Complexes of Alkali Metal Cations and Molecular Hydrogen: Potential Energy Surfaces and Bound States

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Abstract

Complexes between metal cations and molecular hydrogen are systems quite amenable for precise spectroscopic and theoretical studies and, at the same time, they are relevant for applications in hydrogen storage and astrochemistry. In this work we report new intermolecular potential energy surfaces and rovibrational states calculations for complexes involving molecular hydrogen and alkaline metal cations, M^+-H_2 ($M^+=Na^+$, K^+ , Rb^+ , Cs^+). The intermolecular potentials, formulated in an internally consistent way to emphasize differences in the properties of the systems, are represented by simple analytical expressions whose parameters have been optimized from comparison with accurate *ab initio* calculations. Properties of the low-lying bound states -binding energies, frequencies, rotational constants- are compared with previous measurements or computations and an overall good agreement is achieved, supporting the reliability of the present formulation. Variations of these properties as a function of the cation size and isotopic substitution, with a proper sequence of *ortho* and *para* rotational levels, are also discussed.

Introduction

Interactions between cations of metallic atoms and molecular hydrogen (M^+-H_2) are appealing in several respects. First, they are amenable for accurate computational determinations of the (generally) non-covalent forces involved in these systems as well as of the corresponding quantum-mechanical bound states, which in turn can be eventually tested against precise spectroscopic data.^{1,2} In addition, in the study of the interstellar medium there is interest in processes involving ubiquitous H_2 molecules and relatively abundant metallic cations.³⁻⁵ Another motivation for studying these systems is their application in processes of reversible storage of hydrogen in porous materials,⁶⁻¹⁰ where dopant metal cations act as centers to which hydrogen molecules attach and isotopic substitution effects (D_2 by H_2) have been found to be relevant.¹¹ In all these cases, it is also interesting to study the differences in the interaction depending on whether the molecule is in the ground rotational state (*para*- H_2 , *ortho*- D_2) or in the first rotationally excited state (*ortho*- H_2 , *para*- D_2), as has been found in related works.^{2,12}

M^+-H_2 complexes where the metal is an alkaline atom have been extensively investigated, particularly those involving the lighter ions.¹³⁻²² Vitillo *et al.*¹⁶ studied the equilibrium properties of M^+-H_2 with $M^+ = Li^+, Na^+, K^+, Rb^+$ by means of MP2 *ab initio* and density functional theory (DFT) calculations and various basis sets. It was found that the interaction can be mainly described by attractive charge-quadrupole and charge-induced dipole forces at long range and a exchange-repulsion contribution at short range, and that charge transfer is negligible. In all cases, the equilibrium geometry was found to be T-shaped due to the role of the charge-quadrupole contribution. Computed formation enthalpies were found to be in reasonable agreement with experimental determinations.^{13,14} Poad *et al.* performed a joint experimental and computational study of Na^+-H_2 ¹⁷ and Na^+-D_2 .²⁰ A new potential energy surface (PES) was developed based on CCSD(T)/aug-cc-pVQZ *ab initio* computations, and subsequent rovibrational energy levels were obtained by variational calculations and compared with rotationally resolved infrared spectrum recorded in the H-H(D-D) stretch regions. The computations were found in quite good agreement with the experiment for both complexes and confirmed their T-shape equilibrium geometries. Likewise, Page *et al.* reported properties of the rovibrational states of Na^+-H_2/D_2 based on a CCSD(T) calculations,¹⁸ and

it is also worth mentioning their detailed electronic structure study of complexes with $M^+ = \text{Li}^+, \text{Na}^+, \text{K}^+$, including high level methods such as CCSDT and MRCI.¹⁹

In a recent work²³ we presented a new analytical PES for the $\text{Cs}^+\text{-H}_2$ complex in the context of quantum Monte Carlo calculations of binding energies of $(\text{H}_2)_n\text{Cs}^+$ and $(\text{D}_2)_n\text{Cs}^+$ clusters and comparisons with mass spectrometry of these clusters after electron impact ionization of $\text{Cs}/\text{H}_2(\text{D}_2)$ -doped helium nanodroplets, also reported therein. A quite good agreement between calculations and the most prominent features (magic numbers) of the measured ion abundances was achieved, supporting the reliability of the interaction model which assumed pairwise $\text{Cs}^+\text{-H}_2$ and $\text{H}_2\text{-H}_2$ additive interactions plus inclusion of three-body $\text{H}_2\text{-Cs}^+\text{-H}_2$ induction contributions. In particular, the $\text{Cs}^+\text{-H}_2$ was represented using point charges to describe the charge-quadrupole electrostatic contribution and a non-covalent (induction + van der Waals) component given by Improved Lennard Jones (ILJ) functions²⁴ within an atom-bond model.²⁵ Parameters of these functions were fine-tuned against high level CCSD(T) *ab initio* calculations using large basis sets.

In this work, the above mentioned formulation is extended to represent in an internally consistent way the interaction of hydrogen with the Na^+ , K^+ , Rb^+ and Cs^+ cation series. Rovibrational bound state calculations of the complexes between these ions and H_2 are then reported. The goal is to test this approach against experimental data and previous calculations, more abundant for the lighter atoms Na^+ and K^+ , to eventually gain confidence in the reliability of the PES for the complexes involving the heavier cations. We also aim to study the evolution of different properties and effects with the size of the cation: the substitution of H_2 by D_2 , *ortho* vs *para* H_2 binding energies, extent of the stretching/bending motions, etc. The use of the same kind of functional forms for the representations of the interactions will allow us to perform this analysis in a consistent way. Compact interaction potentials are also very useful in cluster science where the evolution of properties with size requires accurate yet simple expressions for the total PES.^{26,27}

The paper is organized as follows. In Section 2, the theoretical model is presented, including the *ab initio* electronic structure calculations, the functional form of the PES and the details of the rovibrational bound state calculations. In Section 3, features of the new PESs as well as of those of the $M^+\text{-H}_2$ bound states (energies, probability distributions,

structural analyses) are reported and discussed in comparison with previous calculations and experiments. A conclusion is given in Section 4. Supporting material is gathered in the Supporting Information (SI).

Theoretical methods

Hamiltonian model

Present M^+H_2 systems are represented using Jacobi coordinates $\vec{r}$ and $\vec{R}$, where $\vec{r}$ is the vector joining the H nuclei, $\vec{R}$ is the vector joining the center of mass of H_2 with the cation M^+ and θ is the angle formed between those vectors. The Hamiltonian can be written as

$$H = -\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\hbar^2 \hat{l}^2}{2\mu R^2} + H_r + \frac{\hbar^2 \hat{j}^2}{2mr^2} + V(R, \theta, r), \quad (1)$$

where m and μ are the reduced masses of H_2 and M^+-H_2 , $\hat{j}$ and $\hat{l}$ are angular momenta associated to $\vec{r}$ and $\vec{R}$, respectively, $V(R, \theta, r)$ is the M^+-H_2 intermolecular potential (approaching zero for $R \rightarrow \infty$) and

$$H_r = -\frac{\hbar^2}{2mr} \frac{\partial^2}{\partial r^2} r + U(r) \quad (2)$$

is the rotationless Hamiltonian of the isolated H_2 diatom. The fast motion of the r coordinate, compared with the intermolecular motion, allows us to apply the well-known vibrational diabatic decoupling approximation (VDA),^{17,28,29} where the total Hamiltonian is averaged over a chosen H_2 vibrational state $\chi_v(r)$, solution of H_r ,

$$H_v = \langle \chi_v | H | \chi_v \rangle = \varepsilon_v - \frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + B_v \hat{j}^2 + \frac{\hbar^2 \hat{l}^2}{2\mu R^2} + V_v(R, \theta), \quad (3)$$

where $B_v = \langle \chi_v | \hbar^2(2mr^2)^{-1} | \chi_v \rangle$, $V_v(R, \theta) = \langle \chi_v | V(R, \theta, r) | \chi_v \rangle$ and ε_v is the eigenvalue associated to $\chi_v(r)$ and is conveniently set to zero. This approach, which eliminates the r coordinate from the Hamiltonian, has proved to work quite well in complexes formed between H_2 and different metallic cations, with uncertainties in the binding energies of 1-3% with respect to the full dimensional calculation,³⁰⁻³³ In a further approximation, aimed at

avoiding a costly calculation of $V(R, \theta, r)$ in a grid of r points and a subsequent averaging over this coordinate, $V_v(R, \theta)$ is estimated by computing the intermolecular potential just at the averaged value of r in the corresponding vibrational state,^{34,35}

$$\begin{aligned} V_v(R, \theta) &\approx V(R, \theta, r_v), \\ r_v &= \langle \chi_v | r | \chi_v \rangle. \end{aligned} \quad (4)$$

The rationale of this model, termed as VDA- r_v , becomes clear if one considers a Taylor expansion of $V(R, \theta, r)$ around r_v . In that case, $V_v(R, \theta)$ approaches $V(R, \theta, r_v)$ if the quadratic and higher terms of the expansion are negligible,^{35,36} since the linear term is identically zero as $\langle \chi_v | (r - r_v) | \chi_v \rangle = 0$. For example, for Ar-HF($v=0$)³⁶ and Cl-HF($v=0$)³⁷ complexes, binding energies using VDA- r_v were found to be within ~ 1 -2% with respect to those using the more accurate VDA; in any case the errors were smaller than those using the HF equilibrium distance (VDA- r_e) or a distance extracted from the vibrationally averaged rotational constant. More proposals for the choice of an effective intramolecular distance are discussed elsewhere.^{33,36}

In this work we apply the VDA- r_v model for the ground vibrational state of H_2 , $v = 0$. The vibrationally averaged rotational constant and H_2 distance, taken from Ref.,³⁴ are $B_0 = 59.3220 \text{ cm}^{-1}$ and $r_0 = 0.76664 \text{ \AA}$, respectively. An indication of the adequacy of the model is provided in Fig. S1 of the SI, where it is shown that the dependence of the intermolecular potential on r , around r_0 , is almost perfectly linear (i.e., quadratic and higher order dependencies appear to be negligible).

Potential energy surfaces

The analytical PESs $V(R, \theta, r_0)$ for the M^+-H_2 ($\text{M}^+ = \text{Na}^+, \text{K}^+$ and Rb^+) system have been built in a similar way to that recently reported for the Cs^+-H_2 system.²³ First, accurate *ab initio* estimations of the involved interaction potential have been performed by employing the coupled-cluster with single, double and perturbative triple excitations (CCSD(T)) method. The intramolecular distance was fixed at r_0 and a dense grid along the intermolecular coordinate R was probed for selected angular configurations of the complex ($\theta = 0^\circ, 30^\circ, 60^\circ$ and 90°). In the case of the $\text{H}_2\text{-K}^+$ and $\text{H}_2\text{-Rb}^+$ systems the d-aug-cc-pV6Z³⁸ and

def2-AQVZPP³⁹ basis sets were used for H₂ and the alkali ion, respectively. We have checked that the adopted basis set is sufficiently large to guarantee well converged interaction energies, which, in the global minimum region, are found to deviate $\sim 7 \text{ cm}^{-1}$ ($\sim 1\%$) from those obtained with the d-aug-cc-pV5Z/def2-AQVZPP basis set. As for the H₂-Na⁺ system, a complete basis set (CBS) estimation of the interaction energies has been obtained by exploiting the two-point correlation energy extrapolation of Halkier *et al.*^{40,41} in conjunction with the aug-cc-pVQZ and aug-cc-pV5Z³⁸ basis sets. In post-HF calculations, for the H₂-Na⁺ (H₂-K⁺) complex, only the metal first (first five) inner orbital(s) is (are) considered as frozen, while for H₂-Rb⁺ the employed basis set includes the ECP28MWB⁴² effective core potential for the alkali atom. Therefore, for the latter system just the Rb outer five orbitals, as well as the inner shell of H₂, are fully correlated. All reported interaction energies are defined as the energy difference between the complex and infinitely separated monomers having the same geometry than in the aggregate: those energies have been corrected for the basis set superposition error (BSSE) by the counterpoise method of Boys and Bernardi.⁴³ All computations have been performed using the Molpro2012.1 package.⁴⁴

The size of the employed basis set is found to be quite important for the interaction in H₂-Na⁺. As shown in Fig. S2 of the SI, moving from aug-cc-pVQZ to the aug-cc-pVQZ and the CBS estimations, interaction energies near the minimum and the saddle point become more attractive by considerable amounts (5-10% when comparing aug-cc-pV5Z with the CBS limit). In addition, the role of scalar relativistic effects in H₂-K⁺ is studied in Fig. S3 of the SI, where it is found that inclusion of an effective core potential leads to negligible variations in the interaction energy around the absolute minimum.

The *ab initio* interaction energies serve as reference values for the optimization of the analytical representations of the PESs. To this aim the total interaction potential is considered as a sum of electrostatic (V_{elec}) and non-covalent (V_{NC}) contributions,

$$V(R, \theta; r_0) = V_{NC}(R, \theta; r_0) + V_{elec}(R, \theta). \quad (5)$$

First, the electrostatic contribution is built from Coulomb interactions between a monopole (M⁺) and a linear distribution of partial charges for H₂, namely, two charges $q_H = 0.45955$ a.u. placed above each nucleus and a third one, $q_C = -2q_H$, placed on the molecular center

of mass. This charge distribution reproduces an accurate calculation of the H₂ quadrupole, 0.48226 a.u., reported in Ref.²³ where a procedure detailed in Ref.⁴⁵ was followed.

Moreover, the non-covalent term, V_{NC} , which involves both induction and van der Waals interactions, is represented using the atom-bond model²⁵ and the ILJ formulation:²⁴

$$V_{NC}(R, \theta) = \varepsilon(\theta) \left[\frac{m}{n(R, \theta) - m} \left(\frac{R_e(\theta)}{R} \right)^{n(R, \theta)} - \frac{n(R, \theta)}{n(R, \theta) - m} \left(\frac{R_e(\theta)}{R} \right)^m \right], \quad (6)$$

where the long-range exponent m is set to 4 as corresponds to the leading charge-induced dipole interaction^{24,46} in M⁺-H₂ and

$$\begin{aligned} n(R, \theta) &= \beta + 4 \left(\frac{R}{R_e(\theta)} \right)^2 \\ \varepsilon(\theta) &= \varepsilon^\perp \sin^2(\theta) + \varepsilon^\parallel \cos^2(\theta) \\ R_e(\theta) &= R_e^\perp \sin^2(\theta) + R_e^\parallel \cos^2(\theta), \end{aligned} \quad (7)$$

where $\varepsilon^\perp$, $\varepsilon^\parallel$, $R_e^\perp$ and $R_e^\parallel$ are, respectively, well depths and equilibrium distances for the perpendicular and parallel orientations of H₂ with respect to M⁺, and β is a dimensionless parameter related to the hardness of the interaction. These parameters were fine tuned (starting from an initial guess based on known values of monomer polarizabilities^{47–49}) by comparing the total interaction potential $V(R, \theta; r_0)$ and the reference *ab initio* estimations. In any case, the variations of the parameters have been kept within limited ranges (largest allowed changes amount to ~ 15 -20% and 2-3% for $\varepsilon^{\perp, \parallel}$ and $R_e^{\perp, \parallel}$, respectively) in order to maintain proper physical meaning and do not become fitting variables. The optimized values for such parameters are gathered in Table 1. A comparison between the analytical PES and the CCSD(T) calculations is presented in Fig. 1 and in Table S1 of the SI. Parameters and potential curves Cs⁺H₂, reported in Ref.,²³ are added for the sake of completeness. From the analysis of Fig. 1 and Table S1 it is clear that the present analytical representation is capable to provide a very good agreement with the reference *ab initio* interaction energies.

Bound states calculations

Eigenstates of the Hamiltonian of Eq.3 have been computed for all the systems M^+H_2 ($M^+=Na^+, K^+, Rb^+$ and Cs^+) by means of the coupled-channel method of Hutson⁵⁰ as recently implemented in the BOUND package.^{51,52} In this approach, the total wavefunction is expanded in an angular basis which couples the angular momenta $\hat{l} + \hat{j}$ to give the total angular momentum $\hat{J} = \hat{l} + \hat{j}$ within a space-fixed representation. Substitution of this expansion into the Schrödinger equation leads to a set of coupled differential equations for the coefficients of the expansion which depend on the radial coordinate R . The eigenvalues of Eq.3 are determined by propagating the radial functions outwards and inwards from the classically forbidden regions at short and long range, respectively, and imposing continuity conditions in the matching region.⁵⁰ Associated wave functions were obtained following the method of Thornley and Hutson.⁵³

In this work, radial functions were propagated by means the diabatic log-derivative method of Manolopoulos,⁵⁴ which typically ranged from $R= 1.6$ to $9.0 \text{ \AA}$ with a step size of $0.007 \text{ \AA}$ and matching at $R= 3.1 \text{ \AA}$. Angular basis involved $j=0-15$ rotational quantum numbers and as many l values as required to satisfy the triangular condition for a given value of the total angular momentum J , which ranged from 0 to 2. The interaction potential is expanded using Legendre polynomials depending on $\cos \theta$; the radial coefficients $v_\lambda(R)$ ($\lambda= 0, 2, \dots, 14$) are generated numerically using 60 quadrature points for the angular coordinate.⁵¹ Masses of H_2 , $^{23}Na^+$, $^{39}K^+$, $^{85}Rb^+$ and $^{133}Cs^+$ were set to 2.01565, 22.98977, 38.96371, 84.91179, and 132.90543 a.m.u., respectively. The resulting energy levels are converged within $1 \times 10^{-5} \text{ cm}^{-1}$.

The computed bound states were classified for its parity under spatial inversion of the coordinates $p_i = \pm 1$ and under permutation of the H nuclei in H_2 $p_j = \pm 1$. In the case of positive parity under permutation, $p_j = +1$, the wavefunction is made up of a combination of even values of j and corresponds -due to the connection with the symmetry of the nuclear spin- to *para*-hydrogen (*pH*₂) whereas $p_j = -1$ (odd values of j) corresponds to *oH*₂.

Detailed lists of the M^+H_2 rovibrational energy levels are provided in Tables S2, S3, S4 and S5 of the SI, for $M^+= Na^+, K^+, Rb^+$ and Cs^+ , respectively.

Equivalent calculations were performed for the M^+D_2 complexes, taking the $D_2(v=0)$

vibrationally averaged rotational constant, $B_0 = 29.9037 \text{ cm}^{-1}$, from Ref.³⁴ and setting the D_2 mass to 4.02820 a.m.u.. Results for the M^+D_2 energies are provided together with those of M^+H_2 in Tables S2, S3, S4 and S5 of the SI. It should be warned that these calculations are not as reliable as those of H_2 because the same M^+H_2 PESs were used, whereas a more consistent procedure should involve computing new intermolecular potentials using, as effective intramolecular distance r_0 , its vibrational average in the $\text{D}_2(v=0)$ state instead of that of $\text{H}_2(v=0)$. An estimation of the inaccuracies brought by this approach is discussed below along with a report of more consistent calculations for the case of Na^+D_2 .

Results and discussion

Potential energy surfaces

Fig. 1 shows that the cation-hydrogen interaction is rather anisotropic in all the studied systems, with a global minimum at the T-shaped configuration (due to the dominant role of the electrostatic contribution) and a relatively high saddle point for H_2 internal rotation corresponding to the minimum energy of the potential curve for the linear ($\theta = 0^\circ$) configuration. Energies and distances for the global minimum ($\theta = 90^\circ$) as well as for the saddle point of the analytical PESs are reported in Table 2. Our computations show that, for all $\text{M}^+\text{-H}_2$ complexes, the intermolecular distance R at the saddle point is roughly $0.5 \text{ \AA}$ larger than that at equilibrium and that the barrier involved between the minimum and the saddle point is considerably high, as it amounts for about 85% of the well depth of each complex.

Table 2 also gathers some previous *ab initio* calculations^{15–17,19,21} on the interaction energies of these complexes. Unfortunately, it is difficult to perform a proper comparison with our results because, on the one hand, previous calculations correspond to geometries minimizing the total energy, $V + U$ (i.e., including the H_2 intramolecular energy, Eq. 2, hence, involving optimization of the H_2 intramolecular distance). On the other hand, present results refer to the stationary points of the analytical PES of Eq.5 with r fixed to r_0 , the expected value of r in the H_2 ground vibrational state. Even though modifications in r are small (2-3 hundredth of an $\text{\AA}$), the intermolecular energy can vary some tens of a cm^{-1} in that range (see the example of Fig. S1 of the SI). Thus, although it can be seen that there is a good

agreement with some previous studies, quantitative comparisons are not conclusive.

To obtain a more consistent assessment for the case of most studied complex, Na^+H_2 , we carried out a new *ab initio* CCSD(T)/CBS calculation at the optimum geometry found by Poad *et al.*,¹⁷ $(R, \theta, r) = (2.408 \text{ \AA}, 90^\circ, 0.746 \text{ \AA})$, obtaining $V = -1262.3 \text{ cm}^{-1}$. It is seen, on the one hand, that the interaction energy is $\sim 40 \text{ cm}^{-1}$ higher than the one at $r = 0.767 \text{ \AA}$, a result that can be rationalized from the dependence on r of the H_2 quadrupole and polarizability.⁵⁵ On the other hand, present value is $\sim 7\%$ deeper than that of Poad *et al.*, using CCSD(T) with a somewhat smaller basis set (aug-cc-pVQZ(H), cc-pVQZ (Na) + 3s3p2d2f1g bond functions). As shown in Fig. S2 of the SI and already discussed, it is very important to use large basis sets in order to achieve quantitatively accurate interaction energies. In addition, the energy obtained by Page *et al.*¹⁹ using the accurate CCSDT method at a very close geometry, -1345.9, is 7% larger in absolute value than the present estimation. Based in this analysis, one can safely conclude that the other *ab initio* calculations^{15,16,21} of Table 2 tend to underestimate the (absolute values of the) interaction energies due to use of less correlated *ab initio* methods and/or small basis sets.

Bound States

Main results of the bound states calculations are presented in Table 3 in comparison with several experimental^{14,17} and theoretical^{16-18,21} works. Most of the constants indicated therein were worked out from the set of energy levels listed in Tables S2-S5 of the SI.

Binding energies for the more abundant *ortho* species of $\text{M}^+\text{-H}_2$ were computed identifying the lowest energy level with $p_j = -1$ ($j=\text{odd}$) and referring it to the energy of the asymptote $\text{M}^+ + \text{H}_2(j = 1)$. For the *para* species, the $\text{M}^+ + \text{H}_2(j = 0)$ limit is already zero so $D_0(p)$ coincides in absolute value with the energy of the ground ($J = 0$) state. In Table 3 it can be seen that binding energies are larger for *o* H_2 than for *p* H_2 , being the difference $\Delta(D_0)$ the largest for $\text{Na}^+\text{-H}_2$. This feature has been already discussed² and one of the implications is the observation of *ortho:para* ratios larger than the natural 3:1 value in the population of $\text{M}^+\text{-H}_2$ complexes formed in supersonic expansions.^{17,29} Moving on to discuss the binding energies in comparison with previous determinations, it can be seen that they are consistent with the experimental values for $\text{Na}^+\text{-H}_2$ and $\text{K}^+\text{-H}_2$ ¹⁴ and that they are somewhat larger

than those computed by Poad *et al* for $\text{Na}^+\text{-H}_2$.¹⁷ A reason for this difference can be, on the one hand, that the present PES is more attractive probably due to the larger basis sets and CBS used, as discussed above. On the other hand, Poad *et al* used the VDA more accurately, by actually computing an r -dependent PES and averaging it on the $\text{H}_2(v=0)$ state. Following previous discussion on the $\text{VDA}-r_v$ approximation, we believe that the latter factor should play a minor role as compared with the former.

Next columns in Table 3 refer to the anharmonic stretching (ν_s) and bending (ν_b) frequencies. The stretching frequency is obtained from the difference between the ground and the first excited (of the same parity $p_i=+1$) energy levels and the bending frequency, from the difference between the energies of the ground states of different inversion parities. For all systems, bending frequencies are larger than stretching ones, which points to the significant anisotropy of the PESs. Similar results were achieved in Refs.^{17,21} for $\text{Na}^+\text{-H}_2$, although their stretching (bending) frequencies are somewhat smaller (larger) than the present ones. Both types of frequencies decrease with the size of the cation since the corresponding PESs become shallower and less anisotropic (see Table 2). We have checked that the first bending-excited state is below the barrier (at the linear configuration) for internal H_2 rotation for all systems, with the exception of $\text{Cs}^+\text{-H}_2$.

The remaining magnitudes shown in Table 3 concern the structure of the ground vibrational state, with a list of the rotational constants resulting from an asymmetric rotor analysis including centrifugal distortion.⁵⁶ To determine the relevant constants i.e., A , B , C , Δ_J and Δ_{JK} , we employed the three levels of total angular momentum $J=1$ and the three lowest energy levels of $J=2$ (indicated in bold face in the Tables S2-5 of the SI). Excluding the two higher $J=2$ levels (correlating with $K_a=2$) in the fit is analogous to the analysis performed by Poad *et al.*,¹⁷ where the spectrum recorded was found to be dominated by $K_a = 1 - 1$ and (to a lesser extent) $K_a = 0 - 0$ bands. As can be seen in Table 3, $\text{M}^+\text{-H}_2$ behave as nearly prolate rotors. Moreover, the resulting rotational constants for the $\text{Na}^+\text{-H}_2$ are in quite good agreement with both measurements and calculations reported in Refs.^{17,20} We are thus confident that the rotational constants obtained for the remaining systems can serve as an useful guide in future spectroscopy investigations.

Finally, estimations of the averaged $\text{M}^+\text{-H}_2$ distance for the ground state are reported

in the last column of Table 3. It must be noted that, in the present work, this distance is computed as the expectation value of R in the ground vibrational state whereas in a previous work on $\text{Na}^+\text{-H}_2$ ¹⁷ this value was determined from the rotational constant $\bar{B}$ as $R_0 = \hbar(2\mu\bar{B})^{-1/2}$. If we followed the latter procedure, using our value of $\bar{B}$, then the corresponding R_0 would be 2.487 Å, in close agreement with the experimental data.

Properties of complexes with D_2 molecules are reported in Table S6 of the SI. As mentioned above, these results may not be as accurate as those of $\text{M}^+\text{-H}_2$ because the effective distance r_0 used for the *ab initio* calculations is not as adequate for D_2 as for H_2 complexes. For $\text{Na}^+\text{-D}_2$, however, we have built a new intermolecular PES by carrying out *ab initio* calculations using $r_0 = 0.7590$ Å, the average intramolecular distance for the ground vibrational state of D_2 , obtained from the potential of Kołos and Wolniewicz.⁵⁷ This new effective distance is just 0.008 Å smaller than the one used up to this point, so large changes in the PES cannot be expected. In fact, it was found to be sufficiently accurate to modify only two of the parameters of the $\text{Na}^+\text{-H}_2$ potential, namely the perpendicular well depth of the non-covalent term, $\varepsilon^\perp = 766.083 \text{ cm}^{-1}$ and the partial charge of the electrostatic component, $q_H = 0.46137$ a.u. (the latter reproducing the calculation of the quadrupole at the new intramolecular distance, being $Q = 0.47457$ a.u.). A comparison of the new analytical PES with the *ab initio* calculations is shown in Fig. S4 of the SI. $\text{Na}^+\text{-D}_2$ binding energies, frequencies and rotational constants corresponding to the new PES are also shown (bold face) in Table S6 of the SI. It can be seen that binding energies and frequencies from the less accurate PES agree within 1% with the new values, the uncertainty being reduced to 0.1% for the rotational constants. These inaccuracies are of the same order than those expected from the quality of the *ab initio* calculations and subsequent fits. We expect a similar degree of confidence for the properties of the remaining $\text{M}^+\text{-D}_2$ systems shown in that Table. Taking these conclusions into account, other properties of $\text{M}^+\text{-D}_2$ will be discussed in the following along those corresponding to the hydrogenated complexes.

More insight into the structure of these systems is obtained by plotting wave functions, as shown in Fig. 2 for the ground state of $\text{Na}^+\text{-H}_2$. The average geometry is T-shaped, as expected from the PES topography but it can be noticed that this state exhibits large amplitude motions (particularly along the angular coordinate) and that both radial and

angular modes are quite correlated.

Moreover, radial $D(R) = \int |\Psi(R, \theta)|^2 d(\cos(\theta))$ and angular $D(\theta) = \int |\Psi(R, \theta)|^2 R^2 dR$ distributions have been computed for the ground rovibrational wave function Ψ and the results are depicted in Fig. 3(a) and (b), respectively. On the one hand, radial distributions are seen to become wider as M^+ goes from Na^+ to Cs^+ ; a larger anharmonicity is also noticed in the $M^+-\text{H}_2$ distributions as compared with $M^+-\text{D}_2$, since they are less symmetrical than their deuterated counterparts. On the other hand, all angular distributions of Fig.3(b) are centered at $\theta = 90^\circ$ (T-shape equilibrium geometry) but they are quite extended, particularly those for the K^+-H_2 , Rb^+-H_2 , and Cs^+-H_2 , where a non negligible amplitude at the linear configuration $\theta = 0^\circ, 180^\circ$ is discernible. Thus, for these systems, H_2 molecules can tunnel through the barrier at the linear geometry and undergone complete rotation within the complex with a non negligible probability.

Finally, it is interesting to explore the correlation between R_0 and other representative magnitudes for the systems under scrutiny. Fig. 4(a) shows the ionic radius of the isolated cations M^+ , taken from Ref.,⁵⁸ versus the average intermolecular distance in the ground state of $M^+-\text{H}_2/\text{D}_2$, R_0 , taken from Table 3. Although a high correlation between these two magnitudes is expected, it is striking that they compose an almost perfect straight lines both for $M^+-\text{H}_2$ and for $M^+-\text{D}_2$. On the other hand, Fig. 4(b) depicts the relationship between the binding energy and R_0 for the ground states of $M^+-\text{H}_2/\text{D}_2$ (those states with parity $p_j = +1$, that is $D_0(p)$ for H_2 and $D_0(o)$ for D_2 , also taken from Table 3). These values are compared with the binding energy of a simple classical system dominated by long range electrostatic and induction forces, as similarly done by other authors,^{1,16}

$$D(R) = -V_{elec}(R, \theta = \pi/2; r_0) - \frac{q_M^2 \alpha_\perp}{2R^4} \quad (8)$$

where V_{elec} is the charge-quadrupole interaction -computed using partial charges for H_2 as described in the ‘‘Theoretical methods’’ Section- and the remaining contribution is the charge-induced dipole interaction, q_M being the charge of M^+ and $\alpha_\perp = 0.71 \text{ \AA}^3$, the perpendicular component of the H_2 polarizability. Presently computed binding energies follow a trend similar to that of $D(R)$ but are smaller than the model estimations, especially for the complexes with Na^+ . Overestimation of the binding energies obtained from Eq. 8 is

due to quantum effects (zero-point energy) as well as to the role of the repulsive forces at short range, especially in the case of the $\text{Na}^+\text{-H}_2/\text{D}_2$ complexes. From these trends shown in Fig. 4 it can be said that these systems can be correctly described at a qualitative level by simple intermolecular interactions and an account of the size of the monomers. However, a quantitative description of the interaction needs high level *ab initio* methods, large basis sets and accurate bound state calculations, as already discussed above.

Conclusions

We have reported new analytical intermolecular PESs representing the interaction between H_2 -in its ground vibrational state- and the alkaline cations $\text{M}^+=\text{Na}^+$, K^+ , and Rb^+ . They have been formulated in an internally consistent way and this represents a crucial condition to emphasize differences in binding energies, structural, spectroscopic and dynamical properties of the investigated systems. Moreover, these PESs involve rather simple analytical functions whose parameters, related to electrostatic and induction properties of the monomers, have been optimized from comparisons with high level *ab initio* calculations. The lowest rovibrational bound states of these complexes (and $\text{Cs}^+\text{-H}_2$) have been computed and their features (binding energies, frequencies, wave functions) have been discussed as functions of the size of the cation, isotopic substitution (H_2 vs. D_2) and the spin parity of the diatom (*ortho* vs. *para*). Behavior of these systems range from being almost rigid and exhibiting impeded internal rotation ($\text{Na}^+\text{-D}_2$) to show quite large amplitude motions, as in the case of $\text{Cs}^+\text{-H}_2$.

These properties of the low-lying bound states were found in good agreement with previous experimental and theoretical data. In particular, rotational constants of the vibrational ground state of $\text{Na}^+\text{-H}_2$ compare very well with those derived from rotationally resolved infrared spectra of the mentioned complexes¹⁷ and the computed binding energies for $\text{Na}^+\text{-H}_2$ and $\text{K}^+\text{-H}_2$ are found to be consistent with determinations based on temperature-dependent equilibrium measurements.¹⁴ In addition, these observables, obtained here assuming a constant H_2 intramolecular distance r (fixed to its average in the ground vibrational state), are in overall good agreement with calculations¹⁷ involving somewhat different *ab initio* calculations and interaction potential model.

We are confident that results reported here for systems lacking of experimental/computational data can serve as reliable benchmarks for future investigations of these complexes. Also, we believe that the present PESs are useful for the description of more complex systems such as $M^+-(H_2)_n$ clusters in the gas phase or attached to porous materials.

Supporting Information

Supporting Information includes Figures S1 to S3, presenting various analyses of the *ab initio* calculations, Table S1, with a comparison of the analytical PES with the *ab initio* calculations, Tables S2-S5, reporting the M^+-H_2/D_2 ($M^+=Na^+$, K^+ , Rb^+ , and Cs^+ , respectively) rovibrational energy levels, Table S6, with the properties of the M^+-D_2 bound states and finally, Figure S4, where analytical and *ab initio* calculations for a new M^+-D_2 PES are shown.

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References

- (1) Dryza, V.; Poad, B.; Bieske, E. Attaching Molecular Hydrogen to Metal Cations: Perspectives from Gas-Phase Infrared Spectroscopy. *Phys. Chem. Chem. Phys.* **2012**, *14*, 14954–14965.
- (2) Dryza, V.; Bieske, E. J. Non-Covalent Interactions between Metal Cations and Molecular Hydrogen: Spectroscopic Studies of M^+-H_2 Complexes. *Int. Rev. Phys. Chem.* **2013**, *32*, 559–587.

- (3) Petrie, S.; Dunbar, R. C. Radiative Association Reactions of Na^+ , Mg^+ , and Al^+ with Abundant Interstellar Molecules. Variational Transition State Theory Calculations. *J. Phys. Chem. A* **2000**, *104*, 4480–4488.
- (4) Burrows, A.; Volobuyev, M. Calculations of the Far-Wing Line Profiles of Sodium and Potassium in the Atmospheres of Substellar-Mass Objects. *Astrophys. J.* **2003**, *583*, 985–995.
- (5) Burdakova, D.; Nyman, G.; Stoecklin, T. Formation of Na-containing Complex Molecules in the Gas Phase in Dense Molecular Clouds: Quantum Study of the $\text{Na}^+ + \text{H}_2$ and $\text{Na}^+ + \text{D}_2$ Radiative Association Step. *Mon. Not. R. Astron. Soc.* **2019**, *485*, 5874–5879.
- (6) Chen, P.; Wu, X.; Lin, J.; Tan, K. High H_2 Uptake by Alkali-Doped Carbon Nanotubes Under Ambient Pressure and Moderate Temperatures. *Science* **1999**, *285*, 91–93.
- (7) Cabria, I.; López, M. J.; Alonso, J. A. Enhancement of Hydrogen Physisorption on Graphene and Carbon Nanotubes by Li Doping. *J. Chem. Phys.* **2005**, *123*, 377.
- (8) Dinca, M.; Long, J. R. Hydrogen Storage in Microporous Metal-Organic Frameworks with Exposed Metal Sites. *Angew. Chem. Int. Ed.* **2008**, *47*, 6766–6779.
- (9) Lindoy, L. P.; Kolmann, S. J.; D’Arcy, J. H.; Crittenden, D. L.; Jordan, M. J. T. Path Integral Monte Carlo Simulations of H_2 Adsorbed to Lithium-Doped Benzene: A Model for Hydrogen Storage Materials. *J. Chem. Phys.* **2015**, *143*, 194302.
- (10) Kaiser, A.; Renzler, M.; Kranabetter, L.; Schwärzler, M.; Parajuli, R.; Echt, O.; Scheier, P. On Enhanced Hydrogen Adsorption on Alkali (Cesium) Doped C_{60} and Effects of the Quantum Nature of the H_2 Molecule on Physisorption Energies. *Int. J. Hydrogen Energy* **2017**, *42*, 3078–3086.
- (11) Physick, A. J.; Wales, D. J.; Owens, S. H.; Shang, J.; Webley, P. A.; Mays, T. J.; Ting, V. P. Novel Low Energy Hydrogen-Deuterium Isotope Breakthrough Separation Using a Trapdoor Zeolite. *Chem. Eng. J.* **2016**, *288*, 161 – 168.

- (12) Shagam, Y.; Klein, A.; Skomorowski, W.; Yun, R.; Averbukh, V.; Koch, C. P.; Narevicius, E. Molecular Hydrogen Interacts more Strongly when Rotationally Excited at Low Temperatures Leading to Faster Reactions. *Nat. Chem.* **2015**, *7*, 921–926.
- (13) Wu, C. H. Binding Energies of LiH_2 and LiH_2^+ and the ionization potential of LiH_2 . *J. Chem. Phys.* **1979**, *71*, 783–787.
- (14) Bushnell, J. E.; Kemper, P. R.; Bowers, M. T. $\text{Na}^+/\text{K}^+(\text{H}_2)_{1,2}$ Clusters: Binding Energies from Theory and Experiment. *J. Phys. Chem.* **1994**, *98*, 2044–2049.
- (15) Barbatti, M.; Jalbert, G.; Nascimento, M. A. C. The Effects of the Presence of an Alkaline Atomic Cation in a Molecular Hydrogen Environment. *J. Chem. Phys.* **2001**, *114*, 2213–2218.
- (16) Vitillo, J. G.; Damin, A.; Zecchina, A.; Ricchiardi, G. Theoretical Characterization of Dihydrogen Adducts with Alkaline Cations. *J. Chem. Phys.* **2005**, *122*, 114311.
- (17) Poad, B. L. J.; Wearne, P. J.; Bieske, E. J.; Buchachenko, A. A.; Bennett, D. I. G.; Kłos, J.; Alexander, M. H. The Na^+H_2 Cation Complex: Rotationally Resolved Infrared Spectrum, Potential Energy Surface, and Rovibrational Calculations. *J. Chem. Phys.* **2008**, *129*, 184306.
- (18) Page, A. J.; von Nagy-Felsobuki, E. I. Ab Initio Rovibrational Spectrum of the NaH_2^+ Ion-Quadrupole Complex. *Theor. Chem. Acc.* **2009**, *122*, 87–100.
- (19) Page, A. J.; Wilson, D. J. D.; von Nagy-Felsobuki, E. I. Trends in MH_2^{n+} Ion-Quadrupole Complexes ($\text{M} = \text{Li}, \text{Be}, \text{Na}, \text{Mg}, \text{K}, \text{Ca}$; $n=1, 2$) using Ab Initio Methods. *Phys. Chem. Chem. Phys.* **2010**, *12*, 13788–13797.
- (20) Poad, B. L. J.; Dryza, V.; Kłos, J.; Buchachenko, A. A.; Bieske, E. J. Rotationally Resolved Infrared Spectrum of the $\text{Na}^+\text{-D}_2$ Complex: An Experimental and Theoretical Study. *J. Chem. Phys.* **2011**, *134*, 214302.
- (21) De Silva, N.; Njegic, B.; Gordon, M. S. Anharmonicity of Weakly Bound $\text{M}^+\text{-H}_2$ Complexes. *J. Phys. Chem. A* **2011**, *115*, 3272–3278.

- (22) Pakhira, S.; Sahu, C.; Sen, K.; Das, A. K. Dispersion Corrected Double High-Hybrid and Gradient-Corrected Density Functional Theory Study of Light Cation-Dihydrogen (M^+-H_2 , where $M = Li, Na, B$ and Al) van der Waals Complexes. *Struc. Chem.* **2013**, *24*, 549–558.
- (23) Ortiz de Zárate, J.; Bartolomei, M.; González-Lezana, T.; Campos-Martínez, J.; Hernández, M. I.; Pérez de Tudela, R.; Hernández-Rojas, J.; Bretón, J.; Pirani, F.; Kranabetter, L. et al. Snowball Formation for Cs^+ Solvation in Molecular Hydrogen and Deuterium. *Phys. Chem. Chem. Phys.* **2019**, *21*, 15662–15668.
- (24) Pirani, F.; Brizi, S.; Roncaratti, L.; Casavecchia, P.; Cappelletti, D.; Vecchiocattivi, F. Beyond the Lennard-Jones Model: a Simple and Accurate Potential Function Probed by High Resolution Scattering Data Useful for Molecular Dynamics Simulations. *Phys. Chem. Chem. Phys.* **2008**, *10*, 5489–5503.
- (25) Pirani, F.; Albertí, M.; Castro, A.; Moix Teixidor, M.; Cappelletti, D. Atom-Bond Pairwise Additive Representation for Intermolecular Potential Energy Surfaces. *Chem. Phys. Lett.* **2004**, *394*, 37–44.
- (26) Rastogi, M.; Leidlmair, C.; An der Lan, L.; Ortiz de Zárate, J.; Pérez de Tudela, R.; Bartolomei, M.; Hernández, M. I.; Campos-Martínez, J.; González-Lezana, T.; Hernández-Rojas, J. et al. Lithium Ions Solvated in Helium. *Phys. Chem. Chem. Phys.* **2018**, *20*, 25569–25576.
- (27) Pérez de Tudela, R.; Martini, P.; Goulart, M.; Scheier, P.; Pirani, F.; Hernández-Rojas, J.; Bretón, J.; Ortiz de Zárate, J.; Bartolomei, M.; González-Lezana, T. et al. A Combined Experimental and Theoretical Investigation of Cs^+ Ions Solvated in He_N Clusters. *J. Chem. Phys.* **2019**, *150*, 154304.
- (28) Beswick, J. A.; Delgado-Barrio, G. Influence of Rotation on the Vibrational Predissociation of the van der Waals Molecule HeI_2 . *J. Chem. Phys.* **1980**, *73*, 3653–3659.
- (29) Buchachenko, A. A.; Grinev, T. A.; Kłos, J.; Bieske, E. J.; Szczeniński, M. M.; Chałasiński, G. Ab Initio Potential Energy and Dipole Moment Surfaces, Infrared spec-

- tra, and Vibrational Predissociation Dynamics of the $^{35}\text{Cl}^- \text{H}_2/\text{D}_2$ complexes. *J. Chem. Phys.* **2003**, *119*, 12931–12945.
- (30) Emmeluth, C.; Poad, B. L. J.; Thompson, C. D.; Weddle, G.; Bieske, E. J.; Buchachenko, A. A.; Grinev, T. A.; Kłos, J. The $\text{Al}^+ \text{-H}_2$ Cation Complex: Rotationally Resolved Infrared Spectrum, Potential Energy Surface, and Rovibrational Calculations. *J. Chem. Phys.* **2007**, *127*, 164310.
- (31) Poad, B. L. J.; Dryza, V.; Buchachenko, A. A.; Kłos, J.; Bieske, E. J. Properties of the $\text{B}^+ \text{-H}_2$ and $\text{B}^+ \text{-D}_2$ complexes: A Theoretical and Spectroscopic Study. *J. Chem. Phys.* **2012**, *137*, 124312.
- (32) Artiukhin, D. G.; Kłos, J.; Bieske, E. J.; Buchachenko, A. A. Interaction of the Beryllium Cation with Molecular Hydrogen and Deuterium. *J. Phys. Chem. A* **2014**, *118*, 6711–6720.
- (33) Artiukhin, D. G.; Bieske, E. J.; Buchachenko, A. A. Ab Initio Characterization of the Electrostatic Complexes Formed by H_2 Molecule and Cr^+ , Mn^+ , Cu^+ , and Zn^+ Cations. *J. Phys. Chem. A* **2016**, *120*, 5006–5015.
- (34) Jankowski, P.; Szalewicz, K. Ab Initio Potential Energy Surface and Infrared Spectra of $\text{H}_2\text{-CO}$ and $\text{D}_2\text{-CO}$ van der Waals Complexes. *J. Chem. Phys.* **1998**, *108*, 3554–3565.
- (35) Jankowski, P.; Szalewicz, K. A New Ab Initio Interaction Energy Surface and High-Resolution Spectra of the H_2CO van der Waals Complex. *J. Chem. Phys.* **2005**, *123*, 104301.
- (36) Jeziorska, M.; Jankowski, P.; Szalewicz, K.; Jeziorski, B. On the Optimal Choice of Monomer Geometry in Calculations of Intermolecular Interaction Energies: Rovibrational Spectrum of Ar-HF from Two- and Three-Dimensional Potentials. *J. Chem. Phys.* **2000**, *113*, 2957–2968.
- (37) Fishchuk, A. V.; Groenenboom, G. C.; van der Avoird, A. Ab Initio Treatment of the Chemical Reaction Precursor Complex $\text{Cl}(^2P)\text{-HF}$. 2. Bound States and Infrared Spectrum. *J. Phys. Chem. A* **2006**, *110*, 5280–5288.

- (38) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. Electron Affinities of the First-Row Atoms revisited. Systematic Basis Sets and Wave Functions. *J. Chem. Phys.* **1992**, *96*, 6796.
- (39) Weigend, F. Accurate Coulomb-Fitting Basis Sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.
- (40) Halkier, A.; Helgaker, T.; Jorgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. Basis-set Convergence in Correlated Calculations on Ne, N₂, and H₂O. *Chem. Phys. Lett.* **1998**, *286*, 243–252.
- (41) Halkier, A.; Helgaker, T.; Jorgensen, P.; Klopper, W.; Olsen, J.; Wilson, A. K. Basis-set Convergence of the Energy in Molecular Hartree-Fock Calculations. *Chem. Phys. Lett.* **1999**, *302*, 437–446.
- (42) Leininger, T.; Nicklass, A.; Küchle, W.; Stoll, H.; Dolg, M.; Bergner, A. The Accuracy of the Pseudopotential Approximation: Non-Frozen-Core Effects for Spectroscopic Constants of Alkali Fluorides XF (X = K, Rb, Cs). *Chem. Phys. Lett.* **1996**, *255*, 274 – 280.
- (43) Boys, S.; Bernardi, F. The Calculation of Small Molecular Interactions by the Differences of Separate Total Energies. Some Procedures with Reduced Errors. *Mol. Phys.* **1970**, *19*, 553–566.
- (44) Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Rauhut, G.; Amos, R. D.; Bernhardsson, A. et al. MOLPRO, Version 2012.1, a Package of Ab Initio Programs. 2012; see <http://www.molpro.net>.
- (45) Bartolomei, M.; Carmona-Novillo, E.; Hernández, M. I.; Campos-Martínez, J.; Hernández-Lamoneda, R. Long Range Interaction for Dimers of Atmospheric Interest: Dispersion, Induction and Electrostatic Contributions for O₂-O₂, N₂-N₂ and O₂-N₂. *J. Comp. Chem.* **2011**, *32*, 279–290.
- (46) Maitland, G. C.; Rigby, M.; Smith, E. B.; Wakeham, W. A. *Intermolecular Forces: Their Origin and Determination*; Clarendon Press, Oxford, 1987.

- (47) Olney, T. N.; Cann, N. M.; Cooper, G.; Brion, C. E. Absolute Scale Determination for Photoabsorption Spectra and the Calculation of Molecular Properties Using Dipole Sum Rules. *Chem. Phys.* **1997**, *223*, 59–98.
- (48) Hirschfelder, J. *Intermolecular Forces*; Wiley Interscience, 1967.
- (49) Aquilanti, V.; Cappelletti, D.; Pirani, F. Range and Strength of Interatomic Forces: Dispersion and Induction Contributions to the Bonds of Dications and of Ionic Molecules. *Chem. Phys.* **1996**, *209*, 299–311.
- (50) Hutson, J. M. Coupled Channel Methods for Solving the Bound-State Schrödinger Equation. *Comput. Phys. Commun.* **1994**, *84*, 1–18.
- (51) Hutson, J. M.; Le Sueur, C. R. BOUND and FIELD: Programs for Calculating Bound States of Interacting Pairs of Atoms and Molecules. *Comput. Phys. Commun.* **2019**, *241*, 1 – 8.
- (52) Hutson, J. M.; Le Sueur, C. R. BOUND, *a Program for Bound states of Interacting Pairs of Atoms and Molecules, Version 2019.01*.
- (53) Thornley, A. E.; Hutson, J. M. Bound-State Wave Functions from Coupled Channel Calculations using Log-Derivative Propagators: Application to Spectroscopic Intensities in ArHF. *J. Chem. Phys.* **1994**, *101*, 5578–5584.
- (54) Manolopoulos, D. E. An Improved Log-Derivative Method for Inelastic Scattering. *J. Chem. Phys.* **1986**, *85*, 6425–6429.
- (55) Cappelletti, D.; Pirani, F.; Bussery-Honvault, B.; Gómez, L.; Bartolomei, M. A Bond-Bond Description of the Intermolecular Interaction Energy: the Case of Weakly Bound N₂-H₂ and N₂-N₂ complexes. *Phys. Chem. Chem. Phys.* **2008**, *10*, 4281–4293.
- (56) Zare, R. N. *Angular Momentum. Understanding Spatial Aspects in Chemistry and Physics*; John Wiley and Sons, 1988.
- (57) Kołos, W.; Wolniewicz, L. Potential-Energy Curves for the $X^1\Sigma_g^+$, $b^3\Sigma_u^+$, and $C^1\Pi_u$ States of the Hydrogen Molecule. *J. Chem. Phys.* **1965**, *43*, 2429–2441.

- (58) Rahm, M.; Hoffmann, R.; Ashcroft, N. W. Atomic and Ionic Radii of Elements 1-96. *Chem. Eur. J.* **2016**, *22*, 14625–14632.

Table 1: Optimized parameters for the non-covalent contribution to the M^+H_2 PESs (Eqs. 6 and 7). Parameters for the electrostatic charge-quadrupole component, common to all systems, are indicated in the text. Distances are in Å and energies, in cm^{-1} ; β is dimensionless.

Complex	β	$R_e^\perp$ (Å)	$R_e^\parallel$ (Å)	$\varepsilon^\perp$ (cm^{-1})	$\varepsilon^\parallel$ (cm^{-1})
Na^+H_2	4.7	2.505	2.610	773.744	1023.236
K^+H_2	6.0	3.010	3.060	437.258	596.694
Rb^+H_2	7.5	3.200	3.240	360.629	499.690
$Cs^+H_2^a$	8.0	3.430	3.470	299.146	417.421

^a From Ref. ²³

Table 2: Interaction energies as obtained from the present analytical PES (Eq. 5), in comparison with previous calculations. Present values correspond to the minimum of $V(R, \theta, r_0)$ with $r_0 = 0.767$ Å, whereas data from previous works refer to the value of the intermolecular potential V at the geometry minimizing the total energy (adding the H_2 intramolecular potential to V) for $\theta = 90^\circ$ or the saddle point ($\theta = 90^\circ$). See text for discussion.

		$\theta = 90^\circ$			$\theta = 0$		
Complex		r (Å)	R (Å)	V (cm $^{-1}$)	r (Å)	R (Å)	V (cm $^{-1}$)
Na^+H_2	This work	0.767	2.384	-1302.8	0.767	2.869	-231.1
	a)	0.741	2.45	-1053.3			
	b)	0.743	2.427	-1038.8			
	c)	0.747	2.372	-1345.9	0.742	2.773	-409.7
	d)	0.746	2.408	-1184			
	e)	0.748	2.469	-1063.3			
K^+H_2	This work	0.767	2.883	-741.1	0.767	3.357	-105.1
	a)	0.739	3.06	-509.9			
	b)	0.740	3.099	-409.2			
	c)	0.748	2.885	-728.9			
Rb^+H_2	This work	0.767	3.083	-611.6	0.767	3.527	-81.1
	a)	0.738	3.31	-401.2			
Cs^+H_2	This work	0.767	3.313	-502.5	0.767	3.755	-74.6

a) MP2; aug-cc-pVQZ for H_2 , 6-311+G(d, p) for M^+ (contracted for Rb^+); BSSE corrected “a posteriori”.¹⁶

b) MP4 energies at MP2-optimized geometries; 6-311G(d, p)¹⁵

c) CCSDT for Na^+ (IC-MRCI+Q the saddle), CCSD(T) for K^+ ; ANO-RCC for M^+ , aug-cc-pVQZ for H_2 ¹⁹

d) RCCSD(T), aug-cc-pVQZ for H_2 , cc-pVQZ for Na^+ + bond functions, BSSE corrected¹⁷

e) CCSD(T); cc-pVTZ.²¹

Table 3: Properties of the M^+-H_2 bound states: Binding energies for *ortho* (*o*) and *para* (*p*) species and their difference, $\Delta(D_0) = D_0(o)-D_0(p)$; rotational constants A , B , C , $\bar{B}$, centrifugal distortion constants Δ_J and Δ_{JK} (with exponents indicated within parenthesis) and expected value of the M^+-H_2 distance for the ground vibrational state; stretching and bending frequencies ν_s and ν_b . All values in cm^{-1} unless otherwise specified.

Complex	$D_0(o)$	$D_0(p)$	$\Delta(D_0)$	ν_s	ν_b	A	B	C	$\bar{B}$	Δ_J	Δ_{JK}	$\langle R \rangle$ ($\text{\AA}$)
Na^+-H_2	948.9	902.2	46.7	265.7	450.6	70.50	1.4826	1.4244	1.4535	1.5(-4)	1.3(-3)	2.51
	888	842	46	246	485	71.30	1.4517	1.3949	1.4233	1.7(-4) ^a	-7.6(-4)	2.51
	—	861.0 ^b	—	242 ^c	492 ^c	—	—	—	—	—	—	2.47 ^b
	—	953.0	—	—	—	—	—	—	—	—	—	—
	860 $\pm$ 70 ^e	—	—	—	—	—	1.4760 ^f	1.4168 ^f	1.4464 ^f	1.5(-4) ^f	—	2.49 ^f
$^{39}K^+-H_2$	514.2	474.4	39.9	165.26	310.86	77.80	0.9715	0.9372	0.9544	1.0(-4)	-1.0(-3)	3.05
	—	459.8	—	—	—	—	—	—	—	—	—	—
	507 $\pm$ 70	—	—	—	—	—	—	—	—	—	—	—
$^{85}Rb^+-H_2$	415.0	378.3	36.7	142.8	275.0	81.15	0.8245	0.7958	0.8101	8.2(-5)	-1.0(-3)	3.27
	—	376.2	—	—	—	—	—	—	—	—	—	—
Cs^+-H_2	338.0	304.1	32.9	119.7	242.3	85.06	0.7054	0.6804	0.6929	7.2(-5)	-2.0(-3)	3.52

^a Rovibrational states calculations;¹⁷

^b Rovibrational states calculations;¹⁸

^c Vibrational self-consistent approach;²¹

^d Formation enthalpy calculations;¹⁶

^e Temperature-dependent equilibrium measurements;¹⁴

^f Rotationally resolved infrared spectrum;¹⁷

Graphical TOC Entry

Figure 1: M^+-H_2 interactions potentials (in cm^{-1}) as functions of the intermolecular distance R (in $\text{\AA}$) and angles between the molecular and the intermolecular axes, from linear ($\theta=0^\circ$) to T-shaped ($\theta=90^\circ$) configurations. Circles correspond to the CCSD(T) *ab initio* calculations and solid lines, to the analytical PES.

Figure 2: Contour plots of the Na^+H_2 PES as well as the ground state wavefunction of Na^+H_2 as functions of $X = R \cos(\theta)$ and $Y = R \sin(\theta)$ (in Å). Contours of the PES start at -1200 cm^{-1} with increments of 200 cm^{-1} up to a value of 600 cm^{-1} along the repulsive wall. Wave function is illustrated using a color palette as indicated in the right panel.

Figure 3: (a) Radial and (b) angular distributions of the ground states of M^+-H_2 (solid lines) and M^+-D_2 (dashed lines) for $M^+ = Na^+$ (red), K^+ (black), Rb^+ (green), Cs^+ (blue).

Figure 4: (a) Ionic radius (in Å) of $M^+ = \text{Na}^+$, K^+ , Rb^+ and Cs^+ and (b) Binding energies (in cm^{-1}) versus average intermolecular distance R_0 (in Å). Complexes with $p\text{H}_2$ and $o\text{D}_2$ are shown using filled red circles and red diamonds, respectively. Also in (b), estimation from Eq. 8 of the dissociation energy.