

## **A new, fully ab initio investigation of the ArNO ( $X\ 2\ \Pi$ ) system. II. Bound states of the Ar–NO complex**

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Citation: *The Journal of Chemical Physics* **111**, 7435 (1999); doi: 10.1063/1.480067

View online: <http://dx.doi.org/10.1063/1.480067>

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# A new, fully *ab initio* investigation of the ArNO( $X^2\Pi$ ) system. II. Bound states of the Ar–NO complex

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(Received 30 April 1999; accepted 13 July 1999)

We report an investigation of bound states of the ArNO complex, based on new coupled-cluster [CCSD(T)] *ab initio* potential energy surfaces. The position and relative spacing of the lowest bend–stretch levels of the complex are found to be in noticeable better agreement with available experimental results than the predictions based on earlier ArNO PES's. © 1999 American Institute of Physics. [S0021-9606(99)30238-5]

## I. INTRODUCTION

In inelastic collision dynamics involving open-shell molecules, collisions of noble gases with NO have emerged as the paradigm for a system which can be investigated carefully by both theoreticians and experimentalists.<sup>1</sup> Experimental interest has continued over nearly two decades.<sup>2–8</sup>

Because of the spatial anisotropy of the electronic wave function, two PES's are required to describe the interaction between a diatomic in a  $\Pi$  electronic and a spherical target.<sup>9–12</sup> Pack and co-workers used density functional methods to determine the two PES's for the Ar–NO( $X$ ) system.<sup>13</sup> We subsequently published more accurate *ab initio* PES's<sup>14</sup> determined using the correlated electron pair (CEPA) method.<sup>15,16</sup> These have been used in a number of theoretical determinations of integral<sup>6,14,17–19</sup> and differential<sup>14,19</sup> cross sections for the scattering of NO( $X$ ) by Ar. Recently, we have calculated<sup>20</sup> a substantially more accurate set of PES's for the ArNO system, based on coupled-cluster [CCSD(T)] calculations with a larger basis set than that used in the earlier CEPA calculations.

For the ArNO system, as in the interaction of other radicals in  $^2\Pi$  electronic states with noble gases,<sup>21</sup> spectroscopic investigation of the bound states of the complex provides information on the shape of the PES's in the region of the van der Waals minimum, information which complements that available from inelastic scattering studies.<sup>22</sup> Mills, Western, and Howard<sup>23,24</sup> used microwave and radio-frequency spectroscopy to investigate transitions between a number of multiplet levels associated with the lowest rotational levels of the ArNO complex. Calculations,<sup>25</sup> based on our CEPA ArNO PES's, showed some disagreement with these experimental results.

More recently, Tsuji, Shibuya, and Obi<sup>26</sup> and Meyer<sup>27</sup> have used two-photon electronic excitation spectroscopy to investigate the Ar–NO complex. Although these experiments give information primarily about the electronically excited states of the complex, Tsuji *et al.*<sup>26</sup> were able to extract values of the dissociation energy, vibrational frequency and Ar–NO distance in the ground electronic state. The experimentally derived value of the dissociation energy ( $D_0 = 88 \pm 0.3 \text{ cm}^{-1}$ )<sup>26</sup> is substantially larger than both the value ( $54 \text{ cm}^{-1}$ ) predicted<sup>25</sup> with our earlier PES's<sup>14</sup> and estimated

from molecular beam measurements of the total Ar–NO scattering cross section.<sup>28</sup>

In an attempt to ascertain whether the remaining discrepancies with experiment are due to inadequacies in the ArNO PES's we present a new investigation of the bound states of the ArNO complex, based on the new CCSD(T) PES's.<sup>20</sup> As will be seen below, the agreement with the spectroscopic observations is substantially improved.

## II. POTENTIAL ENERGY SURFACES

The approach of a structureless atom to a molecule in a  $^2\Pi$  electronic state gives rise to two PES's, of  $A''$  and  $A'$  symmetry with respect to reflection in the triatomic plane.<sup>12</sup> If the NO bond distance is held fixed at its equilibrium value [ $r = 1.5077 \text{ Å}$  (Ref. 29)],<sup>29</sup> the PES's is a function of  $R$  (the distance between the Ar atom and the center of mass of the NO molecule) and  $\theta$  (the angle between  $r$  and  $R$ ). In the present investigation we use our recent PES's<sup>20</sup> determined with an unrestricted coupled-cluster (singles and doubles) calculation with the perturbative inclusion of triple excitations [UCCSD(T)].<sup>30</sup> For reference, Table I reproduces from Ref. 20 the positions and depths of the minima on the two ( $A'$  and  $A''$ ) PES's predicted by the earlier CEPA and recent CCSD(T) calculations.

In the treatment of the nuclear motion of the complex, it is convenient to work with the average and half-difference of the PES's for the states of  $A''$  and  $A'$  reflection symmetry, defined as<sup>12</sup>

$$V_{\text{sam}}(R, \theta) = 0.5[V_{A''}(R, \theta) + V_{A'}(R, \theta)] \quad (1a)$$

and

$$V_{\text{dif}}(R, \theta) = 0.5[V_{A''}(R, \theta) - V_{A'}(R, \theta)]. \quad (1b)$$

The dependence on  $\theta$  is then expanded<sup>12</sup> in terms of reduced rotation matrix elements,<sup>31</sup>

$$V_{\text{dif}}(R, \theta) = \sum_{\lambda=0}^{\lambda_{\text{max}}} V_{\lambda 0}(R) d_{00}^{\lambda}(\theta) \quad (2a)$$

and

$$V_{\text{dif}}(R, \theta) = \sum_{\lambda=2}^{\lambda_{\text{max}}} V_{\lambda 2}(R) d_{20}^{\lambda}(\theta), \quad (2b)$$

TABLE I. Minimum geometry and energy of the  $A'$  and  $A''$  states of  $\text{ArNO}(X)$ .<sup>a</sup>

	CEPA <sup>b</sup>	CCDS(T) <sup>c</sup>
$R_e(A')$	6.99	6.76
$R_e(A'')$	7.09	6.92
$\theta_e(A')$	94.1	94.9
$\theta_e(A'')$	73.1	69.9
$D_e(A')$	77.9	115.9
$D_e(A'')$	79.1	111.0

<sup>a</sup>Distances in bohr, angles in degrees, energies in  $\text{cm}^{-1}$ .<sup>b</sup>Reference 14.<sup>c</sup>Reference 20.

where  $\lambda_{\text{max}}=9$ , corresponding to the number of angles in the *ab initio* grid.<sup>20</sup>

### III. BOUND STATES OF THE AR-NO COMPLEX: FORMALISM

To describe the bound state levels of the  $\text{ArNO}$  complex, we expand the complete wave function in a basis formed by products of functions which describe the electronic-rotational states of the NO molecule, multiplied by angular momentum functions which describe the orbital (end-over-end) rotation of the  $\text{ArNO}$  complex.

In a Hund's case (a) basis<sup>32</sup> the electronic-rotational wave functions of the NO molecule in its  $^2\Pi$  electronic state can be written as

$$|\lambda\sigma jm\omega\varepsilon\rangle = 2^{-1/2} [ |jm\omega\rangle |\lambda\sigma\rangle + \varepsilon |jm-\omega\rangle |-\lambda-\sigma\rangle ]. \quad (3)$$

Here  $j$  denotes the total angular momentum of the diatomic molecule, with projections  $m$  and  $\lambda$  along, respectively, the space- and molecule-fixed  $z$ -axes. Also  $|\lambda\sigma\rangle$  designates the electronic component of the wave function where  $\lambda$  and  $\sigma$  denote, respectively, the molecule-frame projections of the electronic orbital and spin angular momenta. The  $\Lambda$ - (or "parity") doublet levels are distinguished by the symmetry index  $\varepsilon$  which can take the value  $+1$  ( $e$ -labeled levels) or  $-1$  ( $f$ -labeled levels).<sup>33</sup> The total parity of the wave functions is given by  $\varepsilon(-1)^{j-1/2}$ .<sup>33</sup> For simplicity in what follows, we will suppress the electronic wave function  $|\lambda\sigma\rangle$  and the  $\lambda$  and  $\sigma$  quantum numbers, except when needed. Our use here of lower case letters to designate the quantum numbers of the diatomic moiety is consistent with the notation of Dubernet *et al.*<sup>34</sup> and Green and Lester<sup>35</sup> and is used for historical continuity.

The  $j \cdot s$  term in the molecular Hamiltonian<sup>32</sup> mixes the  $\omega=1/2$  and  $\omega=3/2$  case (a) basis functions. The mixed diatomic wave functions can be expressed as linear combinations of the definite  $\omega$  functions of Eq. (3), namely,

$$|jmF_i\varepsilon\rangle = \sum_{\omega} D_{F_i\omega\varepsilon}^j |jm\omega\varepsilon\rangle. \quad (4)$$

The expansion coefficients  $D_{F_i\omega\varepsilon}^j$  are obtained by diagonalization of the Hamiltonian of the isolated NO molecule.<sup>32,36,37</sup> The mixed states are denoted  $F_1$  and  $F_2$  in terms of increasing energy.<sup>38</sup> For the NO molecule, where the spin-orbit splitting is much larger than the rotational

constant, the mixing is small at low  $j$ , so that  $\omega$  is a nearly good quantum number. For the NO molecule the  $f\Lambda$ -doublet levels lie slightly ( $\sim 0.01 \text{ cm}^{-1}$ ) higher in energy. Further, for NO the  $\omega=1/2$  spin-orbit manifold lies lower in energy, so that the lowest rotational state is  $j=\omega=1/2$ .

The complete wave function for the  $\text{ArNO}$  system is expanded as

$$\Psi^{JM} = (1/R) \sum_{jLF_i\varepsilon} C_{jLF_i\varepsilon}^{JM}(R) |jF_i\varepsilon LJM\rangle. \quad (5)$$

Here  $J$  is the total angular momentum with space-frame projection  $M$ . The functions  $|jF_i\varepsilon LJM\rangle$  in Eq. (5) are products of the functions which describe the electronic-rotational states of the NO molecule,  $|jmF_i\varepsilon\rangle$ , multiplied by angular momentum functions which describe the orbital (end-over-end) rotation of the  $\text{ArNO}$  complex ( $L=J-j$ ), namely

$$|jF_i\varepsilon LJM\rangle = \sum_{mm_l} (jmLM_L | JM) Y_{LM_L}(\hat{R}) |jmF_i\varepsilon\rangle, \quad (6)$$

where  $Y_{LM_L}(\hat{R})$  is a spherical harmonic and  $(\dots|\dots)$  is a Clebsch-Gordan coefficient.<sup>39</sup>

The expansion coefficients,  $C_{jLF_i\varepsilon}^{JM}(R)$ , in Eq. (5) are independent of  $M$  and satisfy the standard close-coupled (CC) equations. In matrix notation these are

$$\left( \frac{d^2}{dR^2} + W(R) \right) C^J(R) = 0, \quad (7)$$

where

$$W(R) \equiv k^2 - \frac{L^2}{R^2} - \frac{2\mu}{\hbar^2} V(R). \quad (8)$$

Here  $k^2$  designates the diagonal matrix containing the wave vectors of the individual coupled channels, and  $L^2$  and  $V(R)$  are the full matrices of, respectively, the square of the orbital angular momentum ( $L=J-j$ ) and the interaction potential(s). The matrix elements of the interaction potential for a  $^2\Pi$  system in an intermediate coupling basis have been given previously.<sup>12,40</sup>

In the actual calculation of the bend-stretch levels of the  $\text{ArNO}$  complex, we used a distributed Gaussian basis<sup>41</sup> to expand the radial expansion coefficients in Eq. (5). The bound-state energies are then determined variationally.<sup>42</sup> A total of 17 functions with an exponential parameter<sup>41</sup>  $A$  of 0.406 were used, spaced equally over the range  $4.5 \leq R \leq 11$  bohr. The required matrix elements in this Gaussian basis were obtained by numerical integration using a 81 point grid. Convergence of the calculated  $\text{ArNO}$  bend-stretch energies to within better than  $0.01 \text{ cm}^{-1}$  could be obtained by retaining in the expansion all rotational states with  $j \leq 9.5$  and both spin-orbit states. To check the accuracy of our calculation, a comparison was made with the bend-stretch energies determined earlier<sup>25</sup> for the CEPA PES's by means of an entirely different method. Agreement was excellent, within  $0.002 \text{ cm}^{-1}$ .

In the analysis of the bound states of the complex, it is more convenient to use a body-frame expansion, rather than the space-frame expansion of Eqs. (5) and (6). Consistent with the formal work on  $\text{ArOH}(X^2\Pi)$  of Dubernet *et al.*<sup>34</sup>

and Green and Lester,<sup>35</sup> and on NeOH by Yang and Alexander,<sup>43</sup> we use a standard close-coupled (CC) expansion<sup>34,42,44</sup> again built from symmetrized Hund's case (a) rotational-electronic NO basis functions. The complete wave function is written as

$$\Psi^{JM} = (1/R) \sum_{jP\omega\eta} C_{jP\omega\eta}^J(R) |jP\omega\eta JM\rangle, \quad (9)$$

where

$$|jP\omega\eta JM\rangle = 2^{-1/2} (|jP\omega JM\rangle + \eta |j, -P, -\omega, JM\rangle) \quad (10)$$

and

$$|jP\omega JM\rangle = \frac{[(2J+1)(2j+1)]^{1/2}}{4\pi} D_{M,P}^{J*}(\hat{R}) D_{P,\omega}^{j*}(\hat{R}_B) |\lambda\sigma\rangle. \quad (11)$$

Here  $P$  is the projection of both  $J$  and  $j$  along the body axis  $\hat{R}$ . The symmetry index  $\eta$  (designated  $\varepsilon$  by Green and Lester<sup>35</sup> and  $\xi$  by Dubernet *et al.*<sup>34</sup>) can take on the values  $\pm 1$ . Note that the molecular rotational functions are defined here in terms of  $\hat{R}_B$ , which is the orientation of the NO axis with respect to  $\hat{R}$ . The total parity of the  $|jP\omega\eta JM\rangle$  states is  $\eta(-1)^{J-1/2}$ .<sup>34</sup>

The expansion coefficients,  $C_{jP\omega\eta}^J$ , in Eq. (9) satisfy a set of close-coupled (CC) equations, equivalent to Eq. (7). In a BF expansion the potential matrix is block diagonal in  $P$  and independent of  $J$  and the sign of  $P$ . However, the matrix of  $L^2$  has both diagonal and off-diagonal terms. In the centrifugal-decoupling (CD) approximation,<sup>34,45</sup> the off-diagonal terms, which reflect Coriolis coupling between states of differing  $P$ , are neglected.

Additional physical insight can be gained by an examination of the definite- $P$  adiabatic energies, obtained by diagonalization of the unique block of the BFW( $R$ ) matrix corresponding to the chosen value of  $P$ . We note that although the  $W(R)$  matrix is independent of  $P$ , the CD adiabatic energies of the two possible signed  $P\omega$  states ( $P \times \omega > 0$  and  $P \times \omega < 0$ ) are not necessarily degenerate. The definite- $P$  adiabatic energies are defined by

$$w_P(R) = T(R) W_P(R) T(R)^T, \quad (12)$$

where  $T(R)$  is the matrix which diagonalizes the  $P$ th block of the BFW( $R$ ) matrix. The  $R$  dependence of the  $w_P(R)$  adiabatic energies define "adiabatic bender" potentials. These can then be used to investigate the vibrational motion along the van der Waals stretching coordinate  $R$ .<sup>42,46,47</sup> To the extent that off-diagonal matrix elements of the radial kinetic energy operator can be ignored, and the coriolis couplings are small, the energies of these vibrational levels will provide a good first approximation to the bend-stretch states of the ArNO complex.<sup>46</sup>

Figure 1 displays the radial adiabatic bender potentials for the ArNO complex for a total angular momentum  $J = 1/2$  and states of positive parity, determined within the CD approximation. The lowest curves correspond to  $P = 1/2$ . As mentioned above, for each value of  $P$ , there exist two adiabatic bender curves, which correspond to the two possible signs of  $P \times \omega$ . For complexes of OH( $X^2\Pi$ ) with Ar, Green and Lester have suggested labeling these two states "+" and

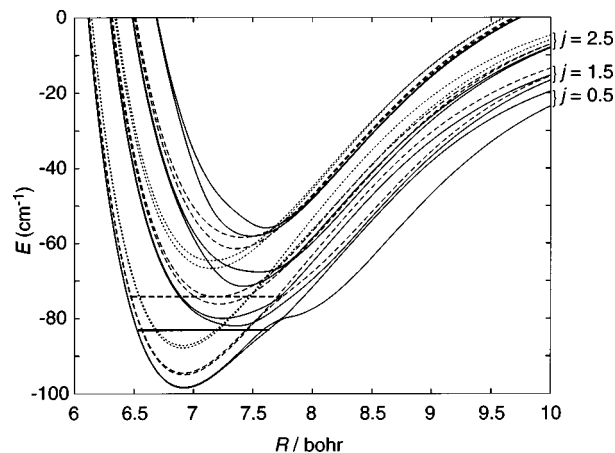


FIG. 1. Centrifugally decoupled (CD) adiabatic bender potentials for the ArNO complex for a total angular momentum of  $J = 1/2$ . The solid, dashed, and dotted curves correspond, respectively, to  $P = 1/2, 3/2$ , and  $5/2$ . For large values of  $R$ , the curves correlate, as shown, with the lowest three rotational levels of NO( $^2\Pi_{1/2}$ ). The curves shown all correspond to positive parity states [ $\eta = +1$  in Eq. (10)]. For each value of  $P$ , there exist two adiabatic bender curves, which correspond to the two possible signs of  $P \times \omega$ . The solid and dashed horizontal lines indicate the energies of the lowest bend-stretch levels with  $P = 1/2$  and  $P = 3/2$  (Table II).

and "−" based on the consideration of which collinear configuration (OHAr or HOAr) is lower in energy. This is especially appropriate for the OH–noble gas complexes, where the minimum lies in collinear geometry. For the Ar–NO complex, in contrast, the minima in the PES's (see Figs. 1–4 of Ref. 20) occur for perpendicular geometry, and, further, the two collinear geometries have nearly identical behavior. Thus the two signed  $P\omega$  adiabatic states have nearly identical energies.

#### IV. BEND-STRETCH LEVELS OF THE COMPLEX

Figure 2 shows the relative position of the lowest levels of the ArNO complex, as predicted by both the CEPA and CCSD(T) PES's. For historical continuity, we also display the  $e/o$  labeling introduced earlier by Howard and

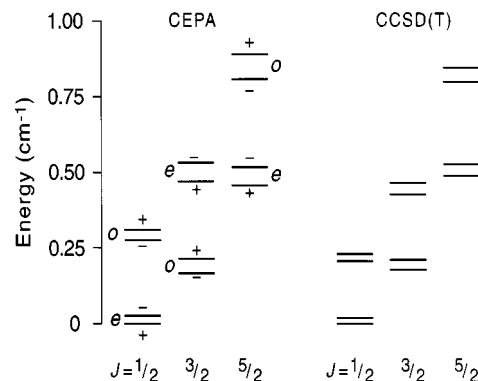


FIG. 2. Relative position of the lowest bend-stretch states of the ArNO complex for  $J = 1/2$ , predicted by from the earlier CEPA PES's as well as by the recent CCSD(T) PES's. The zero of energy is  $-54.398 \text{ cm}^{-1}$  CEPA and  $-83.160 \text{ cm}^{-1}$  [CCSD(T)]. All levels correspond to a nominal value of  $|P| = 1/2$ . The  $e/o$  labeling is identical to that used in earlier studies of the bound states of the ArNO complex (Refs. 24, 25, and 48). The + and − signs indicate the parity of each level.



co-workers<sup>24,48</sup> and used in our earlier theoretical study of the bound states of the ArNO complex.<sup>25</sup> Because the minimum on the two PES's occurs near perpendicular geometry, the lowest energy is associated with bend-stretch levels of low  $P$ . The absolute energies of the low-lying states, including the fundamental levels for  $P=1/2$ ,  $3/2$ , and  $5/2$ , as well as the  $v=1$  states for  $P=1/2$  and  $3/2$  are given in Table II.

For  $J=1/2$ , only  $P=1/2$  is allowed, so that the CD( $P=1/2, J=1/2$ ) and CC( $J=1/2$ ) energies should be identical, to within the small Coriolis mixing between the  $P=1/2$  and  $P=-1/2$  levels which is neglected. For  $J=3/2$ , the CC calculations include both  $P=1/2$  and  $P=3/2$  states in the basis. Comparison with the  $J=1/2$  results then allows us to identify the nominal  $P$  value for each state. This is shown in Table II, as well as a similar identification of the nominally  $P=5/2$  levels.

In comparison with the earlier calculations based on the CEPA PES's,<sup>25</sup> we observe that the zero-point-corrected dissociation energy,  $D_0$ , is larger ( $83.16\text{ cm}^{-1}$  as compared to  $54.40\text{ cm}^{-1}$ ), which is a reflection of the deeper well depth in the CCSD(T) PES's (see Figs. 1–4 of Ref. 20). The lowest  $P=3/2$  level is predicted to lie  $3.73\text{ cm}^{-1}$  above the ground state, quite close to the CEPA prediction of  $3.81\text{ cm}^{-1}$ .

The microwave and radio frequency experiment of Howard and co-workers<sup>24</sup> yield considerable information about the spacings between the lowest  $jP\omega$  multiplet and rotational levels of the ArNO complex shown in Fig. 8. Table III compares the predicted energies for all observed<sup>24</sup> transitions involving rotational levels with  $J', J'' \leq 5/2$ . To compare directly with the experimental results of Howard and co-workers,<sup>24</sup> it is necessary to correct for the hyperfine structure of the initial and final levels, because hyperfine coupling is not included in the present Hamiltonian. To make this correction we use a simple phenomenological Hamiltonian in which we assume that the hyperfine splitting is given by  $aJ \cdot I$ , where  $a$  is an adjustable constant and  $I$  is the nuclear spin ( $I=1$  for the ArNO complex). Thus, an observed transition between levels  $J'F'$  and  $J''F''$ , where  $F$  is the total angular momentum including nuclear spin, is given by

$$E(J', F') - E(J'', F'') = T(J', J'') + \epsilon_{J'F'} - \epsilon_{J''F''}, \quad (13)$$

where

TABLE II. Energies ( $\text{cm}^{-1}$ ) of the lowest bound states of the ArNO complex as predicted by the CCSD(T) PES's.

$P^a$	CD <sup>b</sup> $J=1/2$	CC		
		$J=1/2$	$J=3/2$	$J=5/2$
1/2	-83.141	-83.160	-82.950	-82.672
1/2	-82.950	-82.931	-82.733	-82.316
3/2			-79.430	-79.085
3/2			-79.007	-78.662
5/2				-72.031
5/2				-71.485
1/2	-69.360	-69.367	-69.187	-68.902
1/2	-68.207	-68.200	-68.000	-67.659
1/2	-63.495	-63.413	-63.561	-63.135
1/2	-63.119	-63.196	-62.832	-62.684
3/2			-62.442	-62.109
3/2			-61.915	-61.532
5/2	-56.664	-56.658	-56.562	-56.260
5/2	-55.246	-55.250	-56.297	-56.053

<sup>a</sup>Nominal value of the projection quantum number for each state (see Fig. 1).

<sup>b</sup>Centrifugal decoupling calculation with  $P=1/2$ .

$$\epsilon_{J'F'} = \alpha_{J'}[F'(F'+1) - J'(J'+1) - 2] \quad (14)$$

with a similar expression for  $\epsilon_{J''F''}$ . The constants  $T(J', J'')$ ,  $\alpha_{J'}$ , and  $\alpha_{J''}$  were adjusted to fit the experimental transition energies in Table V of Ref. 24. Here  $T(J', J'')$  is the rotational transition energy, with the hyperfine splitting eliminated. The rms deviation of the fit (involving 30 different transitions) was  $3.6\text{ MHz} = 1.2 \times 10^{-4}\text{ cm}^{-1}$ .

As can be seen in Table III, the calculations with the CCSD(T) PES's give an generally excellent agreement with experiment, noticeably better than the energies predicted by the CEPA PES or PES's adapted by Joswig *et al.*<sup>49</sup> from the earlier electron-gas PES's of Nielsen, Parker, and Pack.<sup>13</sup> Table III also compares predictions for the CEPA PES from our present calculations with those published earlier by Schmelz and co-workers. The agreement is within  $\pm 0.001\text{ cm}^{-1}$  except in the case of the  $J=3/2$ ,  $o(-) \rightarrow 1/2, o(+)$  transition, where Schmelz *et al.*<sup>25</sup> give  $-0.095\text{ cm}^{-1}$ . We believe the discrepancy here is a result of sign and data transcription errors in this earlier paper. A transition energy of  $-0.095\text{ cm}^{-1}$  corresponds to the downward (emission) tran-

TABLE III. Energies ( $\text{cm}^{-1}$ ) of several pure rotational transitions in the ArNO(X) complex.<sup>a</sup>

Transition	JAS <sup>b</sup>	CEPA		CCSD(T) <sup>c</sup>	Expt. <sup>d</sup>
		Ref. 25	Present		
$J=3/2, o(-) \rightarrow 1/2, o(+)$	1.488	-0.095	0.143	0.051	0.014
$J=1/2, o(-) \rightarrow 1/2, o(+)$	0.029	0.034	0.034	0.023	0.020
$J=3/2, o(-) \rightarrow 3/2, o(+)$	-0.011	0.048	0.048	0.032	0.029
$J=1/2, o(-) \rightarrow 3/2, o(+)$			-0.061	0.004	0.035
$J=3/2, o(+ ) \rightarrow 5/2, o(-)$	1.981	0.674	0.674	0.587	0.574
$J=3/2, o(+ ) \rightarrow 3/2, e(-)$	1.701	0.315	0.318	0.255	0.226
$J=3/2, e(+ ) \rightarrow 5/2, e(-)$			0.043	0.099	0.123

<sup>a</sup>See Fig. 8.

<sup>b</sup>PES's of Ref. 13, modified as described in Ref. 49; values taken from Ref. 25.

<sup>c</sup>Present work.

<sup>d</sup>Reference 24, after correction for the hyperfine splittings; see Eq. (13).

TABLE IV. Spectroscopic constants of the ArNO(X) complex.

	$D_0$	$\langle R \rangle (\text{\AA})$	$\omega_{\text{stretch}}^a$	$\omega_{\text{bend}}^b$
CEPA	55, <sup>c</sup> 54.4 <sup>d</sup>	3.904 <sup>c</sup>	11.0 <sup>c,d</sup>	3.7 <sup>c,d</sup>
CCSD(T) <sup>c</sup>	83.2	3.772 <sup>c</sup>	13.8 <sup>f</sup>	3.6 <sup>f</sup>
Experiment	87.8 <sup>g</sup>	3.711 <sup>h</sup>	40 <sup>i</sup>	

<sup>a</sup>Difference between the lowest two  $J=1/2$  states of  $e^+$  symmetry in Table II.

<sup>b</sup>Difference between the lowest  $P=1/2$  and  $P=3/2$  states in Table II.

<sup>c</sup>Reference 25.

<sup>d</sup>Present work.

<sup>e</sup>Obtained as average of  $R$  over the lowest adiabatic-bender wave function.

<sup>f</sup>See Table II.

<sup>g</sup>Reference 26.

<sup>h</sup>Reference 24.

<sup>i</sup>Reference 50.

sition  $J=1/2$ ,  $o(+)\rightarrow 3/2,o(+)$ , which is not experimentally observable because both states have the same parity.

Table IV compares with available experimental values the calculated zero-point dissociation energies, the predicted average Ar–NO distance and the predicted vibrational frequencies of the complex. As can be seen, the agreement between the predictions of the CCSD(T) PES's and experiment is excellent for both  $D_0$  and  $\langle R \rangle$ , considerably better than the agreement with predictions based on the CEPA PES's. For the vibrational frequencies of the complex, the predictions are significantly smaller than the experimental estimate.<sup>50</sup>

## V. DISCUSSION

Despite the similarity in the topology of the CEPA and CCSD(T) Ar–NO potential energy surfaces, the relative position of the lowest bound states predicted by the CCSD(T) PES agrees noticeably better with the available experimental information from radio-frequency and microwave spectroscopy.<sup>24</sup> In addition, because the CCSD(T) calculations recover a greater degree of the correlation energy of the system, the calculated dissociation energy is significantly larger than the CEPA value, and in excellent agreement with the experimental estimate from optical spectroscopy.<sup>26</sup> Both of these experiments give information on the PES's near (or at) the van der Waals minimum. A further test of the calculated PES's would be the experimental determination of the spacing between the lower bend–stretch levels (Table II) which correspond to excitation of the torsional and/or stretching modes of the triatomic complex.<sup>25</sup> Hopefully, future studies of the electronic spectroscopy of the ArNO complex,<sup>26,27</sup> will be able to provide this information.

## ACKNOWLEDGMENT

The author is grateful to the U.S. National Science Foundation for partial support of this research under Grant No. CHE-9971810.

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