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# Intermolecular potential surfaces from electron gas methods. II. Angle and distance dependence of the $A'$ and $A''$ Ar-NO( $X^2\Pi$ ) interactions\*

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Angle dependent intermolecular potential energy surfaces for the two states ( $^2A'$  and  $^2A''$ ) that arise from the interaction of ground ( $X^2\Pi$ ) state NO with Ar are calculated using the electron gas model to obtain the short range interactions. The average and difference of the two interaction energies are fit to analytic forms convenient for use in scattering calculations and joined smoothly onto the long range van der Waals potential previously determined. The results, which appear to be of useful accuracy, and the applicability of the electron gas model to such open shell-closed shell interactions are discussed.

## I. INTRODUCTION

In paper I of this series<sup>1</sup> we reviewed and discussed applications of the electron gas (EG) model—as developed by Gaydaenko and Nikulin,<sup>2</sup> and Gordon and Kim,<sup>3</sup> and modified by Rae,<sup>4</sup> and Cohen and Pack<sup>5</sup>—for calculation of interactions between atoms and molecules when both partners have closed shell electronic structure. We also applied the method to the He-CO<sub>2</sub> and Ar-CO<sub>2</sub> interactions.

In this paper we use the method to calculate the interaction energy between a closed shell atom Ar and an open shell molecule NO. Closed shell-open shell interactions of atoms have been treated with the EG model by Clugston and Gordon<sup>6</sup> who used it to study the noble gas halides. They compared their results with the *ab initio* calculations of Dunning and Hay<sup>7</sup> for KrF and found that the EG results were good for the  $\Pi$  state in which the empty F orbital is perpendicular to the Kr but poor for the  $\Sigma$  state in which the empty F orbital points at the Kr atom. We believe that this is because the EG model cannot account for the charge transfer and mixing<sup>7</sup> of covalent and ionic character that occurs in this state. In applying the model to the Ar-NO system, we are on much safer ground. NO has a much lower electronegativity than F and we expect negligible ionic character or configuration mixing; all the ground state interactions should be of the simple non-bonding type and be adequately described by the EG model.

The electronic structure of ground ( $X^2\Pi$ ) state NO is essentially that of closed shell N<sub>2</sub> with one additional electron in an antibonding  $\pi$  orbital. In the Ar-NO system, which has  $C_s$  symmetry, the degenerate  $\Pi$  state is split into two states: an  $A'$  state (herein called +) in which the wavefunction is symmetric under reflection in the triatomic plane and an  $A''$  state (herein called -) asymmetric about that plane. Using the coordinates of Fig. 1, it is clear that the  $A'$  (+) state is obtained by putting the extra electron on the NO in a  $\pi_y$  orbital lying in the triatomic plane while the  $A''$  (-) is obtained by putting it in a  $\pi_x$  orbital perpendicular to

that plane. This is achieved merely by multiplying the rest of the Hartree-Fock  $\pi$  orbital by an appropriately normalized  $\sin\varphi$  or  $\cos\varphi$ , respectively, to give the proper  $\varphi$  dependence and symmetry.

All calculations and results in this paper are non-relativistic and use a spin-free Hamiltonian. However, intermolecular potentials which incorporate an approximate accounting of spin orbit effects, such as the 121.1 cm<sup>-1</sup> spin orbit splitting<sup>8</sup> between the  $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$  states of NO, can easily be generated from the results of this paper by solving a  $2 \times 2$  secular equation as described in detail in an earlier paper.<sup>9</sup>

## II. CALCULATIONS

### A. Electron gas potentials

The method of calculating the electron gas potential was given in detail in paper I. Herein we will only discuss differences between the present procedure and that one.

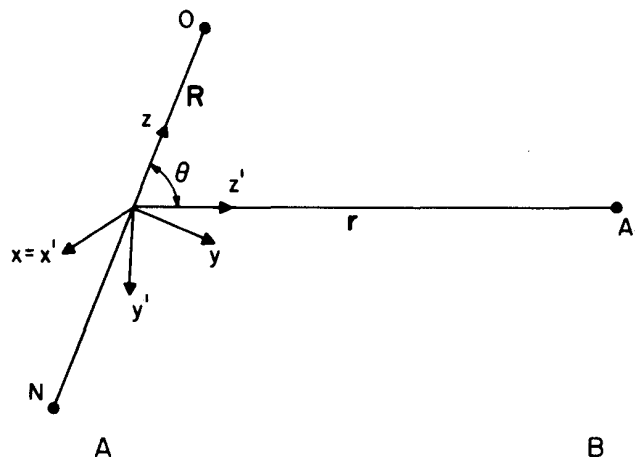


FIG. 1. Coordinate system used in the present work. The NO orbitals are measured relative to the unprimed axes.

The wavefunctions used were the Hartree-Fock functions of Green<sup>10</sup> for NO and of Clementi<sup>11</sup> for Ar. The energies of the  $A'$ (+) and  $A''$ (-) states were calculated by storing the charge density due to the extra  $\pi$  orbital separately from the rest of the NO charge density and putting the pieces together with the different  $\varphi$  dependences discussed in the previous section. The 3-dimensional numerical quadrature<sup>12</sup> was carried out using Gauss-Legendre quadratures similar to those in I; 32 points were used in the  $\phi$  integration, 40 points in the  $\theta$  integration, and a total of 72 points in the  $r$  integration which ran from 0 to  $12.0 a_0$ . The  $r$  integration was split up into 12 intervals with the N and O nuclei and the positions of the Ar atom at the end points of the intervals. The results of the quadrature should be accurate to about 1% at the smaller  $r$  values and about 10% at the largest distances. The calculation was carried out with (see Fig. 1)  $R$  fixed at  $R_0 = 2.1747 a_0$ , at 7 values of  $r$  ranging from  $3-9 a_0$ , and at the  $\theta$  angles of a 12-point Gauss-Legendre quadrature. Rae's<sup>4</sup> correction, which multiplies the  $EG$  exchange energy by 0.518 for Ar-NO, was used.

In the interest of space, detailed tables of the resulting  $EG$  estimates of the  $SCF$  and correlation ( $COR$ ) interaction energies of the two states at each of the 84 points will not be reproduced here, but they are available upon request from one of the authors ( $RTP$ ).

## B. Fitting of $EG$ potentials

The difference between the two interaction energies  $V_+(r, \theta)$  and  $V_-(r, \theta)$  resulting from the calculations described above turned out to be much smaller than (ca. 10%) of either one. To treat this difference accurately in fitting  $V_+$  and  $V_-$  to analytic forms, we chose to fit the average,

$$V_a = \frac{1}{2}(V_+ + V_-), \quad (1)$$

and half the difference,

$$V_d = \frac{1}{2}(V_+ - V_-), \quad (2)$$

instead. The original potentials of the two states:

$$V_{\pm} = V_a \pm V_d, \quad (3)$$

are easily recovered from our fits to  $V_a$  and  $V_d$ , and it turns out that  $V_a$  and  $V_d$  are themselves useful quantities in the theory of scattering of atoms by  $\Pi$ -state mole-

cules.<sup>13</sup> In addition, as we showed in determining van der Waals coefficients for this system,<sup>9</sup> the natural Legendre polynomial expansions of  $V_a$  and  $V_d$  are different as detailed below.

Both these interaction energies are given by the  $EG$  model as the sum of  $SCF$  and correlation ( $COR$ ) contributions:

$$V_i = V_{SCFi} + V_{CORi}, \quad i = a \text{ or } d, \quad (4)$$

and each of these was fit separately.  $V_a$  was first expanded in Legendre polynomials,

$$V_{ja} = \sum_{n=0} v_n^{ja}(r) P_n(\cos\theta), \quad j = SCF \text{ or } COR, \quad (5)$$

and the coefficients determined by Gaussian quadrature as in Paper I. This is equivalent to a least squares fit using optimized points and weights. However, as we showed elsewhere,<sup>9</sup>  $V_d$  is best expanded in associated Legendre polynomials  $P_n^m$  with  $m = 2$ :

$$V_{jd} = \sum_{n=2} v_n^{jd}(r) P_n^2(\cos\theta). \quad (6)$$

Now the  $P_n^2$  form a complete set but are not orthogonal under ordinary Gauss-Legendre quadrature. Hence the  $v_n^{jd}$  here had to be determined by ordinary linear least squares fitting. Thus we are not assured as good a fit to  $V_d$  as to  $V_a$ , but the fit is probably as good as justified by the size and accuracy of the original  $V_d$ .

As in paper I, the  $v_n^{ji}(r)$  were fit to the analytic forms:

$$v_n^{SCFi}(r) = A_{n1}^i \exp(A_{n2}^i r + A_{n3}^i r^2), \quad (7)$$

and

$$v_n^{CORi}(r) = -B_{n1}^i \exp(B_{n2}^i r + B_{n3}^i r^2), \quad (8)$$

where  $i = a$  or  $d$ . In this fitting, the  $EG$  results at  $r = 9a_0$  were not used because they were less stable and accurate than the rest of the data. In addition, it was found that at  $r = 3a_0$ ,  $V_d$  was negative at several of the angles and somewhat irregular. Whether this is a real physical effect, an artifact of the  $EG$  model, or just due to the fact that  $V_d$  is so much smaller than  $V_a$  at small  $r$  as to be in the noise of the quadrature was not clear, and some data at  $r = 3$  was omitted in doing the fitting. This close-in region of the potential energy surface is

TABLE I. Parameters for the average Ar-NO interaction potential  $V_a = (V_+ + V_-)/2$ . The  $A_n$  and  $B_n$  were obtained directly from fitting the electron gas results; the van der Waals coefficients are from Ref. 9; and the  $r_n$  and  $B_n'$  are defined in the text. All are in Hartree atomic units. The numbers following each entry are exponents.

$n =$	0	1	2	3	4	5	6
$A_{n1}^a$	0.228311E+02	-0.374060E-01	0.191494E+02	-0.129877E+00	0.156797E+01	-0.199150E-02	0.423932E-02
$A_{n2}^a$	-0.900993E+00	0.469850E+00	-0.848736E+00	-0.758019E-01	-0.547978E+00	0.951085E+00	0.920948E+00
$A_{n3}^a$	-0.816737E-01	-0.157335E+00	-0.801656E-01	-0.117222E+00	-0.115781E+00	-0.236344E+00	-0.273503E+00
$B_{n1}^a$	0.247943E+00	-0.476424E-02	0.121053E+00	-0.552338E-02	0.238035E-03	-0.307187E-04	0.346671E-08
$B_{n2}^a$	-0.765576E+00	-0.176886E+00	-0.713292E+00	-0.535382E+00	0.107794E+01	0.997173E+00	0.512894E+01
$B_{n3}^a$	-0.259343E-01	-0.514367E-01	-0.286123E-01	-0.264962E-01	-0.243921E+00	-0.236564E+00	-0.741895E+00
$C_8(n)$	69.		9.9				
$r_n^a$	5.66384	$\infty$	5.75480	$\infty$	$\infty$	$\infty$	$\infty$
$B_{n1}^d$	0.366976E+00		0.426280E-01				

TABLE II. Parameters for the Ar-NO difference potential  $V_d = (V_+ - V_-)/2$ . Notation is the same as in Table I.

$n =$	2	3	4	5	6
$A_{n1}^d$	0.151076E-01	-0.959842E-03	0.977523E-04	-0.143591E-09	0.308462E-04
$A_{n2}^d$	-0.380142E-01	0.362915E+00	0.979587E+00	0.432678E+01	0.233850E+00
$A_{n3}^d$	-0.118531E+00	-0.137587E+00	-0.182474E+00	-0.416412E+00	-0.108864E+00
$B_{n1}^d$	0.105201E-02	-0.163794E-03	0.103033E-03	-0.238730E-04	0.162300E-04
$B_{n2}^d$	-0.472957E+00	-0.366790E+00	-0.410274E+00	-0.691294E+00	-0.809847E+00
$B_{n3}^d$	-0.279202E-01	-0.296739E-01	-0.229925E-01	0.0	-0.251704E-02
$D_6$	1.24				
$r_n^d$	6.96258	$\infty$	$\infty$	$\infty$	$\infty$
$B_{n1}^{d'}$	0.133436E-02				

only sampled in high energy collisions and should not affect properties at thermal energies. The resulting parameters are given by the first six lines of Tables I and II. When these are used in Eq. (4)-(8) they reproduce  $V_a$  at all the original points with  $4 \leq r \leq 8$  with a standard fractional deviation of 3%. (They also reproduce the omitted  $V_a$  data at  $3 a_0$  to within about 15%). They reproduce  $V_d$  at  $4 \leq r \leq 8$  with a standard fractional deviation of 17%. This large error is primarily due to the fact that even at  $4a_0$ ,  $V_d$  is so much smaller than  $V_a$  as to be almost in the noise of the quadrature. The parameters reproduce  $V_d$  on  $5 \leq r \leq 8$  to within 9% which is about as good as justified since  $V_d \sim 0.1 V_a$ , and the original points were calculated only to an accuracy of about 1% in  $V_a$ .

### C. Inclusion of van der Waals potential

The van der Waals  $C_6$  and  $D_6$  coefficients for NO interactions were determined in a previous paper<sup>9</sup>; accuracy and availability of data prevented our calculating the higher coefficients<sup>14</sup> which are calculable for other molecules such as  $\text{CO}_2$ , so that the form obtained was:

$$V_{vdw} = -r^{-6} [C_6(0) + C_6(2)P_2(\theta) \pm D_6P_2^2(\theta)]. \quad (9)$$

As in Paper I, we joined each of these terms smoothly onto the appropriate term of  $V_{COR}$  of Eq. (8) by first finding the points  $r_n^i$  where the two forms have equal logarithmic derivatives in order to assure a continuous slope and then determining  $B_{n1}^{i'}$  that would make Eq. (8) and the van der Waals potentials equal at  $r_n^i$ . However, instead of replacing the  $B_{n1}^i$  by the  $B_{n1}^{i'}$  as we did in Paper I, we adopt a more flexible procedure which allows us to approximately mock up the effects of the missing  $r^{-6}$  and  $r^{-10}$  terms with terms that extend to large  $r$  but die faster than  $r^{-6}$ . This is done by using the following forms for the correlation terms:

$$v_n^{CORi} = -B_{n1}^i \exp(B_{n2}^i r + B_{n3}^i r^2), \quad r \leq r_n^i, \quad (10)$$

$$= -C_6^i(n) r^{-6} - (B_{n1}^i - B_{n1}^{i'}) \exp(B_{n2}^i r + B_{n3}^i r^2), \quad r \geq r_n^i,$$

where  $C_6^i(n) = C_6(n)$  and  $C_6^i(2) = D_6$  from Eq. (9). This form assures one of a continuous potential and derivative everywhere for arbitrary  $B_{n1}^i$  so that the  $B_{n1}^i$  can be ad-

justed at will empirically as more information becomes available, and it also assures one of a potential which is asymptotically of the correct van der Waals form.

This completes the description of the determination of the *a priori* intermolecular potentials for the Ar-NO interactions. The parameters are in Tables I and II.

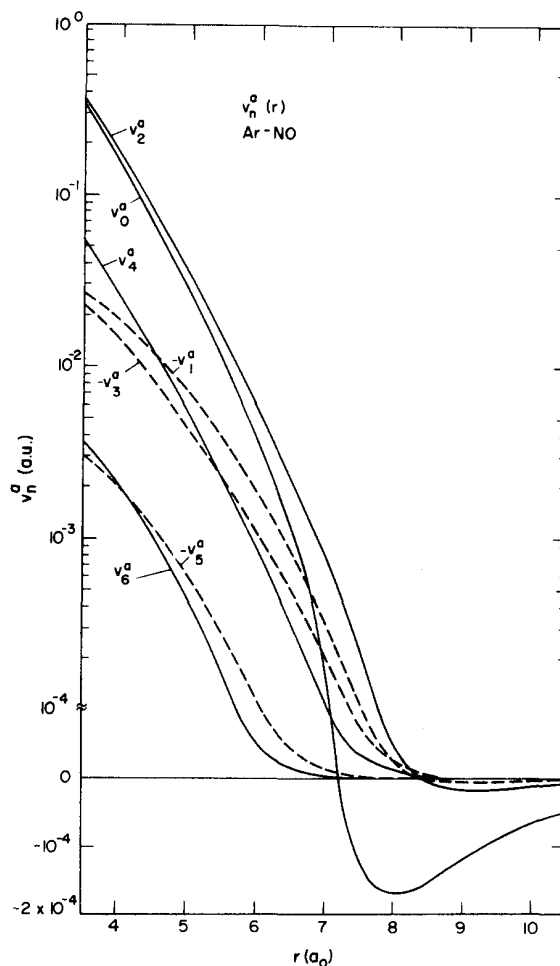


FIG. 2. Coefficients  $v_n^a$  in the Legendre polynomial expansion of the average potential  $V_a$ . The negatives of the  $v_n^a$  for odd  $n$  are plotted. All quantities are in Hartree atomic units.

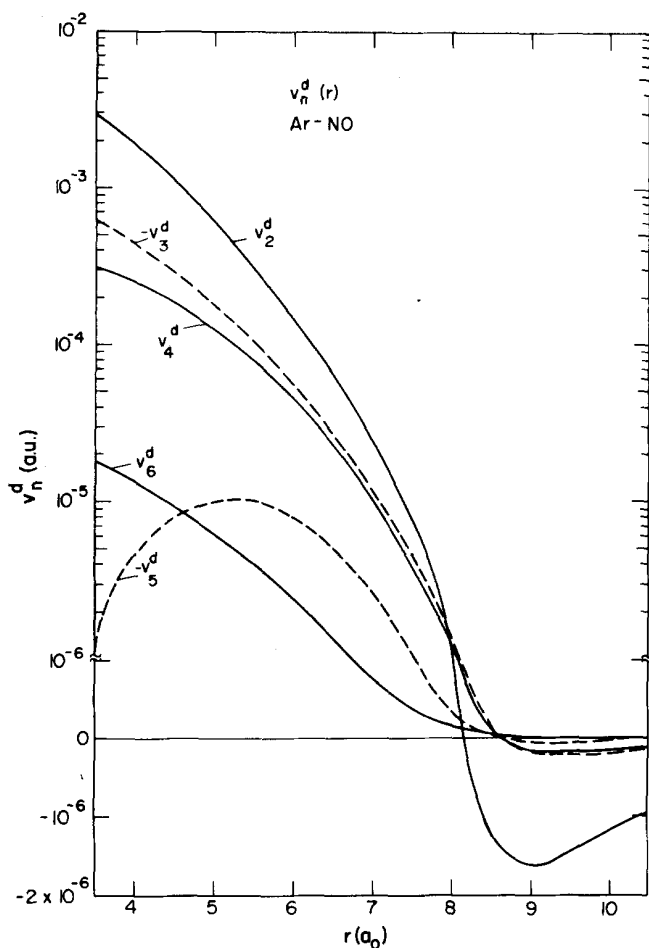


FIG. 3. Coefficients  $v_n^d$  in the associate Legendre polynomial expansion of the difference potential  $V_d$ . The negatives of the odd  $n$   $v_n^d$  are plotted. Hartree atomic units.

### III. RESULTS AND CONCLUSIONS

#### A. Results

From Tables I and II we see that  $B_{01}^{a'} > B_{01}^a$  and  $B_{21}^{d'} > B_{21}^d$ . If these values are used for the  $B_{n1}^i$  and  $B_{n1}^{i'}$  in Eq. (10) they will tend to make the attractive wells shallower than they would be with the van der Waals  $r^{-6}$  term alone. And we already expect that well to be too shallow because of the absence of the  $r^{-8}$  and  $r^{-10}$  terms. Hence, to make the results more realistic, we replaced  $B_{01}^a$  by  $B_{01}^{a'}$  and  $B_{21}^d$  by  $B_{21}^{d'}$  everywhere before constructing plots.

Figure 2 is a plot of our fits to the coefficients  $v_n^a$  of the Legendre polynomials  $P_n$  in the expansion of the average potential  $V_a$ . Each  $v_n^a$  is the sum of SCF and COR contributions. We note that  $v_2^a > v_0^a$  in the repulsive region; with this much anisotropy any treatment of the interaction as spherical is of doubtful value. It should also be noted that, because of the small dipole moment of NO, the coefficients with odd  $n$  (whose negative is plotted) are smaller in magnitude than the neighboring coefficients with even  $n$ , but they are certainly not negligible. Coefficients with  $n > 6$  are negligible.

Figure 3 is a plot of our fits to the coefficients  $v_n^d$  of the associated Legendre polynomials  $P_n^m$ ,  $m=2$ , in the expansion of the difference potential  $V_d$ . Each contains both SCF and COR contributions, and the negative of the  $v_n$  for odd  $n$  is plotted. The coefficients with  $n > 6$  were negligible everywhere. We note that the behavior of the  $v_n^d$  is similar to that of the  $v_n^a$ , except for their smaller magnitudes and the interesting small  $r$  behavior of  $v_5^d$  which may be an artifact of the quadrature and fitting procedure already discussed.

Figure 4 is a contour plot of the average potential  $V_a = (V_+ + V_-)/2$ . It has the usual shape; like the Ar-CO surface,<sup>15</sup> it is quite anisotropic but not so anisotropic as the Ar-CO<sub>2</sub> surface.<sup>1</sup> With the present parameterization, the minimum in the well occurs at  $r = 7.43 a_0$  and  $\theta = 89.3^\circ$  and is  $2.30 \times 10^{-4}$  a.u. (72.6 °K) deep. As we discuss below, this is still too shallow.

Figure 5 is a contour plot of the potential difference  $V_d = (V_+ - V_-)/2$ , and one sees that its shape is very interesting and at least qualitatively right. It goes to zero for all  $r$  at  $\theta = 0^\circ$  and  $180^\circ$  because the two  $\Pi$  components are degenerate for a linear molecule. For  $\theta$

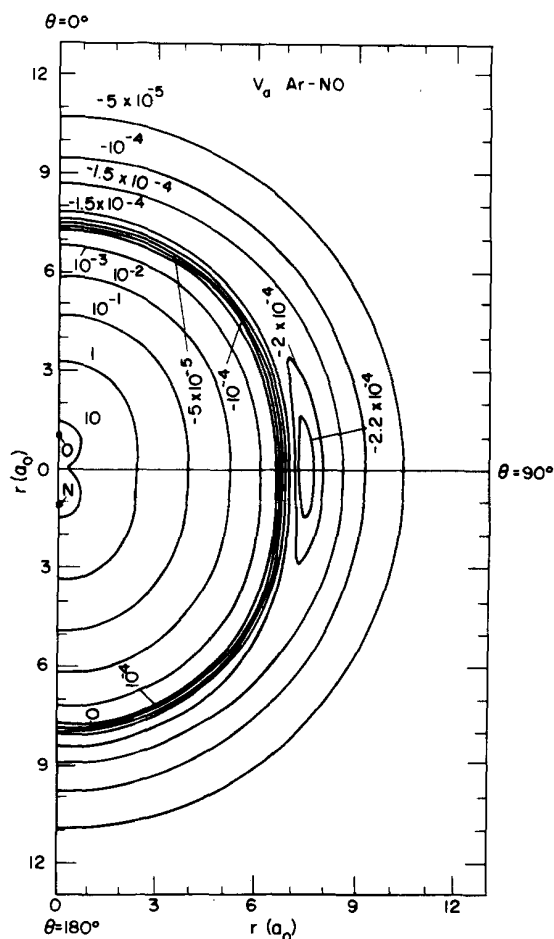


FIG. 4. Contour plot of the average Ar-NO potential energy  $V_a$ . The N and O atoms lie on the  $z$  axis as shown, and the contours give the potential energy in a.u. felt by the Ar at any  $r$  or  $\theta$ . In terms of the coordinates of Fig. 1,  $y = r \sin \theta$  and  $z = r \cos \theta$  are the abscissa and ordinate, respectively.

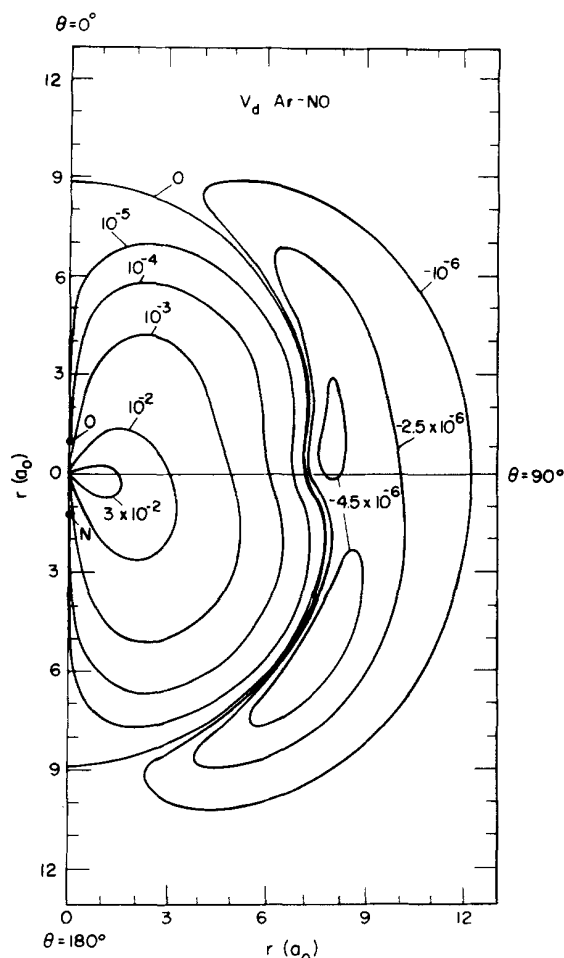


FIG. 5. Contour plot of the Ar-NO difference potential energy  $V_d$ . The notation and coordinates are those of Fig. 2.

$\neq 0^\circ$  or  $180^\circ$  and small  $r$ , it is positive because the  $\pi$  orbital in the  $A'$ (+) state is in the plane of the Ar giving greater overlap and repulsion. For  $\theta \neq 0^\circ$  or  $180^\circ$  and larger  $r$  it goes negative because of the greater polarization of the  $\pi$  orbital in the  $A'$ (+) state. However, the maximum well depth ( $4.5 \times 10^{-6}$  a.u. or  $1.4^\circ\text{K}$ ) in  $V_d$  is very small. Because our van der Waals  $D_6$  coefficient is only a rough estimate,<sup>9</sup> this well depth is only qualitatively correct. Clearly,  $V_d$  is small compared to  $V_a$ .

### B. Use of these potentials

We conclude that while our potential difference  $V_d$  is reasonable and qualitatively correct, it is unlikely to be any more than qualitatively accurate and any potential user should keep that in mind. Further experiments or *ab initio* calculations are needed to determine  $V_d$  more accurately. Measurement of the cross section for the  ${}^2\Pi_{1/2} \rightarrow {}^2\Pi_{3/2}$  transition in Ar-NO collisions would be very helpful because that cross section can be shown<sup>13</sup> to depend directly on  $V_d$ .

As it presently stands, even with the modifications made in making the plots,  $V_d$  has too shallow an attractive well. Based on the empirical similarities<sup>16</sup> between Ar, NO, and CO, we expect that the well depth of

$V_a$  should be at least  $120^\circ\text{K}$ . To achieve that, we note that our work on  $\text{CO}_2^1$  and  $\text{CO}^{15}$  indicated that the Rae correction may overcorrect somewhat and that one might approximately account for that by multiplying all the  $A_{n1}$  by a factor of 0.7–0.8. In addition, all our work<sup>1,5</sup> with the EG model has indicated that the  $B_{n1}$  need to be multiplied by a factor of 2–3. Unfortunately, virial coefficient or other data which would directly specify these factors more closely do not seem to be available. Recent scattering calculations<sup>17</sup> using the Ar- $\text{CO}_2$  potential from paper I indicate that the EG model gives a good description of the anisotropy of the surface, so that with these modifications of the  $A_{n1}$  and  $B_{n1}$  (which we suggest be incorporated in any use of the present results), we believe that the resulting  $V_a$  would provide a realistic description of the average Ar-NO interaction. Some molecular beam data is available<sup>18</sup> which could be used together with detailed scattering calculations to test this hypothesis. Wenn time permits, we plan to do such calculations. Such results would also be interesting because the theory of scattering by a  ${}^2\Pi$  molecule<sup>13</sup> predicts curious effects in the cross section for the  ${}^2\Pi_{1/2} \rightarrow {}^2\Pi_{3/2}$  transition, similar to those seen in  $\Delta j = 1$  transitions in  ${}^1\Pi$  state molecules.<sup>19</sup>

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