

The ν_1 and ν_2 bands of $\text{Ar}\cdots\text{HN}_2^+$: A joint theoretical/experimental study

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A combined theoretical and experimental study of the ν_1 and ν_2 stretching vibrations of $\text{Ar}\cdots\text{HN}_2^+$ is presented. These correlate asymptotically with the almost local NH and NN stretching vibrations of free HN_2^+ , but undergo mode mixing and are strongly influenced by vibrational anharmonicity in the complex. The first observation of the strong ν_2 band by means of diode laser absorption spectroscopy in a supersonic planar plasma is reported. Its band origin is found at $2041.1802(3)\text{ cm}^{-1}$. New results are presented for the ν_1 band with origin at $2505.5000(2)\text{ cm}^{-1}$. The ground-state rotational constant is determined from both band systems as $0.080\,868(6)\text{ cm}^{-1}$.

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I. INTRODUCTION

Several studies, both experimental¹⁻⁴ and theoretical,^{3,5} have been carried out for the linear proton-bound ionic complex $\text{Ar}\cdots\text{HN}_2^+$. Pure rotational spectra were reported in an unpublished microwave study¹ and rotationally resolved vibration spectra were obtained by infrared predissociation^{2,3} and infrared direct absorption experiments.⁴ Three $\Sigma-\Sigma$ type bands, all originating from the ground vibrational state, were observed with origins at $2505.4998(4)$,⁴ $2707.34(5)$, and $2755.62(5)\text{ cm}^{-1}$.² The second band was left unassigned but the first and third were assigned to the $\nu_1 + \nu_s$ and $\nu_1 + 2\nu_s$ combination bands, respectively. Here, ν_s is the intermolecular stretching vibration and ν_1 is the intramolecular stretching vibration with highest wave number which is an almost local NH stretching vibration in free HN_2^+ . This assignment was based on the approximately linear relationship between the complexation induced red-shift of the ν_1 fundamental and the proton affinity of the rare gas (rg) partner found for other ionic complexes.^{6,7} This gives a red-shift of roughly 950 cm^{-1} from the free monomer value at 3233.95 cm^{-1} .^{8,9} Consequently, the ν_1 fundamental in the complex was expected around 2285 cm^{-1} , consistent with a theoretically predicted value of $2330\pm 100\text{ cm}^{-1}$.⁵ The latter result was obtained by MP2 calculations and a one-dimensional treatment of vibrational anharmonicity supplemented by an empirical correction taken over from free HN_2^+ . The error estimate was claimed to be conservative. However, even after scanning systematically the $2200\text{--}2400\text{ cm}^{-1}$ range, the ν_1 fundamental was not found,¹⁰ even though this band is expected to be considerably stronger in intensity than the $\nu_1 + \nu_s$ combination band. A solution to this problem appears to be possible through state-of-the-art quantum chemical calculations including the major effects of vibrational anharmonicity. In this paper new results obtained by large-scale coupled cluster calculations are presented which necessitate a reassignment of the previous work. The predictions are confirmed by experimental data.

II. METHODS

The present *ab initio* calculations make use of the coupled cluster variant CCSD(T) (Ref. 11) which involves single and double excitation operators and includes the effects of connected triple substitutions in an economical non-iterative way. Large basis sets of 219 and 368 contracted Gaussian-type orbitals (cGTOs) are employed. The former consists of the aug-cc-pVQZ basis for argon¹² plus the slightly modified cc-pVQZ basis¹³ for the atoms constituting the HN_2^+ fragment. The hydrogen *f* functions are of little importance and were left off. The hydrogen *s* functions were left uncontracted, in order to somewhat increase the flexibility of the wave function at the proton site. The larger basis corresponds to the aug-cc-pV5Z basis for argon and the cc-pV5Z basis for HN_2^+ . Valence electrons were correlated in the CCSD(T) calculations which were carried out with the MOLPRO suite of programs.¹⁴

The details of the experimental setup have been described.¹⁵ Vibration-rotation spectra of $\text{Ar}\cdots\text{HN}_2^+$ were obtained in direct absorption, using a tunable diode laser and employing production modulation in a supersonic planar plasma that is generated by electron impact ionization of an $\text{Ar:N}_2:\text{H}_2$ expansion (90:5:5 mixing ratio). The production is optimized by monitoring the plasma online using a quadrupole mass spectrometer. The absolute accuracy is estimated to be better than 0.002 cm^{-1} by simultaneously recording marker etalons and reference gas spectra. The other experimental conditions are basically identical to those given in Ref. 4.

III. RESULTS

A. CCSD(T) calculations for $\text{Ar}\cdots\text{HN}_2^+$

Table I lists results of the present CCSD(T) calculations in comparison with earlier work carried out at the MP2 level.^{3,5} The results of the CCSD(T) calculations for the two different basis sets are close and it is expected that those obtained with the larger basis set are almost converged.

TABLE I. Calculated equilibrium structures, equilibrium rotational constants, harmonic vibrational wave numbers, and equilibrium dissociation energies for $\text{Ar}\cdots\text{HN}_2^+$.

	MP2 ^a	MP2/full ^b	CCSD(T) ^a	
	125 cGTO ^c	203 cGTO ^d	219 cGTO	368 cGTO
$R_{\text{Ar}\cdots\text{H}}^{(e)}/\text{\AA}$	1.8346	1.8363	1.8923	1.8871
$R_{\text{HN}}^{(e)}/\text{\AA}$	1.0831	1.0838	1.0748	1.0755
$R_{\text{NN}}^{(e)}/\text{\AA}$	1.1081	1.1070	1.0956	1.0949
B_e/cm^{-1}	0.08136	0.08126	0.07952	0.07972
ω_1/cm^{-1}	2659	2603	2788	2783
ω_2/cm^{-1}	2049	2042	2195	2195
ω_3/cm^{-1}	213	210	190	191
ω_4/cm^{-1}	942	919	882	876
ω_5/cm^{-1}	172	212	157	156
D_e/cm^{-1}	3088	2881	2800	2819

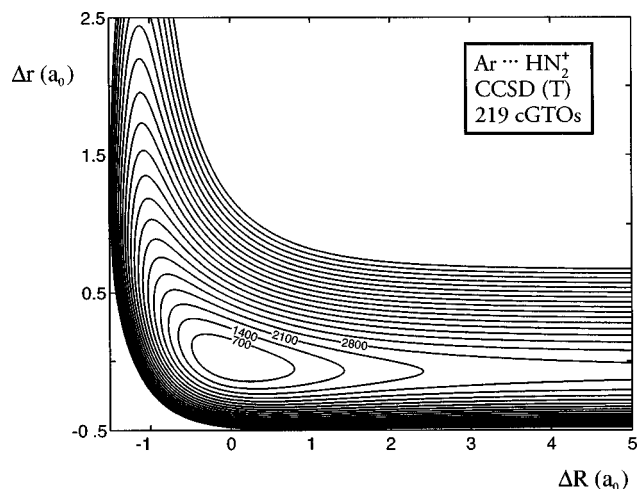
^aValence electrons correlated.^bAll electrons correlated.^cReference 5.^dReference 3.

Compared to CCSD(T) calculations with the cc-pV5Z basis for free HN_2^+ , the harmonic stretching vibrational wave numbers in the complex are lowered by 623 cm^{-1} for ω_1 (\sim NH stretch) and 99 cm^{-1} for ω_2 (\sim NN stretch) to 2783 cm^{-1} and 2195 cm^{-1} , respectively. The previous MP2 calculations severely underestimate the values in the complex. In the free HN_2^+ this is quite different; here the MP2 value for ω_1 is only 17 cm^{-1} smaller than the corresponding CCSD(T) value.¹⁶ Consequently, the assumption made in Ref. 5 that the MP2 values of the NH stretching vibrational wave number in $\text{Ar}\cdots\text{HN}_2^+$ and free HN_2^+ have similar errors has no sound basis. The approximately 150 cm^{-1} MP2 error in ω_2 is not very different from the value of 135 cm^{-1} calculated for free HN_2^+ (Ref. 16) and illustrates the well-known poor performance of this method for triple bonds.

The intermolecular harmonic stretching vibrational wave number is predicted to be $\omega_3=191\text{ cm}^{-1}$ (CCSD(T)/cc-pV5Z) with an estimated uncertainty of 1%. The previous MP2 calculations overestimate this value by approximately 10%.

Although the quadratic HNN bending force constant is smaller in $\text{Ar}\cdots\text{HN}_2^+$ compared to free HN_2^+ by 7%, the HNN bending vibrational wave number in the complex (ω_4) is larger by 179 cm^{-1} . Within the familiar GF matrix formalism,¹⁷ the major part of the increase results from a large value of the off-diagonal G matrix element G_{45} . The off-diagonal quadratic force constant F_{45} has a value of $-0.013\text{ aJ \AA}^{-2}$ (CCSD(T)/cc-pV5Z) and contributes 40 cm^{-1} to the above shift in wave number. The negative sign of the force constant means that a *cis*-like bent configuration of the four nuclei in the complex is energetically more favorable than a *trans*-like structure.

While the MP2 values of Kolbuszewski⁵ for the intermolecular harmonic bending vibrational values differ from the present CCSD(T) values by only $14\text{--}16\text{ cm}^{-1}$ or $\approx 10\%$, the value of $\omega_5=212\text{ cm}^{-1}$ reported by Dopfer *et al.*³ is too high by $\approx 35\%$. This is probably due to the fact that all electrons were correlated in their MP2 calculations, but the chosen

FIG. 1. CCSD(T) potential energy surface for $\text{Ar}\cdots\text{HN}_2^+$: dependence on $\text{Ar}\cdots\text{H}$ (ΔR) and NH (Δr) stretching coordinates. Contour lines are given in intervals of 700 cm^{-1} .

basis set did not provide the necessary flexibility to allow for a proper description of core–valence and core–core correlation effects.

The equilibrium dissociation energy D_e for dissociation into the fragments Ar and HN_2^+ is predicted to be 2819 cm^{-1} (CCSD(T)/368 cGTO). The D_e value reduces to 2767 cm^{-1} when the basis set superposition error (BSSE) is taken into account by means of the familiar counterpoise procedure¹⁸. It is likely that the true value for D_e lies between the BSSE corrected and uncorrected values, yielding $D_e=2800\pm 30\text{ cm}^{-1}$ which is in very good agreement with the experimental D_o value of $2781.5\pm 1.5\text{ cm}^{-1}$.² Not unexpectedly, the zero-point vibrational contribution to the dissociation energy is thus rather small since the stretching and bending contributions to $D_e - D_0$ tend to cancel each other almost completely.

Effects of vibrational anharmonicity were explicitly taken into account for the stretching vibrations within a well-established three-dimensional model.¹⁹ A stretch-only vibrational Hamiltonian of the form

$$\hat{H}_{\text{vib}} = \frac{-\hbar^2}{2} \sum_{i=1}^3 \frac{\partial^2}{\partial Q_i^2} + V_{\text{anh}}(Q_i, \text{ normal coordinates})$$

was diagonalized in a sufficiently large basis set of harmonic oscillator product functions. The anharmonic potential energy function V_{anh} employed is based on 414 CCSD(T) energy points with linear arrangement of the nuclei (219 cGTO basis). While the NN stretching potential is almost independent of the intermolecular separation $R_{\text{Ar}\cdots\text{H}}$, the NH stretching potential varies strongly with decreasing $R_{\text{Ar}\cdots\text{H}}$ and becomes increasingly more anharmonic (see Fig. 1). This shifts the wave number of the fundamental NH stretching vibration down towards the region of the NN stretching vibration. As a consequence, mode mixing occurs and both vibrations become significantly more anharmonic than in the free HN_2^+ . This behavior is graphically illustrated in Fig. 2 which displays the harmonic and anharmonic vibrational wave numbers as a function of the mass of the hydrogen atom, m_{H} , which is taken to be a variable. Within the har-

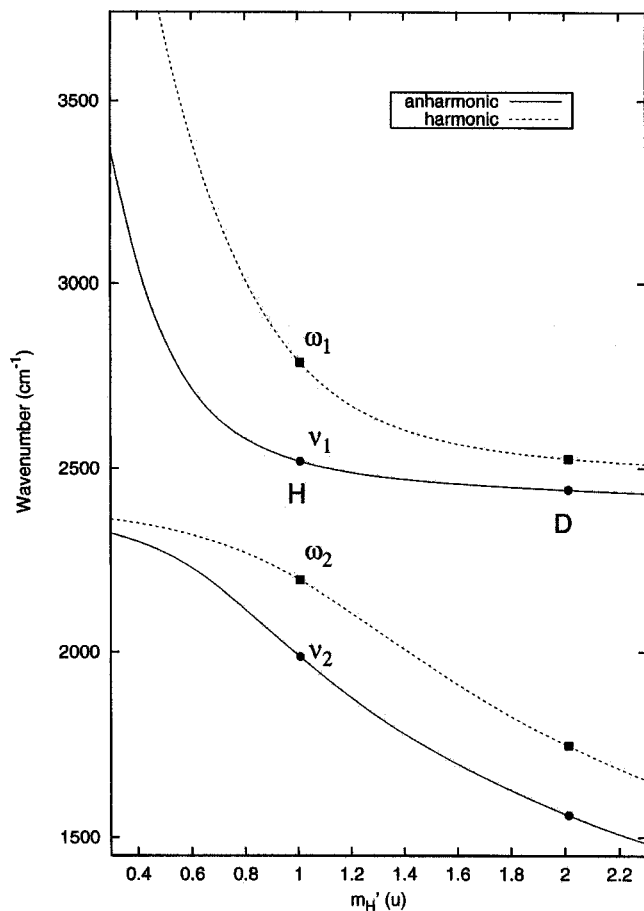


FIG. 2. Dependence of the two highest harmonic and anharmonic stretching vibrational wave numbers on the mass of the hydrogen atom $m_{H'}$, taken to be a variable.

monic approximation, ω_1 depends more strongly on $m_{H'}$ around $m_{H'} \approx 1$ u than is the case for ω_2 and consequently the harmonic stretching vibration with highest wave number is predominantly NH stretching in character. The situation becomes reversed when vibrational anharmonicity is taken into account. The anharmonic vibration ν_2 shows a rather strong dependence on $m_{H'}$ and the difference $\omega_2 - \nu_2$ is calculated to be as large as 208 cm^{-1} .

The equilibrium electric dipole moment of $\text{Ar} \cdots \text{HN}_2^+$, evaluated in the center-of-mass coordinate system, is 4.112 D (CCSD(T)/219 cGTO). Such a large value facilitates the investigation of pure rotational transitions of the cluster ion.¹ The variation of the electric dipole moment with the three internal stretching vibrational coordinates is shown in Fig. 3. All three curves have rather large slopes at equilibrium and exhibit relatively little curvature. In order to calculate vibrational transition moments, a three-dimensional analytical electric dipole moment function was obtained by least-squares fit to 106 CCSD(T) dipole moment values.

Results of the 3D variational calculations, including calculated vibrational transition moments, are listed in Table II. Restriction to linear nuclear configurations implies that the interaction between Ar and HN_2^+ is likely to be overestimated on average by the present calculations and, consequently, the anharmonic interaction between vibrational

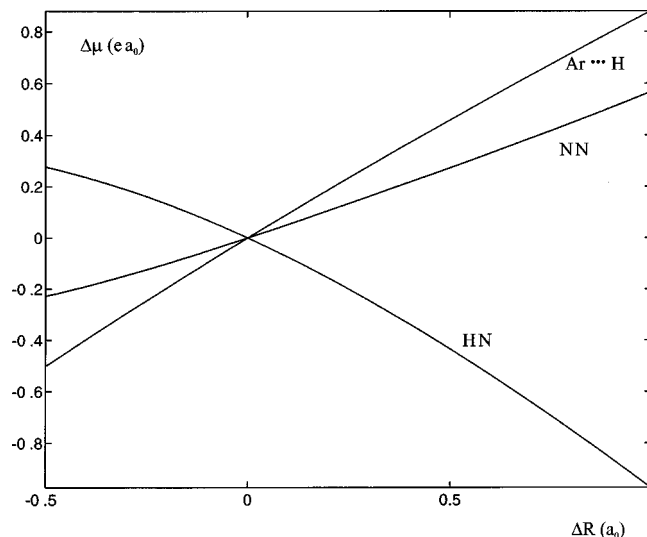


FIG. 3. Variation of the electric dipole moment of $\text{Ar} \cdots \text{HN}_2^+$, evaluated in the center-of-mass coordinate system, with the internal stretching vibrational coordinates.

states ν_1 and ν_2 is expected to be overestimated as well. The calculated difference $\nu_1 - \nu_2$ is therefore expected to be too large. The origin of the ν_1 band with predicted transition moment of 0.434 D is calculated at 2519 cm^{-1} , only 14 cm^{-1} above the origin of the strongest band observed so far. The band observed at 2505 cm^{-1} is therefore assigned to the fundamental with highest wave number (ν_1). For the ν_2 band with calculated origin at 1987 cm^{-1} an exceptionally large transition moment of 0.611 D is predicted. The corresponding harmonic vibrational wave number (cf. Table I) is $\omega_2 = 2195 \text{ cm}^{-1}$ and the $\mu(\omega_2)$ value obtained within the familiar double-harmonic approximation is 0.339 D . The double-harmonic value for the NN stretching vibration of free HN_2^+ is only 0.016 D . The combination tone $\nu_1 + \nu_s$ in the complex is calculated at 2756 cm^{-1} with a transition moment of 0.074 D . The observed band with origin at $2755.62(5) \text{ cm}^{-1}$ (Ref. 2) is therefore assigned to $\nu_1 + \nu_s$.

B. IR diode laser absorption spectroscopy

Guided by the present *ab initio* calculations the ν_2 band of $\text{Ar} \cdots \text{HN}_2^+$ was located around 2041 cm^{-1} . In total 81

TABLE II. Wave numbers and transition moments of most intense stretching vibrational transitions of $\text{Ar} \cdots \text{HN}_2^+$ from 3D variational calculations.^a

Band	$\text{Ar} \cdots \text{HN}_2^+$	
	$\tilde{\nu}/\text{cm}^{-1}$	$ \mu /\text{D}$
ν_s	205	0.389
$2\nu_s$	402	0.045
ν_2	1987	0.611
$\nu_2 + \nu_s$	2226	0.016
$\nu_2 + 2\nu_s$	2448	0.046
ν_1	2519	0.434
$\nu_2 + 3\nu_s$	2658	0.033
$\nu_1 + \nu_s$	2756	0.074
$\nu_1 + 2\nu_s$	2983	0.021

^aCCSD(T)/219 cGTO.

TABLE III. Observed line positions (in cm^{-1}) within the ν_1 and ν_2 bands $\text{Ar}\cdots\text{HN}_2^+$.

J	ν_2				ν_1			
	P branch	Δ (10^{-4}) ^a	R branch	Δ (10^{-4}) ^a	P branch	Δ (10^{-4}) ^a	R branch	Δ (10^{-4}) ^a
0			2041.3455	13			2505.6627 ^b	17
1	2041.0185	0	2041.5117	13	2505.3373 ^b	-11	2505.8285	-2
2	2040.8592	2	2041.6808	19	2505.1780 ^b	-2	2505.9957	1
3	2040.7021	3	2041.8502	6	2505.0184 ^b	-16	2506.1639	-3
4	2040.5466	-3	2042.0228	2	2504.8632 ^b	-2	2506.3349	3
5	2040.3947	5	2042.1980	2	2504.7089 ^b	3	2506.5075	9
6	2040.2439	2	2042.3742	-10	2504.5564 ^b	9	2506.6805	0
7	2040.0965	10	2042.5545	-4	2504.4048 ^b	7	2506.8563	4
8	2039.9499	3	2042.7362	-6	2504.2530 ^b	-15	2507.0327	-5
9	2039.8065	6	2042.9219	10	2504.1056 ^b	-10	2507.2113	-8
10	2039.6650	5	2043.1089	16	2503.9596 ^b	-8	2507.3914	-14
11	2039.5256	3	2043.2978	19	2503.8181 ^b	21	2507.5750	-2
12	2039.3890	6	2043.4830	-38	2503.6753 ^b	20	2507.7594	1
13	2039.2545	7	2043.6788	-10	2503.5324 ^b	0	2507.9445	-6
14	2039.1215	1	2043.8687	-64	2503.3932 ^b	-1	2508.1329	3
15	2038.9906	-7	2044.0749	23	2503.2549 ^b	-10	2508.3221	2
16	2038.8560	-74	2044.2737	14	2503.1202 ^b	0	2508.5121	-8
17	2038.7380	2	2044.4760	18	2502.9873 ^b	10	2508.7075	19
18	2038.6150	6	2044.6797	13	2502.8559 ^b	17	2508.8997	-3
19	2038.4928	-5	2044.8857	10			2509.0958	-4
20	2038.3727	-18	2045.0931	-2	2502.5938 ^b	-5	2509.2954	13
21	2038.2569	-10	2045.3021	-19	2502.4669 ^b	-7	2509.4942 ^b	5
22	2038.1434	-2	2045.5160	-9	2502.3425 ^b	-9	2509.6952 ^b	2
23	2038.0312	-3	2045.7315	-6			2509.8968 ^b	-13
24	2037.9226	9	2045.9468	-26				
25	2037.8143	1	2046.1702	13	2501.9755 ^b	-22		
26	2037.7077	-12	2046.3905	0	2501.8608 ^b	9		
27	2037.6059	1	2046.6147	3	2501.7480 ^b	8		
28	2037.5053	3	2046.8392	-12				
29	2037.4078	14	2047.0688	2				
30	2037.3112	11	2047.2986	-3				
31	2037.2166	6	2047.5323	9				
32	2037.1247	5	2047.7668	7				
33	2037.0357	11	2048.0040	11				
34	2036.9479	6	2048.2425	7				
35	2036.8628	7	2048.4834	5				
36	2036.7793	0	2048.7261	0				
37	2036.6984	-2	2048.9729	14				
38	2036.6235	33	2049.2183	-7				
39	2036.5424	-16	2049.4675	-11				
40	2036.4668	-32	2049.7197	-6				

^aObserved-calculated, using constants of Table IV.^bReference 4.

rather strong lines could be found. Their positions are listed in Table III. The band system exhibits a spectral feature typical for a $\Sigma-\Sigma$ transition of a linear molecule with regular P - and R -branches and a band gap of approximately $4B$. This is shown in Fig. 4. The ground and excited state parameters are evaluated by fitting the line positions to the expression

$$\nu_{\text{obs}} = \nu_0 + (B' + B'')m + (B' - B'' - D' + D'')m^2 - 2(D' + D'')m^3 - (D' - D'')m^4$$

with $m = -J$ for P and $m = J+1$ for R branch transitions. The resulting set of spectroscopic constants is listed in Table IV. They reproduce the wave numbers of the observed transitions well within the estimated experimental uncertainty of 0.002 cm^{-1} , apart from the transitions ending at $J' = 15$ where a small perturbation of unknown nature may be involved. In addition, further R -branch lines within the ν_1 band

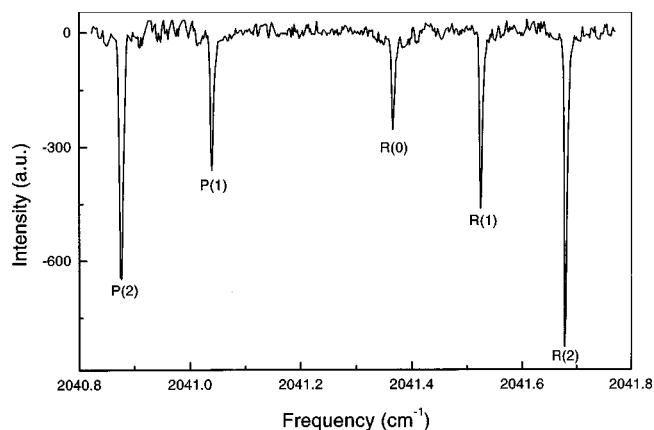


FIG. 4. The ν_2 band of $\text{Ar}\cdots\text{HN}_2^+$ around its origin recorded in direct absorption by tunable diode laser spectroscopy in a supersonic planar plasma.

TABLE IV. Spectroscopic constants (in cm^{-1}) for the ν_1 and ν_2 stretching vibrations of $\text{Ar}\cdots\text{HN}_2^+$. The values in parentheses correspond to 1σ deviations in terms of the least significant digit.

	ν_2	ν_1
ν_0	2041.1802(3)	2505.5000(2)
B''	0.080861(10)	0.080872(5)
D''	$5.5(4)\cdot 10^{-8}$	$5.5(2)\cdot 10^{-8}$
B'	0.081986(10)	0.081734(5)
D'	$5.9(4)\cdot 10^{-8}$	$4.9(2)\cdot 10^{-8}$

were found which are included in Table III. Combining them with the earlier data from diode laser absorption spectroscopy⁴ and predissociation spectroscopy²⁰ under appropriate weighting, the spectroscopic constants given in Table IV were obtained. As both observed bands originate from the ground state, the values for B'' and D'' should overlap within their (1σ) uncertainties, which is clearly the case. From the two parameter sets a final ground state value of $B''=0.080\,868(6)\text{ cm}^{-1}$ is derived. Combining the latter value with the difference B_e-B_0 of $-0.000\,887\text{ cm}^{-1}$ as calculated from the cubic CCSD(T)/219 cGTO force field by conventional second-order perturbation theory an estimate for B_e of $0.079\,989\text{ cm}^{-1}$ is found. This differs from the B_e value obtained with the large basis set (cf. Table I) by only 0.3%. The rotational constants in the two singly excited stretching vibrational states ν_1 and ν_2 are very similar. The corresponding band origins are determined as $\nu_1=2505.5000(2)\text{ cm}^{-1}$ and $\nu_2=2041.1802(3)\text{ cm}^{-1}$. Using the harmonic vibrational wave numbers obtained with the large basis set (cf. Table I) and the experimental anharmonic values, anharmonicity contributions of 277 and 154 cm^{-1} are calculated for ν_1 and ν_2 , respectively. The corresponding values in free HN_2^+ are 169 and 38 cm^{-1} (Ref. 16) and thus very different.

The red-shift in the NH stretching vibration arising upon complex formation is either 728.45 cm^{-1} or 1192.77 cm^{-1} , depending on whether one correlates ν_1 (HN_2^+) with ν_1 or ν_2 in the complex, respectively. Either choice is in poor agreement with a linear extrapolation involving data for $\text{He}\cdots\text{HN}_2^+$ (Ref. 21) and $\text{Ne}\cdots\text{HN}_2^+$.²² Although successful for less strongly bound species, this procedure fails in a situation of strong mode mixing and anharmonic interaction as is the case for $\text{Ar}\cdots\text{HN}_2^+$.

Guided by the present *ab initio* calculations, the strong ν_2 band of $\text{Ar}\cdots\text{DN}_2^+$ was recently found around 1594

cm^{-1} , 35 cm^{-1} above the CCSD(T) prediction within the 3D anharmonic approximation. The analysis of the observed lines is in progress and will be published separately. Future theoretical work will be devoted to an extension of the CCSD(T) potential energy function to all six dimensions and the calculation of rovibrational states by means of a variant of the DVR-DGB method.²³

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