | 1419.9 | | –182.3 |
| 0,0,1,1,0,\( A''_2 \) | 1485.0 | | –117.2 |
| 0,0,1,2,0,\( A''_2 \) | 1532.0 | | –70.3 |
| 0,0,1,3,0,\( A''_2 \) | 1563.8 | | –38.5 |
| 0,0,1,4,0,\( A''_2 \) | 1583.7 | | –18.7 |
| 0,0,1,5,0,\( A''_2 \) | 1595.1 | | –7.2 |
| 0,0,1,6,0,\( A''_2 \) | 1600.6 | | –1.7 |
| 0,0,1,7,0,\( A''_2 \) | 1602.3 | | –0.01 |
| \( D_{00} \) | 1602.3 | | |

\( a \) Asymptotic energy of \( \text{D}^+ + \text{D}_2 \) (\( v_d = 0, j = 0 \)) dissociation.

\( b \) Asymptotic energy of \( \text{D}^+ + \text{D}_2 \) (\( v_d = 0, j = 1 \)) dissociation.
magnitude and negative, $D_X$ being the smallest (in magnitude) and positive. The choice of negative $D_Z$ at large $R$ corresponds to the $Z$-axis oriented from the center of mass of the molecule toward the $H^-$ ion. For small values of $R$ (for fixed $\gamma$ and $r$) the two components $D_Z$ and $D_X$ become comparable in magnitude. For such geometries they are identified by ensuring a smooth variation of the components with decreasing $R$. Notice that because the principal axes of inertia for $H_3 \equiv H_3^-$ are the same, the obtained PDMS are the same for the two species.

Figures 8 and 9 show $ab\ initio$ values of the $D_Z$ and $D_X$ PDM components for $\gamma = 30^\circ$ for all nine values of $r = 0.8, 1, \cdots, 2.4$ a.u. as a function of $R$. As one can see from the figures, the sampling grid of $ab\ initio$ geometries is dense enough to perform an interpolation procedure in order to calculate $D_Z$ and $D_X$ at any arbitrary geometry. Therefore, in the central region in Fig. 1, we interpolate the $D_Z$ and $D_X$ PDMS using the same 3D B-spline procedure as for the PES interpolation.

In region II, when $R \rightarrow \infty$, the analytical behavior of the largest component $D_Z$ is known: It decreases with increasing $R$ as (in a.u.) $D_Z = e r_{cm-H} = -2R/3$, where $r_{cm-H}$ is the distance between the center of mass of $H_3^-$ and the $H^-$ ion, and $e = -1$ is the electron charge. The $ab\ initio$ $D_Z$ values confirm this behavior, so the same formula is used for extrapolation of $D_Z$ in region II. Outside the central region in Fig. 1, the PDMS (except the $D_Z$ components in region II) are extrapolated using an empirical analytical formula. The empirical formula is obtained by inspecting the PDMS variations close to the boundaries of the $ab\ initio$ region. The smallest component $D_X$ varies at large $R$ as $k_x(r, \gamma)/R$, where $k_x(r, \gamma)$ is fixed by the value of the PDMS at the final point $R_f = 56.4227$ a.u. of the grid, i.e., $k_x=V(R_f; r, \gamma)R_f$. As previously, we obtain a surface for the $k_x(r, \gamma)$ function, which is computed at any geometry using a 2D B-spline interpolation. For the extrapolation of the PDMS in region I we found (empirically) a quadratic (for $D_Z$) and linear (for $D_X$) dependencies along $r$ with coefficients depending on $R$ and $\gamma$, which are evaluated from the corresponding boundary values of $D_Z$ and $D_X$, respectively. Similarly, in region III and IV, we assumed a linear dependency along $r$ and $R$, respectively, with coefficients fixed by the boundary values of the PDMS.

VI. SUMMARY AND CONCLUSIONS

In the present study we have obtained accurate potential energy surface and components of the permanent dipole moment for the $H_3^-$ molecular ion. The surfaces were calculated on a large number of geometries that covers short, intermediate, and long-range regions. In total, the $ab\ initio$ calculations were made for 3024 geometries. The large basis and grid used in the calculations allows us to suggest that the obtained PES is more accurate than the results of the previous study. Comparison of the long-range behavior of the obtained PES with the expected analytical behavior of the PES confirms this conclusion. No previous data on the dipole moment of $H_3^-$ is available.

The obtained $ab\ initio$ values for potential energy surface and the dipole moment components were used to construct FORTRAN interpolation/extrapolation subroutines that calculate the energies and dipole moments for any arbitrary geometry. The subroutines interpolate the surfaces using B splines inside the region of $ab\ initio$ geometries and extrapolate the surfaces outside of the region using analytical formulas based on the theoretical asymptotic behavior. The subroutines are available in the supplementary material. The energy surface can be used for all isotopologues of $H_3^-$, the dipole moment surfaces in the present form can only be used for $H_2D^-$ and $D_3^-$ isotopologues. For the $H_2D^-$ and $D_3^-$ molecules, the dipole moments should be transformed to account for the different orientation of axes of inertia. Using the new potential surfaces, we have calculated the bound states for the $H_3^-$ and $D_3^-$ isotopologues.

A relatively large magnitude $|D| \sim 4$ a.u. of the dipole moment near equilibrium positions for bound vibrational states and a large size of the electronic clouds of $H^-$ suggest that the cross section for the formation of $H_3^-$ stable molecules by the RA between $H_2$ and $H^+$ is significant. A rela-
tively large dipole moment and the existence of several bound levels suggests also that the H$_3^-$ can be detected using IR photoabsorption spectroscopy.

The calculated energies of H$_3^-$ bound states can also be used to search for H$_3^-$ in the cold ISM with a large fraction of ionized hydrogen (to have enough free electrons). We have developed a model for the formation of H$_3^-$ in RA collisions between H$_2$ and H$^-$. In the model, H$^-$ is formed by dissociative attachment of the electron to H$_2$. If a photoabsorption signal from H$_3^-$ (in mm range) is detected, this would also be a signal for the presence of H$^-$ in the ISM: H$^-$ itself cannot be detected directly. The details of the model as well as the calculated rates of RA collisions between H$_2$ and H$^-$ will be discussed in a forthcoming publication.

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APPENDIX: ON THE ACCURACY OF THE PRESENT AB INITIO RESULTS

1. Comparison between MRCI and CEPA-2 methods

In this appendix, we discuss briefly the comparison of the results obtained using the CEPA-2 and multi reference configuration interaction (MRCI) ab initio methods. The CEPA method has been introduced about thirty years ago by Meyer and collaborators. Although the CEPA methods provide accurate results (at least, for certain molecules) and are not very expensive numerically (see, for instance, the recent review of Ref. 66), they have never been very popular in quantum chemistry calculations, even if a small part of the quantum chemistry community is still developing CEPA-type methods.  

To demonstrate the accuracy of the CEPA-2 method that has been employed for the present study, we have also performed calculations with the MRCI method using the same basis in the CEPA-2 calculation. In the MRCI calculations, all four electrons of H$_3^-$ are treated as active. We have used four active (self consistent field) orbitals. We have also verified that further increase of the number of active orbitals does not change the obtained energies for the geometries of interest. As pointed out above, at small distances near equilateral geometries the ion is unstable due to the electron autodetachment. Therefore, CEPA-2 and MRCI are not converging at such geometries with the employed basis.

The result of the comparison is given in Figs. 10 and 11. Figure 10 compares the ab initio energies of H$_3^-$ obtained using CEPA-2 and MRCI methods for fixed values of $\gamma=0$ and $r=1.4$ and different values of $R$. The figures includes also the results of MRCI calculations with Pople and Davidson corrections included (see Ref. 70 and references therein). The asymptotic limits of the four curves are quite different. The CEPA-2 asymptotic energy is the closest one above the “best available” estimation 1.702 191 8 for the sum of H$_2$ and H$^-$ energy (see Table I). We recall that CEPA-2 method gives the energy of H$_3^-$ at $R \to \infty$ that is exactly equal to the sum of H$_2$ and H$^-$ energies calculated separately for H$_2$ and H$^-$ (see Table I). Based on this observation, we conclude that CEPA-2 provides better results than the corrected or uncorrected MRCI method.

Figure 11 shows the same curves as Fig. 10 but the asymptotic limits of the four curves are brought to the same value. As one can see the agreement between energies relative to the dissociation limit is much better than the agreement in terms of absolute energies. Notice that the potential well depth in Fig. 11 strongly depends on the correction added to the bare MRCI value, the latter being very close to the CEPA-2 one.
The remaining inaccuracy (≈100 cm⁻¹ for CEPA-2) in the absolute energies should probably be attributed to the limited basis used in the present study.

2. On the diagonal non-Born–Oppenheimer correction

Here, we discuss the diagonal non-Born–Oppenheimer correction (DNBOC) to the obtained H₂⁺ PES, which may be expected to have a significant contribution due to the low H₂⁺ mass. As mentioned above, the H₂⁺ molecule is a loosely bound H₂⁺+H⁺ complex. Therefore, for the estimation of DNBOC we can model it as the H₂ dimer with the internuclear distance r perturbed by the presence of H⁺ located at the distance R with the angle γ. Therefore, the DNBO correction, ε(r, R, γ), can be represented as ε₀(r) + ε₁(r, R, γ), where ε₀(r) is DNBOC of the dimer, and ε₁(r, R, γ) is the correction caused by the perturbation of the dimer due to the presence of H⁺; ε₁(r, R, γ) → 0 when R → ∞. We can estimate the order of magnitude of ε₁(r, R, γ) term for geometries of the interest (near the minimum of H₂) as ε₁(r, R, γ)/ε₀(r) ≤ ΔU(H₂)/U(H₂), where ΔU(H₂) is the change in H₂ energy due to the perturbation, i.e., the depth of the potential well of the H₂⁺+H⁺ complex, and U(H₂) is the energy of the unperturbed H₂ dimer near the equilibrium. For U(H₂) it is reasonable to take the energy of chemical bond of H₂, i.e., 0.174 475 7 a.u. Using these numbers we obtain ε₀(r=1.4) is about 100 cm⁻¹ 55,71 which gives the estimation for ε₁(r, R, γ) of the order of 0.5 cm⁻¹. It is comparable to the accuracy of the present calculation (in terms of energies relative to the H₂ + H⁺ dissociation limit).

The function ε₀(r) is known 55,71 and can be added to the Born–Oppenheimer PES obtained in the present study. In calculation of bound states of H₂⁺ we did not include DNBOC. For the all bound states of H₂⁺ and D₂⁺, the state of the dimer is the ground rovibrational level. Therefore, the binding energies shown in Tables II and III are insensitive to the inclusion of the correction. The inclusion of DNBOC is expected to have a significant contribution due to the low H₂⁺ mass. As mentioned above, the H₂⁺ molecule is a loosely bound H₂⁺+H⁺ complex. Therefore, for the estimation of DNBOC we can model it as the H₂ dimer with the internuclear distance r perturbed by the presence of H⁺ located at the distance R with the angle γ. Therefore, the DNBO correction, ε(r, R, γ), can be represented as ε₀(r) + ε₁(r, R, γ), where ε₀(r) is DNBOC of the dimer, and ε₁(r, R, γ) is the correction caused by the perturbation of the dimer due to the presence of H⁺; ε₁(r, R, γ) → 0 when R → ∞. We can estimate the order of magnitude of ε₁(r, R, γ) term for geometries of the interest (near the minimum of H₂) as ε₁(r, R, γ)/ε₀(r) ≤ ΔU(H₂)/U(H₂), where ΔU(H₂) is the change in H₂ energy due to the perturbation, i.e., the depth of the potential well of the H₂⁺+H⁺ complex, and U(H₂) is the energy of the unperturbed H₂ dimer near the equilibrium. For U(H₂) it is reasonable to take the energy of chemical bond of H₂, i.e., 0.174 475 7 a.u. Using these numbers we obtain ε₀(r=1.4) is about 100 cm⁻¹ 55,71 which gives the estimation for ε₁(r, R, γ) of the order of 0.5 cm⁻¹. It is comparable to the accuracy of the present calculation (in terms of energies relative to the H₂ + H⁺ dissociation limit).

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