Theoretical Spectroscopy of the N_2HAr^+ Complex

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The six-dimensional potential energy surface of the electronic ground state of N_2HAr^+ is determined by ab initio computations at the CCSD(T) level of theory. The potential energy surface is used to derive a set of spectroscopic data for N_2HAr^+ and N_2DAr^+ using second order perturbation theory. Full six-dimensional (6-D) rotation−vibration computations are also carried out using an analytical representation of the surface for J=0 and 1, in order to deduce the rovibrational spectra of N_2HAr^+ and its deuterated isotopomer. Our variationally determined anharmonic wavenumbers differ by less than 15 cm^{-1} from the most accurate experimental values. Strong anharmonic resonances are found between the rovibrational levels of both cations even at low energies.

I. Introduction

The proton-bound ionic complex N_2HAr^+ was predicted to exist in 1995 by Kolbuszewski at the MP2 level of theory[1] with a relatively deep potential well toward dissociation into N_2H^+ and Ar (dissociation energy $D_e \approx 3000$ cm^{-1}). Two years later, the group at Basel[2−4] has characterized experimentally for the first time this cation by means of InfraRed PhotoDissociation (IRPD) spectroscopy and has accurately deduced its dissociation energy, $D_0 = 2781.5 \pm 1.5$ cm^{-1}, not far from the theoretical prediction. From the analysis of their IRPD spectra and the comparison to the available theoretical data,[1] these authors have tentatively determined the ν_1 fundamental (NH stretch) at ∼ 2255 cm^{-1} and the ν_s (=ν_3) fundamental (HAr stretch) at ∼250 cm^{-1}. However, the IRPD spectral assignments proposed there were revised later, since this ν_1 value was completely out of the range of the CCSD(T) predictions of Botschwina and Oswald,[5] ν_1= 2519 cm^{-1}. Moreover, the previously derived value for ν_1 was also far from the direct absorption spectroscopy value of 2505.5000 cm^{-1}, which is, however, the new commonly accepted evaluation of this stretching mode.[6] The ν_2 band origin (NN stretch) was also precisely determined at 2041.1802 cm^{-1}.[6] Finally, several combination modes have been identified. Readers are referred to the recent review of Bieske and Dopfer[7,8] for more details.

In addition to the MP2 computations of Kolbuszewski[1] and the CCSD(T) three-dimensional (3-D) stretch-only vibrational Hamiltonian variational calculations of Botschwina and Oswald[5,6] discussed above, MP2/aug-cc-pVTZ calculations have been carried out for this cation by Dopfer et al.,[4] who have generated the 2-D intermolecular potential energy surface of the N_2HAr^+ dimer and deduced a set of spectroscopic parameters, including equilibrium geometry and harmonic wavenumbers. Generally, previous computations have noticed the existence of anharmonic resonances between the stretchings because of the mixed character of these modes that should be described as a combination of NH, NN and HAr elongation motions. Finally, an accurate experimental/theoretical equilibrium structure has been deduced by Verdes et al.[9] from the analysis of the rotationally resolved spectra obtained by IRPD and direct absorption and ab initio computations, yielding R_e(NN) = 1.0929 Å, R_e(NH) = 1.0752 Å, and R_e(HAr) = 1.8854 Å. These distances are in good accord with the most recent values deduced by Seki et al.[10] from their Fourier Transform microwave pure rotational spectra of six different isotopomers of N_2HAr^+.

For the deuteron-bound N_2DAr^+ complex, similar investigations as for N_2HAr^+ were performed. Briefly, these works have located the fundamentals at ν_1 (NN stretch) = 2436.272 cm^{-1},[11] and ν_2 (ND stretch) = 1593.6058 cm^{-1}.[9] A combination mode $\nu_2 + 4\nu_s$, which is found to strongly interact with ν_1, occurs at 2435.932 cm^{-1}.

Despite this significant amount of experimental and theoretical data on N_2HAr^+ and N_2DAr^+ in the literature, little is known about the bending modes, except their harmonic frequencies. The reliable pattern of the bending levels can, however, only be deduced from full 6-D variational calculations on a six-dimensional potential energy surface of the electronic ground state of this cationic species. Hence, accurate ab initio methods are used here in order to generate the 6-D potential energy surface (6-D PES) of the ground electronic state of N_2HAr^+ covering its equilibrium geometry and the lowest dissociation pathway, leading to $N_2H^+(X^1\Sigma^+)$ and $Ar(^1S)$. Moreover, an analytical expression is deduced for this 6-D PES and used to derive a set of spectroscopic parameters for N_2HAr^+ and its deuterated isotopomer using second order perturbation theory. This analytical expansion is also incorporated in full 6-D variational calculations using the method of Carter and Handy.[12,13] The rovibrational spectra of N_2HAr^+ and N_2DAr^+ are then deduced for $J = 0$ and 1, allowing for reliable predictions for these two cations.

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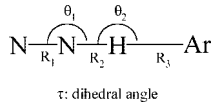

Figure 1. Definition of the internal coordinates of N_2HAr^+.

II. Computational Methods

a. Electronic Problem. Sheng and Leszczynski[14] were emphasizing the importance of electron correlation in the treatment of N_2HNg^+ molecular systems, where Ng is a rare gas. These authors came to the conclusion that DFT approaches are failing in treating these species and that only highly correlated methods, such as Coupled Cluster and Configuration Interaction methods, should be used for that purpose. Here, the 6-D PES of N_2HAr^+ ($X^1\Sigma^+$) was mapped using the coupled cluster method, CCSD(T), implemented in the MOLPRO program suite.[15] These calculations were carried out with two different basis sets. (1) In the larger basis set, the *spdfg* aug-cc-pV5Z basis set of Dunning was used for N and Ar, whereas the *spdf* aug-cc-pV5Z basis set was employed for H, resulting in 381 contracted Gaussian functions. (2) The smaller *spd(f)* cc-pV5Z basis subset resulted in 222 contracted Gaussian functions.[16,17] These two basis sets were employed in order to compare the effect of the diffuse part of the basis sets on the electronic structure, the equilibrium geometry, and the rovibrational level pattern of N_2HAr^+. This effort is connected closely to the polarizability of Ar, which is better described with the larger basis set. Indeed, this quantity is computed to be ~10.08 bohr^3 at the *spdf(g)* aug-cc-pV5Z/CCSD(T) level of theory, in close agreement with the experimental determination of 10.09 bohr^3.[18] In contrast, similar calculations using the smaller basis set lead to ~8.8 bohr^3, a value that is 20% smaller than the experimental result. The counterpoise correction was also computed for the larger basis set in order to compare the influence of Basis Set Superposition Error (BSSE) on the spectroscopy of this cation. These three 6-D PESs were generated in the internal coordinates defined in Figure 1, comprising the three stretching coordinates R_1 (R_{NN}), R_2 (R_{NH}), and R_3 (R_{HAr}), the two in-plane bending angles θ_1 (NNH) and θ_2 (NHAr), and the torsional angle τ between the NNH and NHAr planes. We calculated energies corresponding to different nuclear positions in the vicinity of the equilibrium geometry of $N_2HAr^+(X^1\Sigma^+)$ and along the lowest energy fragmentation pathway, which leads to the lowest dissociation limit, $N_2H^+(X^1\Sigma^+) + Ar(^1S)$. The geometries considered were in the ranges (in Å and degrees) $0.9 \le R_1 \le 1.3$, $0.85 \le R_2 \le 1.35$, $1.6 \le R_3 \le 2.8$, $50° \le \theta_{1,2} \le 180°$, and $0° \le \tau \le 180°$, resulting in more than 300 geometries. For $2 \le R_3 \le 2.8$, a step of 0.1 Å is used for choosing the points. The constructed PES covers the energies up to ~15 000 cm^{-1} above the minimum of $N_2HAr^+(X^1\Sigma^+)$ and ~2700 cm^{-1} along the R_3 coordinate. Subsequently, the calculated energies were fitted to the following polynomial expansion, where all points are equally weighted,

$$V(R_1, R_2, R_3, \theta_1, \theta_2, \tau) = \sum_{ijklmn} c_{ijklmn} Q_1^i Q_2^j Q_3^k Q_4^l Q_5^m \cos(nQ_6) \quad (1)$$

with the three reduced stretching coordinates, $Q_u = (R_u - R_u^{ref})/R_u$, for $u = 1-3$, the two bending coordinates, $Q_u = \theta_{u-3} - \theta_{u-3}^{ref}$, for $u = 4,5$ ($0° \le \theta_{u-3} \le 180°$), and the torsional angle, $Q_6 = \tau - \tau^{ref}$ ($0° \le \tau \le 360°$). The index "ref" refers to the reference geometry used during the fit (cf. Table 1). For the fit, the exponents in the expansion were restricted to $i + j + k + l + m \le 4$ and $n \le 2$. For $n \ne 0$, only the terms, for which $l \ne 0$, $m \ne 0$ and l, m and n have the same parity, were taken into account (see ref 19). Eventually, in total 71 c_{ijklmn} coefficients were optimized using a least-squares procedure and the final values are listed in ref 20. The root-mean-square of the fit was less than 10 cm^{-1}. Readers are referred to refs 21−27 for

TABLE 1: Equilibrium Distances (R_i, in Å), Rotational Constants (B_e and D_J, in cm^{-1}), Harmonic Wavenumbers (ω_e, in cm^{-1}) and the Decomposition of the Normal Modes into the Internal Coordinates of $N_2HAr^+(X^1\Sigma^+)$ and $N_2DAr^+(X^1\Sigma^+)$

	N_2HAr^+		N_2DAr^+
R_1	1.094[a]		
	1.094[b]		
	1.096[c]		
	1.1081[d]		
	1.1070[e]		
	1.0949[f]		
	1.098[g]		
R_2	1.071[a]		
	1.074[b]		
	1.082[c]		
	1.0831[d]		
	1.0838[e]		
	1.0755[f]		
	1.074[g]		
R_3	1.920[a]		
	1.898[b]		
	1.852[c]		
	1.8346[d]		
	1.8363[e]		
	1.8871[f]		
	1.909[g]		
B_e	0.0785[a]		0.0784[a]
	0.0793[b]		0.0793[b]
	0.0810[c]		0.0809[c]
	0.08136[d]		0.07965[i]
	0.08126[e]		
	0.07972[f]		
D_J	0.607×10^{-7}[a]		0.611×10^{-7}[a]
	0.579×10^{-7}[b]		0.583×10^{-7}[b]
	0.500×10^{-7}[c]		0.503×10^{-7}[c]
ω_1 (σ^+)	2823[a]	$0.82\,R_1 - 0.57\,R_2$	2542[a]
	2784[b]	$0.85\,R_1 - 0.53\,R_2$	2534[b]
	2694[c]	$0.88\,R_1 - 0.46\,R_2$	2494[c]
	2659[d]		2527[h]
	2603[e]		
	2783[f]		
ω_2 (σ^+)	2220[a]	$0.97\,R_1 + 0.25\,R_2$	1778[a]
	2204[b]	$0.96\,R_1 + 0.27\,R_2$	1747[b]
	2146[c]	$0.94\,R_1 + 0.31\,R_2$	1674[c]
	2049[d]		1743[h]
	2042[e]		
	2195[f]		
ω_3 (σ^+)	173[a]	$0.33\,R_1 + 0.65\,R_2 + 0.68\,R_3$	171[a]
	180[b]	$0.33\,R_1 + 0.65\,R_2 + 0.68\,R_3$	178[b]
	200[c]	$0.32\,R_1 + 0.65\,R_2 + 0.68\,R_3$	197[c]
	213[d]		189[h]
	210[e]		
	191[f]		
ω_4 (π)	882[a]	$-0.90\,\theta_1 + 0.43\,\theta_2$	667[a]
	889[b]	$-0.89\,\theta_1 + 0.45\,\theta_2$	671[b]
	923[c]	$-0.84\,\theta_1 + 0.53\,\theta_2$	693[c]
	942[d]		661[h]
	919[e]		
	876[f]		
ω_5 (π)	138[a]	$0.80\,\theta_1 + 0.60\,\theta_2$	130[a]
	143[b]	$0.80\,\theta_1 + 0.59\,\theta_2$	134[b]
	150[c]	$0.81\,\theta_1 + 0.58\,\theta_2$	143[c]
	172[d]		148[h]
	212[e]		
	156[f]		

[a] This work: CCSD(T)/*spdf(g)* aug-cc-pV5Z including BSSE (381 cGTO) calculations. [b] This work: CCSD(T)/*spdf(g)* aug-cc-pV5Z (381 cGTO) calculations. [c] This work: CCSD(T)/*spd(f)* cc-pV5Z (222 cGTO) calculations. [d] MP2 (125 cGTO) calculations.[1] [e] MP2/full (203 cGTO) calculations.[4] [f] CCSD(T) (368 cGTO) calculations.[6] [g] Experimental value estimated from the analysis of the Fourier Transform microwave pure rotational spectra of six different isotopomers.[10] [h] CCSD(T) (368 cGTO) calculations[9]

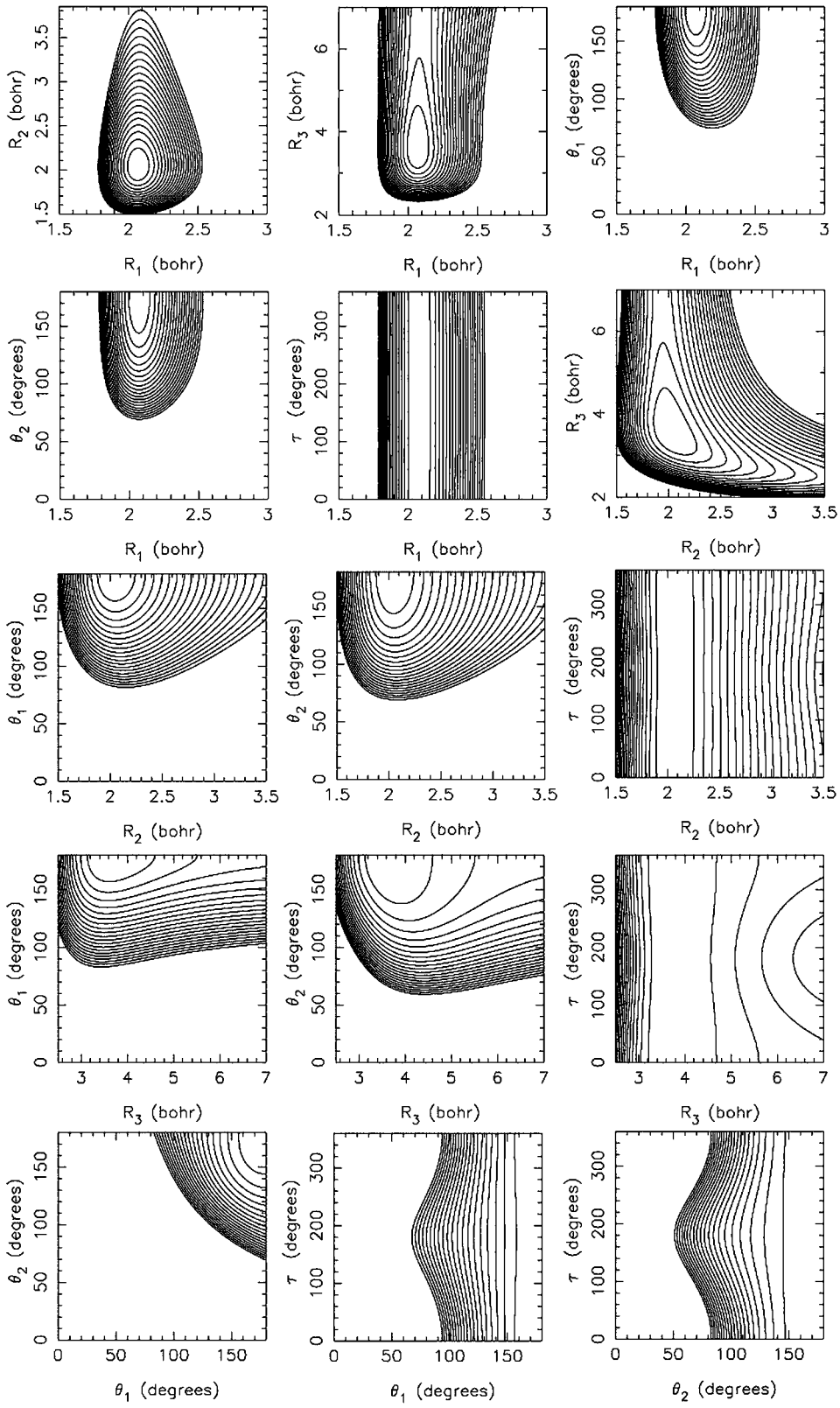

Figure 2. 2-D cuts through the 6-D PES of $N_2HAr^+(X^1\Sigma^+)$, obtained at the *spdf(g)* aug-cc-pV5Z/CCSD(T) level including the BSSE correction, for all 15 combinations of two of the internal coordinates. The other internal coordinates are kept fixed at their equilibrium values (cf. Table 1), except the contours involving τ, which are given for θ_1 and/or $\theta_2 = 150°$. The steps between the contours are 1000 cm^{-1}.

similar treatments of other linear tetratomic molecules, for which close agreement between calculations with accurate experimental data is achieved, further validating our theoretical approach.

b. Nuclear Motion Problem. The analytical representations of the 6-D PES were incorporated into perturbative and variational treatments of the nuclear problem. In the perturbative approach, the 6-D PES was derived as a quartic force field in internal coordinates, which was subsequently transformed by L-tensor algebra into a quartic force field in dimensionless normal coordinates. This procedure enables the evaluation of the spectroscopic constants up to the fourth order, using the formula developed in refs 28 and 29. In the variational approach,

TABLE 2: Variationally Calculated Rovibrational Levels of $N_2HAr^+(X^1\Sigma^+)$ and Their Tentative Assignment[a]

$J = 0$				$J = 1$	
σ^+		σ^-		π	
$(v_1,v_2,v_3,v_4^{l4},v_5^{l5})$	energy	$(v_1,v_2,v_3,v_4^{l4},v_5^{l5})$	energy	$(v_1,v_2,v_3,v_4^{l4},v_5^{l5})$	energy
$(0,0,0,0^0 0^0)$	0	$(0,0,0,1^1,1^1)$	1001	$(0,0,0,0^0,1^1)$	162
$(0,0,1,0^0,0^0)$	230	$(0,0,1,1^1,1^1)$	1228	$(0,0,1,0^0,1^1)$	394
$(0,0,0,0^0,2^0)$	314	$(0,0,0,1^1,3^1)$	1323	$(0,0,0,0^0,3^1)$	568
$(0,0,2,0^0,0^0)$	493	$(0,0,2,1^1,1^1)$	1485	$(0,0,2,0^0,1^1)$	660
$(0,0,1,0^0,2^0)$	546	$(0,0,1,1^1,3^1)$	1558	$(0,0,1,0^0,3^1)$	803
$(0,0,3,0^0,0^0)$	682	$(0,0,3,1^1,1^1)$	1696	$(0,0,0,1^1,0^0)$	828
$(0,0,2,0^0,2^0)$	784	$(0,0,2,1^1,3^1)$	1783	$(0,0,3,0^0,1^1)$	973
$(0,0,1,0^0,4^0)$	834	$(0,0,1,1^1,5^1)$	1853	$(0,0,1,1^1,0^0)$	1051
$(0,0,4,0^0,0^0)$	929	$(0,0,4,1^1,1^1)$	1947	$(0,0,2,0^0,3^1)$	1065
$(0,0,0,1^1,1^1)$	985	$(0,0,0,2^0,2^0)$	1960	$(0,0,4,0^0,1^1)$	1081
$(0,0,2,0^0,4^0)$	1100	$(0,0,3,1^1,3^1)$	2116	$(0,0,0,1^1,2^0)$	1177
$(0,0,5,0^0,0^0)$	1199	$(0,0,5,1^1,1^1)$	2172	$(0,0,3,0^0,3^1)$	1303
$(0,0,1,1^1,1^1)$	1206	$(0,0,1,2^0,2^0)$	2203	$(0,0,0,0^0,7^1)$	1313
$(0,0,4,0^0,2^0)$	1221	$(0,0,4,1^1,3^1)$	2239	$(0,0,2,1^1,0^0)$	1344
$(0,0,0,1^1,3^1)$	1277	$(0,0,0,2^0,4^0)$	2305	$(0,0,5,0^0,1^1)$	1361
$(0,0,3,0^0,4^0)$	1314	$(0,0,3,1^1,5^1)$	2335	$(0,0,1,1^1,2^0)$	1435
$(0,0,2,1^1,1^1)$	1456	$(0,0,2,2^0,2^0)$	2437	$(0,0,0,1^1,4^0)$	1468
$(0,0,5,0^0,2^0)$	1475	$(0,0,5,1^1,3^1)$	2489	$(0,0,4,0^0,3^1)$	1578
$(0,0,1,1^1,3^1)$	1501	$(0,0,1,2^0,4^0)$	2501	$(0,0,3,1^1,0^0)$	1588
$(0,0,0,1^1,5^1)$	1586			$(0,0,3,0^0,5^1)$	1647
$(0,0,7,0^0,0^0)$	1595			$(0,0,2,1^1,2^0)$	1662
$(0,0,0,2^0,0^0)$	1621			$(0,0,5,0^0,3^1)$	1673
$(0,0,6,0^0,2^0)$	1724			$(0,0,1,1^1,4^0)$	1734
$(0,0,2,1^1,3^1)$	1772			$(0,0,4,0^0,5^1)$	1760
$(0,0,1,1^1,5^1)$	1826			$(0,0,2,0^0,7^1)$	1806
$(0,0,1,2^0,0^0)$	1857			$(0,0,4,1^1,0^0)$	1830
$(0,0,4,0^0,6^0)$	1893			$(0,0,0,2^0,1^1)$	1868
$(0,0,3,0^0,8^0)$	1909			$(0,0,7,0^0,1^1)$	1880
$(0,0,8,0^0,0^0)$	1938			$(0,0,3,1^1,2^0)$	1912
$(0,0,4,1^1,1^1)$	1962			$(0,0,6,0^0,3^1)$	1961
$(0,0,3,1^1,3^1)$	1970			$(0,0,2,1^1,4^0)$	1968
$(0,1,0,0^0,0^0)$	2056			$(0,0,1,2^0,1^1)$	2033
$(0,0,2,1^1,5^1)$	2064			$(0,0,1,1^1,6^0)$	2082
$(0,0,2,2^0,0^0)$	2078			$(0,0,4,0^0,7^1)$	2118
$(0,0,5,0^0,6^0)$	2131			$(0,0,8,0^0,1^1)$	2146
$(0,0,4,0^0,8^0)$	2149			$(0,0,3,1^1,3^1)$	2175
$(0,0,9,0^0,0^0)$	2186			$(0,0,4,1^1,2^0)$	2183
$(0,0,5,1^1,1^1)$	2201			$(0,0,7,0^0,3^1)$	2221
$(0,0,4,1^1,3^1)$	2220			$(0,0,3,1^1,4^0)$	2224
$(0,0,8,0^0,2^0)$	2255			$(0,0,0,2^0,3^1)$	2236
$(0,1,1,0^0,0^0)$	2284			$(0,1,0,0^0,1^1)$	2244
$(0,0,3,1^1,5^1)$	2332			$(0,0,6,0^0,5^1)$	2265
$(0,0,3,2^0,0^0)$	2367			$(0,0,2,1^1,5^1)$	2285
$(0,1,0,0^0,2^0)$	2376			$(0,0,2,2^0,1^1)$	2305
$(0,0,6,0^0,6^0)$	2409			$(0,0,5,1^1,0^0)$	2348
$(0,0,5,0^0,8^0)$	2412			...	...
$(0,0,10,0^0,0^0)$	2418			$(0,1,0,1^1,0^0)$	2937
$(0,0,6,1^1,1^1)$	2437				
$(0,0,5,1^1,3^1)$	2476				
$(0,0,9,0^0,2^0)$	2496				
$(1,0,0,0^0,0^0)$	2518				
...	...				
$(0,2,3,0^0,0^0)$	2719				
$(1,0,1,0^0,0^0)$	2740				
$(1,0,0,0^0,2^0)$	2848				
$(1,0,2,0^0,0^0)$	3025				
$(1,0,3,0^0,0^0)$	3272				

[a] These data are derived from the 6-D PES obtained at the *spdf*(*g*) aug-cc-pV5Z/CCSD(T) level including the BSSE correction. See text for more details. All values are in cm^{-1}.

the method of Carter and Handy was employed,[12,13] which takes all couplings between all angular momenta into account, leading to relatively large Hamiltonian matrices for tetratomic species. To reduce the size of these matrices, the following contraction scheme was employed. First, 2-D contractions were done for R_1 and R_3, and the resulting functions were then combined with the stretching functions associated with R_2. The 3-D stretching functions were contracted and stocked for later use. Four different contractions were performed for the bending coordinates, two by combining the θ_1 and θ_2 basis functions with $\cos(0\tau)$ and $\cos(1\tau)$ and two with $\sin(1\tau)$ and $\sin(2\tau)$. The resulting functions were then contracted to the primitive τ

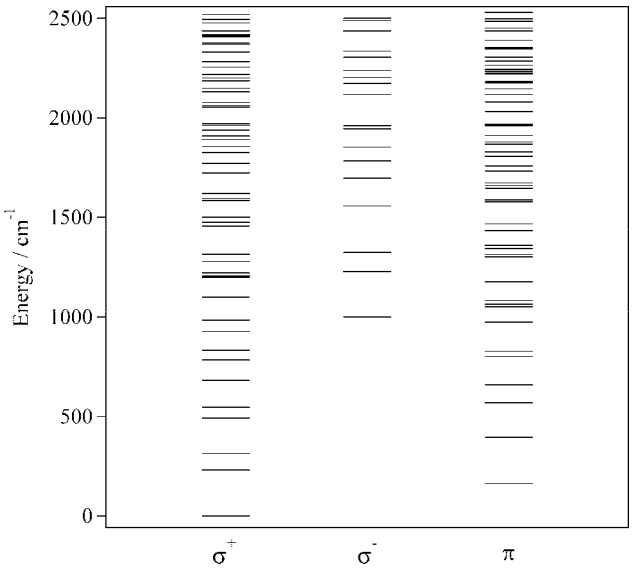

Figure 3. Pattern of the variationally calculated rovibrational levels of $N_2HAr^+(X^1\Sigma^+)$ for $J = 0$ and $J = 1$ (cf. Table 2).

functions, $\cos(0\tau)$ to $\cos(M\tau)$ and $\sin(1\tau)$ to $\sin(M\tau)$. The rovibrational levels were then obtained after diagonalization of the Hamiltonian matrix written in the basis formed by the 3-D contracted stretching functions and the contracted bending functions (for $J = 0$) and the eigenfunctions of the rigid rotor (for $J \neq 0$). Consequently, the resulting Hamiltonian matrix is formed only by 1-D or 2-D integrals, reducing the cost for the variational calculations.[12,13] Details of the basis set used for these calculations are given in refs 22, 27, 30, and 31. The accuracy of these calculations is $\sim$1 cm^{-1} for the converged levels. The accuracy of the computed rovibrational energies is better than 20 cm^{-1} for the converged levels. The rotational constants are believed to be accurate to within 0.01 cm^{-1}.

III. Results and Discussion

a. Characteristics of the Six-Dimensional Potential Energy Surface (6-D PES) of $N_2HAr^+(X^1\Sigma^+)$. Figure 2 depicts the 2-D cuts through the 6-D PES of $N_2HAr^+(X^1\Sigma^+)$, obtained at the *spdf(g)* aug-cc-pV5Z/CCSD(T) level and including the BSSE correction, along two of the internal coordinates, with the remaining internal coordinates kept fixed at their equilibrium values (cf. Table 1), except for those involving the torsion τ, which are given for θ_1 and/or $\theta_2 = 150°$. In each cut, 20 contours are plotted in steps of 1000 cm^{-1}. The 2-D cuts were also generated through the 6-D PES without the BSSE correction and through the 6-D PES computed with the smaller basis set. Comparison between these 2-D cuts reveals that these three PESs present similar shapes so that the following discussion is valid for three of them. Inspection of Figure 2 reveals that, with the exception of the NN (R_1) stretching, this PES is very flat along all internal coordinates, in particular, the cuts involving R_2 (NH) and R_3 (HAr). Hence, low anharmonic wavenumbers are expected for some of the normal modes. The cuts along the R_3 distance display a shallow minimum, corresponding to the equilibrium geometry of $N_2HAr^+(X^1\Sigma^+)$, with a slow rise in energy for large R_3 distances up to the lowest intermolecular dissociation limit. By bending both in-plane angles, local minima can be found along the torsion coordinate for $\tau \approx 90°$ and 270°. These minima are located higher in energy than the global linear minimum of $N_2HAr^+(X^1\Sigma^+)$ and correspond to transient species formed during the isomerization of linear N_2HAr^+ toward less stable isomers of the same sum formula. Similar behavior has already been noticed in the 6-D PESs of some linear tetratomic molecules, such as NCCN,[21] C_3O,[24] CCNN,[25] and C_3S.[26]

TABLE 3: Variationally Calculated Anharmonic Wavenumbers (ν_i, in cm^{-1}) of $N_2HAr^+(X^1\Sigma^+)$ and $N_2DAr^+(X^1\Sigma^+)$ and Comparison to Experimental Values

ν_1 (σ^+)	2517.9[a]	2438.8[a]
	2522.1[b]	2438.7[b]
	2478.2[c]	2423.3[c]
	2519.0[d]	2441[g]
	2505.5000[e]	2436.272[h]
ν_2 (σ^+)	2056.4[a]	1611.6[a]
	2062.8[b]	1597.8[b]
	2055.5[c]	1617.8[c]
	1987.0[d]	1559[g]
	2041.1802[e]	1593.6058[h]
ν_3 (σ^+)	230.0[a]	197.7[a]
	236.0[b]	202.7[b]
	256.4[c]	230.8[c]
	205.0[d]	195[g]
	199.2[f]	
ν_4 (π)	828.3[a]	633.0[a]
	841.9[b]	640.8[b]
	910.0[c]	680.2[c]
ν_5 (π)	162.0[a]	142.3[a]
	163.5[b]	144.5[b]
	168.9[c]	157.7[c]
$\nu_1 + \nu_3$	2739.9[a]	
	2748.2[b]	
	2777.0[c]	
	2756.0[d]	
	2755.62[i]	
$\nu_2 + 3\nu_3$	2718.5[a]	
	2715.6[b]	
	2658.0[b]	
	2707.34[i]	
$\nu_2 + 4\nu_3$		2420.2[a]
		2422.8[b]
		2408.4 (2442.6)[j]
		2435.932[k]

[a] This work: CCSD(T)/*spdf(g)* aug-cc-pV5Z including BSSE (381 cGTO) calculations. [b] This work: CCSD(T)/*spdf(g)* aug-cc-pV5Z (381 cGTO) calculations. [c] This work: CCSD(T)/*spd(f)* cc-pV5Z (222 cGTO) calculations. [d] CCSD(T) (368 cGTO) calculations.[6] [e] Experimental value.[6] [f] Experimental value estimated from the analysis of the Fourier Transform microwave pure rotational spectra of six different isotopomers.[10] [g] CCSD(T) (368 cGTO) calculations.[9] [h] Experimental data.[9] [i] Experimantal value.[2] [j] CCSD(T) calculations.[11] [k] Experimental data.[11]

Close examination of the cuts in Figure 2 shows couplings between several internal coordinates. For example, the NN (R_1) and NH (R_2) elongations are slightly coupled together. Much stronger couplings are identified between the NH (R_2) and the HAr (R_3) bonds. The two bendings are also coupled together and with the HAr stretch coordinate. These couplings are confirmed by the decomposition of the normal modes into the internal coordinates (cf. Table 1 for more details). In particular, the ν_3 mode is a strong mixture of the NN, HN, and HAr displacements. The resulting anharmonic resonances complicate the assignments of vibrational quantum numbers to the rovibrational levels observed in both the experimental and theoretical spectra (vide infra). The bendings are coupled with the HN and HAr stretches. Finally, the torsion is coupled with all the other internal coordinates.

Table 1 compares the linear equilibrium geometry of $N_2HAr^+(X^1\Sigma^+)$ deduced from the present analysis with previous theoretical and experimental determinations. Our parameters, $R_1 = 1.094$ (1.094) Å, $R_2 = 1.074$ (1.071) Å, and $R_3 = 1.898$

TABLE 4: Variationally Calculated Rovibrational Levels of $N_2DAr^+(X^1\Sigma^+)$ and their Tentative Assignment[a]

$J = 0$				$J = 1$	
σ^+		σ^-		π	
$(\nu_1,\nu_2,\nu_3,\nu_4^{l4},\nu_5^{l5})$	energy	$(\nu_1,\nu_2,\nu_3,\nu_4^{l4},\nu_5^{l5})$	energy	$(\nu_1,\nu_2,\nu_3,\nu_4^{l4},\nu_5^{l5})$	energy
$(0,0,0,0^0,0^0)$	0	$(0,0,0,1^1,1^1)$	788	$(0,0,0,0^0,1^1)$	142
$(0,0,1,0^0,0^0)$	198	$(0,0,1,1^1,1^1)$	982	$(0,0,1,0^0,1^1)$	339
$(0,0,0,0^0,2^0)$	288	$(0,0,0,1^1,3^1)$	1081	$(0,0,0,0^0,3^1)$	471
$(0,0,2,0^0,0^0)$	401	$(0,0,2,1^1,1^1)$	1182	$(0,0,2,0^0,1^1)$	541
$(0,0,1,0^0,2^0)$	481	$(0,0,1,1^1,3^1)$	1272	$(0,0,0,1^1,0^0)$	633
$(0,0,0,0^0,4^0)$	597	$(0,0,0,1^1,5^1)$	1393	$(0,0,1,0^0,3^1)$	666
$(0,0,3,0^0,0^0)$	620	$(0,0,3,1^1,1^1)$	1402	$(0,0,3,0^0,1^1)$	761
$(0,0,2,0^0,2^0)$	682	$(0,0,2,1^1,3^1)$	1478	$(0,0,1,1^1,0^0)$	833
$(0,0,0,1^1,1^1)$	775	$(0,0,0,2^0,2^0)$	1544	$(0,0,2,0^0,3^1)$	840
$(0,0,1,0^0,4^0)$	796	$(0,0,1,1^1,5^1)$	1595	$(0,0,0,1^1,2^0)$	873
$(0,0,3,0^0,2^0)$	869	$(0,0,3,1^1,3^1)$	1655	$(0,0,1,0^0,5^1)$	928
$(0,0,0,0^0,6^0)$	922	$(0,0,0,1^1,7^1)$	1732	$(0,0,4,0^0,1^1)$	1003
$(0,0,2,0^0,4^0)$	970	$(0,0,2,1^1,5^1)$	1742	$(0,0,2,1^1,0^0)$	1023
$(0,0,1,1^1,1^1)$	973	$(0,0,1,2^0,2^0)$	1759	$(0,0,3,0^0,3^1)$	1041
$(0,0,5,0^0,0^0)$	1008			$(0,0,0,0^0,7^1)$	1045
$(0,0,0,1^1,3^1)$	1063			$(0,0,1,1^1,2^0)$	1110
$(0,0,1,0^0,6^0)$	1141			$(0,0,2,0^0,5^1)$	1136
$(0,0,3,0^0,4^0)$	1177			$(0,0,0,1^1,4^0)$	1215
$(0,0,2,1^1,1^1)$	1189			$(0,0,3,1^1,0^0)$	1255
$(0,0,0,2^0,0^0)$	1233			$(0,0,4,0^0,3^1)$	1270
$(0,0,6,0^0,0^0)$	1250			$(0,0,1,0^0,7^1)$	1276
$(0,0,1,1^1,3^1)$	1269			$(0,0,2,1^1,2^0)$	1296
$(0,0,5,0^0,2^0)$	1319			$(0,0,3,0^0,5^1)$	1338
$(0,0,3,1^1,1^1)$	1397			$(0,0,0,0^0,9^1)$	1356
$(0,0,1,0^0,8^0)$	1406			$(0,0,0,2^0,1^1)$	1370
$(0,0,1,2^0,0^0)$	1421			$(0,0,6,0^0,1^1)$	1412
$(0,0,7,0^0,0^0)$	1440			$(0,0,4,1^1,0^0)$	1430
$(0,0,3,0^0,6^0)$	1458			$(0,0,5,0^0,3^1)$	1442
$(0,0,2,1^1,3^1)$	1487			$(0,0,2,0^0,7^1)$	1464
$(0,0,0,2^2,2^2)$	1499			$(0,0,3,1^1,2^0)$	1488
$(0,0,0,2^0,2^0)$	1510			$(0,0,4,0^0,5^1)$	1520
$(0,0,6,0^0,2^0)$	1551			$(0,0,1,2^0,1^1)$	1534
$(0,1,0,0^0,0^0)$	1611			$(0,0,1,0^0,9^1)$	1546
$(0,0,4,1^1,1^1)$	1618			$(0,0,2,1^1,4^0)$	1589
$(0,0,2,2^0,0^0)$	1636			$(0,0,7,0^0,1^1)$	1611
$(0,0,8,0^0,0^0)$	1659			$(0,0,5,1^1,0^0)$	1630
$(0,0,4,0^0,6^0)$	1676			$(0,0,6,0^0,3^1)$	1657
$(0,0,3,1^1,3^1)$	1698			$(0,0,4,1^1,2^0)$	1678
$(0,0,1,2^2,2^2)$	1720			$(0,0,5,0^0,5^1)$	1701
$(0,0,1,2^0,2^0)$	1729				
...					
$(0,1,2,0^0,0^0)$	2030				
$(1,0,0,0^0,0^0)$	2439				
$(0,1,4,0^0,0^0)$	2420				

[a] These data are derived from the 6-D PES obtained at the *spdf(g)* aug-cc-pV5Z/CCSD(T) level including the BSSE correction. See text for more details. All values are in cm^{-1}.

(1.920) Å obtained at the *spdf(g)* aug-cc-pV5Z/CCSD(T) level of theory without and with (in parentheses) BSSE correction agree quite well with the previous MP2 (125 cGTO), MP2 (203 cGTO) and the CCSD(T) results of Kolbuszewski,[1] Dopfer et al.,[4] and Botschwina et al.,[6] respectively (Table 1). When compared to the equilibrium structure deduced from the microwave spectra of Seki et al.,[10] our values for R_1 and R_2 differ by less than 0.004 Å from theirs. For R_3, the difference between our (with and without the BSSE correction) and their value reaches 0.011 Å, probably due to the flatness of the PES along this coordinate, which is better described in our 6-D treatment as compared to previous theoretical efforts. Using the smaller basis set (i.e., *spd(f)* cc-pV5Z without BSSE correction), a surprisingly good agreement with previous works is also noticeable, despite the fact that this basis set not fully describes the polarizability of Ar, which is the main relevant quantity for the formation of this complex (via charge-induced dipole interaction).

When compared to their corresponding diatomic and triatomic fragments, the R_1 separation (NN stretch) in N_2HAr^+ of 1.098 Å (see Table 1) is slightly longer than the NN distance in the neutral $N_2(X^1\Sigma_g^+)$ diatomic (1.09768 Å[32]) but remains distinctly shorter than in $N_2^+(X^2\Sigma_g^+)$ (1.11642 Å[32]). The weakening of the NN bond in the N_2HAr^+ complex is most likely a signature of a charge transfer occurring during the formation of the bonds between N_2, H, and Ar in this complex. Then, the HAr distance ($R_3 = 1.852$ Å) of this complex is strongly shortened compared to the neutral HAr diatomic ($R_e = 3.6$ Å for HAr(X)[33]) but still longer than the equilibrium distance (of 1.28 Å[32]) in HAr^+. Again, this is consistent with the partial electron transfer from N_2 to HAr^+. Finally, the NN and NH distances in N_2HAr^+ are slightly longer than those of N_2H^+, probably because of small electron transfer to the weak HAr bond. Similar effects have already been observed for other charge-transfer complexes. Interested readers are referred to refs 22, 23 for further examples.

The dissociation energy (D_0) of the N_2HAr^+ complex was measured precisely as 2781.5 ± 1.5 cm^{-1}.[2] This value is in good agreement with the D_e value of ~2820 (2720) cm^{-1} deduced from our 6-D PES, obtained at the *spdf(g)* aug-cc-pV5Z/CCSD(T) without (with) BSSE correction. The accuracy of the calculated value is expected to be ~100 cm^{-1}, according to previous calculations and due to our experience in calculating this quantity.[22,23] When compared to previous theoretical data, our dissociation energy is in close accord with both the MP2 (203 cGTO) and the CCSD(T) (368 cGTO) determinations of Dopferet al. (D_e = 2881 cm^{-1})[4] and of Botschwina et al.[6] (D_e = 2819 cm^{-1}), respectively. The less precise MP2 calculations of Kolbuszewski[1] lead, however, to a quite high value (D_e = 3088 cm^{-1}), which is out of the range of our and the other previous determinations.

b. Spectroscopic Properties and Rovibrational Spectrum of $N_2HAr^+(X^1\Sigma^+)$. The N_2HAr^+ ($X^1\Sigma^+$) cation has five vibrational modes, namely three stretching modes, ν_{1-3} (σ^+), and two doubly degenerate bending modes, ν_{4-5} (π). If the bending modes are excited, then there are two vibrational angular momenta l_4 and l_5, for which only the projection of $\boldsymbol{l} = \boldsymbol{l_4} + \boldsymbol{l_5}$ has to be considered. The variable l varies from $|l_4 - l_5|$ to $l_4 + l_5$ in steps of two. The rotational angular momentum J needs to be greater or equal to l ($J = l, l + 1, l + 2,...$). Table 1 lists the rotational constants (B_e and D_J) and the harmonic wavenumbers (ω_i) for $N_2HAr^+(X^1\Sigma^+)$. This table gives also a comparison between our computed data and the corresponding previously determined quantities. Concerning the harmonic wavenumbers, our values computed at the *spdf(g)* aug-cc-pV5Z/CCSD(T) level of theory with and without BSSE correction, compare relatively well with previous CCSD(T) calculations. The differences are less than 25 cm^{-1} with previous works.

Let us now concentrate on the comparison of our three 6D-PESs computed at the *spd(f)* cc-pV5Z/CCSD(T) level and the *spdf(g)* aug-cc-pV5Z/CCSD(T) level with and without BSSE correction. As expected, Table 1 shows that the inclusion of diffuse functions is crucial for a better description of the bonding, the electronic structure, and therefore, the spectroscopy of this complex. For instance, the values for ω_1, ω_2, and ω_4 derived at the *spd(f)* cc-pV5Z/CCSD(T) level of theory are quite different from the others, whereas ω_3 and ω_5 show relatively better accord with previous calculations. More generally, such discrepancies between the data obtained using a smaller or larger basis set are expected for these molecular systems due to the flatness of the PESs along the corresponding coordinates and of the importance of electron correlation in the description of their bonding. For instance, electron correlation effects should change drastically the shape of the PESs, especially near the equilibrium minimum, leading to different second order derivatives and consequently to quite different ω values. For these molecular systems, only full-dimensional variationally computed spectra on 6-D PESs can lead to reliable spectroscopic information, which can directly be compared to the experimental data (see below).

Table 2 lists the variationally calculated rovibrational spectrum of the 6-D PES of $N_2HAr^+(X^1\Sigma^+)$ for $J = 0$ and $J = 1$ obtained at the *spdf(g)* aug-cc-pV5Z/CCSD(T) level including the BSSE correction. Figure 3 displays the pattern of these levels up to 2500 cm^{-1} above the zero point energy. The accuracy of the variationally determined wavenumbers is expected to be ~20 cm^{-1}, comparably to similar works on other tetratomic systems.[21-27] Table 2 and Figure 3 clearly show the high density of rovibrational levels even for energies as low as 1500 cm^{-1} above the zero point vibrational energy, favoring their mutual interactions and resulting anharmonic resonances. The anharmonic resonances are mixing the initial rovibrational wave functions, making their equivocal assignment a quite difficult task. In our assignment, we were also guided by the perturbatively computed spectrum using the 6-D PESs. Table 2 lists the tentatively assigned spectrum for all rovibrational levels up to 2500 cm^{-1} above the zero point vibrational energy and for the pure ($1,0,\nu_3,0^0,0^0$) and ($0,\nu_2,0,0^0,0^0$) stretching series up to 3200 cm^{-1} above the zero point vibrational energy.

As can be seen in Table 3, our fundamentals computed at the *spdf(g)* aug-cc-pV5Z/CCSD(T) level (without BSSE correction) are ν_1 (NH stretch) = 2522.1, ν_2 (NN stretch) = 2062.8, ν_3 (HAr stretch) = 236.0, ν_4 (trans bending) = 841.9 and ν_5 (cis bending) = 163.5 (all values are in cm^{-1}), respectively. These values change to ν_1 = 2517.9, ν_2 = 2056.4, ν_3 = 230.0, ν_4 = 828.3 and ν_5 = 162.0 when including the BSSE correction. The above-mentioned differences between data derived from the 6-D PES for the harmonic wavenumbers with and without BSSE are clearly reduced when considering the 6-D variationally computed anharmonic wavenumbers. Our results represent reliable predictions for the bending modes. When compared to the N_2H^+ monomer, the NH and NN stretches show substantial redshifts of 712 and 195 cm^{-1}, respectively. These are indicative of the perturbation of the corresponding bonds arising from the formation of this complex.

In the following, we will be discussing only the data derived from our 6D-PES computed at the *spdf(g)* aug cc-pV5Z/CCSD(T) level and including the BSSE correction. For the ν_1 and ν_2 modes, our values agree quite well with the most precise experimental determinations of these quantities, with differences of less than 16 cm^{-1} (Table 3). Such differences are within the expected accuracy of our computations. In order to further rationalize this observation, we have also generated the 3-D PES of the ground-state of $N_2H^+(X^1\Sigma^+)$ at the Coupled Cluster level of theory using the same basis set (*spdf(g)* aug-cc-pV5Z). The details of these calculations and of the corresponding theoretical data will be published separately.[34] Briefly, these computations show that the NH stretch (ν_1) of $N_2H^+(X^1\Sigma^+)$ is calculated at 3234 cm^{-1}, matching with the experimental value of Keim et al.[35] The N_2H^+ $X^1\Sigma^+$ ν_2 mode (NN stretch) is calculated to be 2265 cm^{-1}, which is 7 cm^{-1} higher than the experimental value of Foster and McKellar.[36]

The HAr stretch wavenumber (ν_3) in N_2HAr^+ is calculated to be 230.0 cm^{-1}, which may be compared to the experimental estimate of 199 cm^{-1} derived from the analysis of the rotational spectrum.[10] Interestingly, Table 2 shows that the ($0,0,\nu_3,0,0$) vibrational series presents an inverted anharmonicity character. Indeed, one can clearly see that its corresponding harmonic ω value (ω_3 = 173 cm^{-1}) value is lower than its anharmonic ν value (ν_3 = 230 cm^{-1}). This is closely related to the flatness of the PES along the corresponding normal coordinate. Similarly, the ($0,0,0,0,\nu_5$) vibrational series exhibits such an inverted anharmonicity behavior. Here again, ω_5 (=138 cm^{-1}) is lower than ν_5 (=162 cm^{-1}), which is also a signature of the flatness of the PES along this bending coordinate. These features are commonly occurring for the low frequency modes in charge-transfer molecular systems, such as N_2CO^+ and N_4^+.[23,24] Generally, the harmonic approximation is not appropriate to generate accurate rovibrational spectra for this type of molecular species.

Dealing with combination modes, the $\nu_1 + \nu_3$ band has been identified at 2755.62 cm^{-1} by Nizkorodov et al.[2] This value is differing by ~16 cm^{-1} from our computed value of 2740 cm^{-1} (cf. Table 2). This deviation is still within the expected accuracy

of our computations. Hence, the couplings between the vibrational modes, at least between the ν_1 and ν_3 stretch, are well described by our 6-D PES. Similarly, our computed wavenumber for $\nu_2 + 3\nu_3$ (= 2718.5 cm^{-1}, cf. Table 2) shows a good agreement with the experimental value of 2707.34 cm^{-1}, signature here again of the good description of the couplings between the ν_2 and ν_3 modes.

c. Spectroscopic Properties and Rovibrational Spectrum of $N_2DAr^+(X^1\Sigma^+)$. In Tables 1 and 4 are listed a set of spectroscopic parameters and the variationally calculated spectrum for N_2DAr^+ ($X^1\Sigma^+$), respectively. The isotopic shifts (in cm^{-1}) are computed variationally to be $\Delta\nu_1 = 79$, $\Delta\nu_2 = 445$, $\Delta\nu_3 = 32$, $\Delta\nu_4 = 195$ and $\Delta\nu_5 = 20$. Hence, the five vibrational modes are significantly affected by substituting the H atom by D, since the H atom is located in the middle of this tetratomic molecule and because of the mixing of all five modes together (cf. the decomposition of the normal modes into the internal coordinates given in Table 1). Concerning the accuracy of the ω and the ν values given in these tables, we refer to the discussion carried out above for N_2HAr^+. Shortly, using the parameters evaluated for the 6-D PES obtained at the *spdf(g)* aug-cc-pV5Z/CCSD(T) level with BSSE correction, our ν_1 and ν_2 wavenumbers are computed to be 2438.8 and 1611.6 cm^{-1}, respectively, which are displaced by less than $\sim$20 cm^{-1} from the most accurate experimental determinations of Verdes et al.[9] and Verbraak et al.[11] However, our ν_3 anharmonic wavenumber computed at 197.7 cm^{-1} is very close to the value deduced from the CCSD(T) computations of Verdes et al.[9] (see Table 3). As for the normal isotopomer, a high density of rovibrational states is noticed, which allows anharmonic resonances to occur. This has been confirmed recently, for instance, by the IR spectrum of N_2DAr^+ in the energy domain 2400−2500 cm^{-1}, where a strong Fermi interaction between the ν_1 and $\nu_2 + 4\nu_3$ bands is reported by Verbraak et al.[11] More generally, the features pointed out for N_2HAr^+ and detailed in the previous sections are also valid for the deuterated species.

IV. Conclusions

Large-scale ab initio computations are performed in order to generate the 6-D PES of the electronic ground-state of the N_2HAr^+ cationic species using the Coupled Cluster methods and different basis sets and corrections. The analytical forms of these 6-D PESs are incorporated later into pertubative and full 6-D variational treatments of the nuclear motions, in order to derive a set of spectroscopic data for the N_2HAr^+ and N_2DAr^+ isotopomers and their rovibrational spectra up to 3200 cm^{-1}. Our data, obtained at the largest level of theory, are in good agreement with the most accurate experimental measurements. Surprisingly, our computations show a very minor effect of the BSSE correction on the spectroscopy of this charge transfer complex. The simulation of the IR spectrum of these species requires the generation of the 6-D dipole moment surface of N_2HAr^+ and our PES and a variational treatment, which will be done in the near future.

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Supporting Information Available: Table of polynomial expansion coefficients. This material is available free of charge via the Internet at http://pubs.acs.org.

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