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Glen C. Nielson

Gregory A. Parker
parker@nhn.ou.edu

Russell T. Pack

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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*

Glen C. Nielson[†] and Gregory A. Parker[‡]

Department of Chemistry, Brigham Young University, Provo, Utah 84602

Russell T Pack[§]

Theoretical Division, University of California Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545

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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 series¹ we reviewed and discussed applications of the electron gas (EG) model—as developed by Gaydaenko and Nikulin,² and Gordon and Kim,³ and modified by Rae,⁴ and Cohen and Pack⁵—for calculation of interactions between atoms and molecules when both partners have closed shell electronic structure. We also applied the method to the He-CO₂ and Ar-CO₂ 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 Gordon⁶ who used it to study the noble gas halides. They compared their results with the *ab initio* calculations of Dunning and Hay⁷ for KrF and found that the EG results were good for the Π state in which the empty F orbital is perpendicular to the Kr but poor for the Σ 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 mixing⁷ 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 N₂ with one additional electron in an antibonding π orbital. In the Ar-NO system, which has C_s symmetry, the degenerate Π 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 π_y orbital lying in the triatomic plane while the A'' (-) is obtained by putting it in a π_x orbital perpendicular to

that plane. This is achieved merely by multiplying the rest of the Hartree-Fock π orbital by an appropriately normalized $\sin\varphi$ or $\cos\varphi$, respectively, to give the proper φ 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⁻¹ spin orbit splitting⁸ 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 2×2 secular equation as described in detail in an earlier paper.⁹

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.

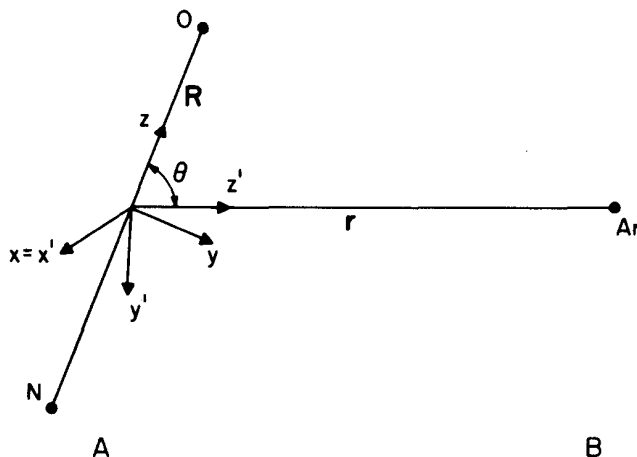


FIG. 1. Coordinate system used in the present work. The NO orbitals are measured relative to the unprimed axes.

The wavefunctions used were the Hartree-Fock functions of Green¹⁰ for NO and of Clementi¹¹ for Ar. The energies of the A' (+) and A'' (-) states were calculated by storing the charge density due to the extra π orbital separately from the rest of the NO charge density and putting the pieces together with the different φ dependences discussed in the previous section. The 3-dimensional numerical quadrature¹² was carried out using Gauss-Legendre quadratures similar to those in I; 32 points were used in the ϕ integration, 40 points in the θ 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 $R_0 = 2.1747a_0$, at 7 values of r ranging from 3–9 a_0 , and at the θ angles of a 12-point Gauss-Legendre quadrature. Rae's⁴ 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 Π -state mole-

cules.¹³ In addition, as we showed in determining van der Waals coefficients for this system,⁹ 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,

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

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,⁹ V_d is best expanded in associated Legendre polynomials P_n^m with $m = 2$:

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

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 | ∞ | 5.75480 | ∞ | ∞ | ∞ | ∞ |
| 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 | ∞ | ∞ | ∞ | ∞ |
| $B_{n1}^{d'}$ | 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 paper⁹; accuracy and availability of data prevented our calculating the higher coefficients¹⁴ which are calculable for other molecules such as 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.

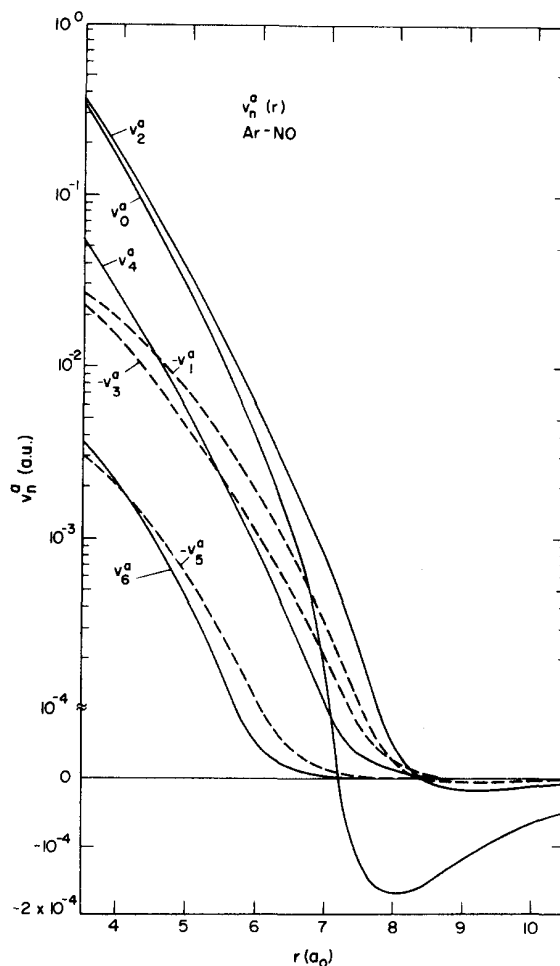


FIG. 2. Coefficients v_n^a in the Legendre polynomial expansion of the average potential V_a . The negatives of the v_n^a for odd n are plotted. All quantities are in Hartree atomic units.

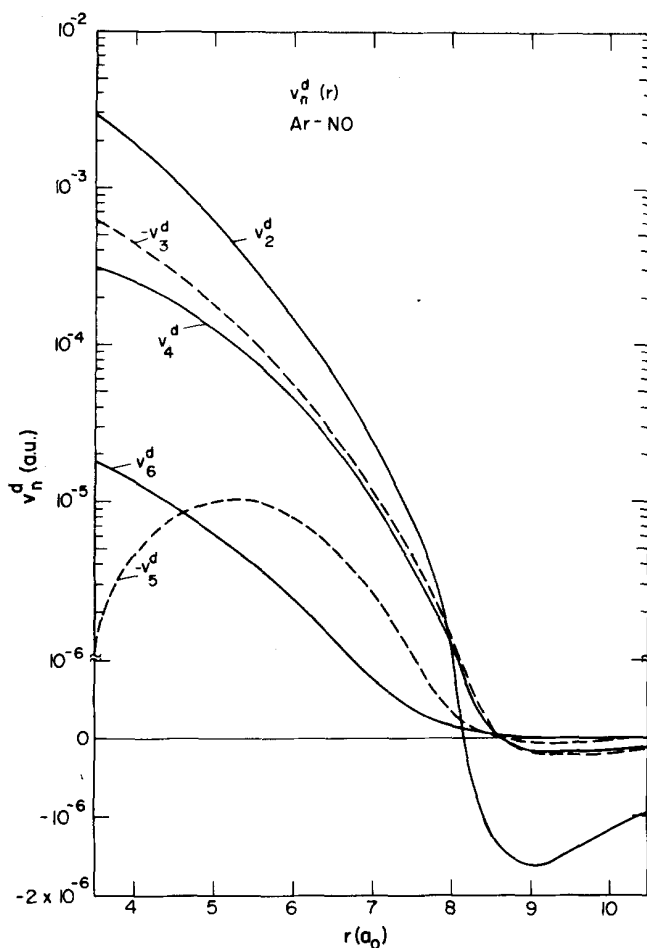


FIG. 3. Coefficients v_n^d in the associate Legendre polynomial expansion of the difference potential V_d . The negatives of the odd v_n^d are plotted. Hartree atomic units.

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^d 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,¹⁵ it is quite anisotropic but not so anisotropic as the Ar-CO₂ surface.¹ With the present parameterization, the minimum in the well occurs at $r = 7.43 a_0$ and $\theta = 89.3^\circ$ and is 2.30×10^{-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° because the two Π components are degenerate for a linear molecule. For θ

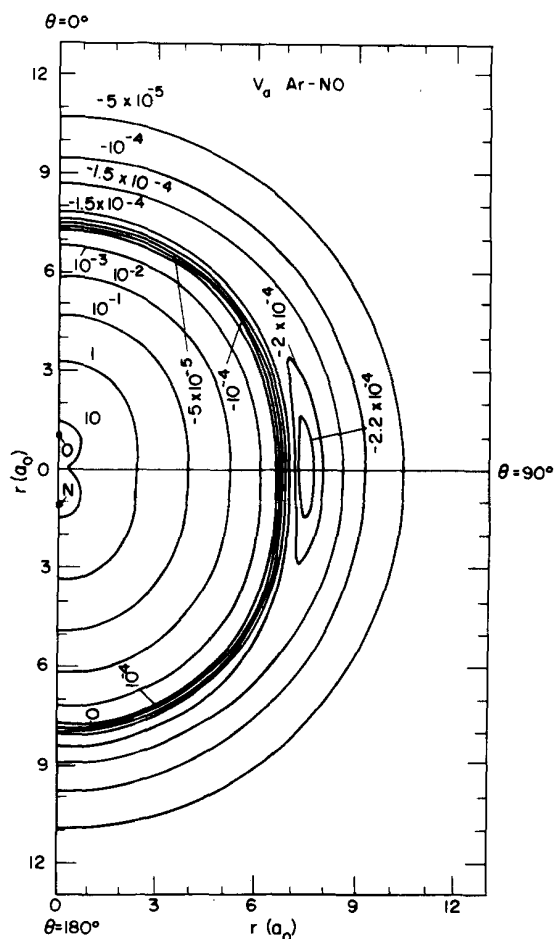


FIG. 4. Contour plot of the average Ar-NO potential energy V_a . The N and O atoms lie on the z axis as shown, and the contours give the potential energy in a.u. felt by the Ar at any r or θ . In terms of the coordinates of Fig. 1, $y = r \sin \theta$ and $z = r \cos \theta$ are the abscissa and ordinate,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

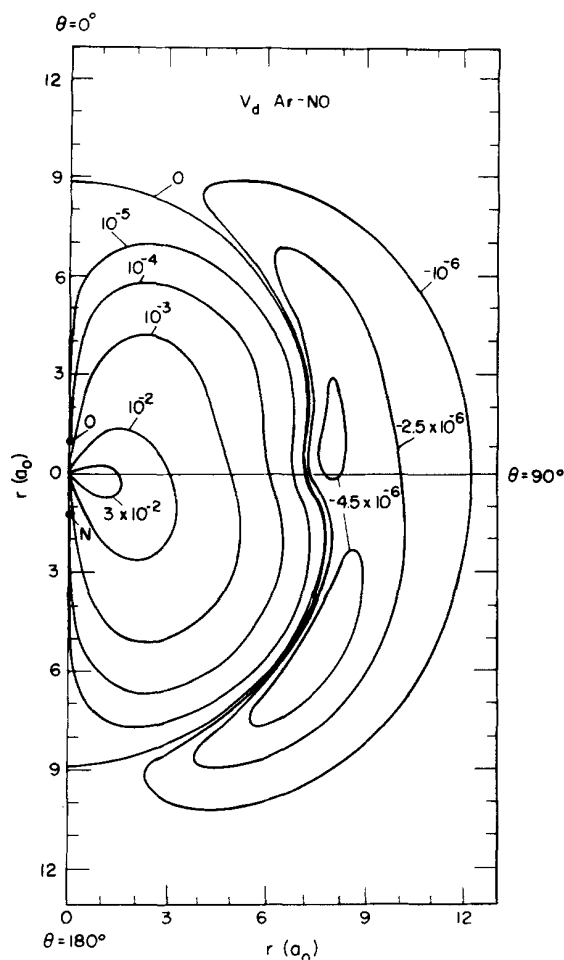


FIG. 5. Contour plot of the Ar-NO difference potential energy V_d . The notation and coordinates are those of Fig. 2.

$\neq 0^\circ$ or 180° and small r , it is positive because the π orbital in the A' (+) state is in the plane of the Ar giving greater overlap and repulsion. For $\theta \neq 0^\circ$ or 180° and larger r it goes negative because of the greater polarization of the π orbital in the A' (+) state. However, the maximum well depth (4.5×10^{-6} a.u. or 1.4°K) in V_d is very small. Because our van der Waals D_6 coefficient is only a rough estimate,⁹ 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 shown¹³ 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 similarities¹⁶ between Ar, NO, and CO, we expect that the well depth of

V_a should be at least 120°K . To achieve that, we note that our work on CO_2^1 and 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^{1,5} 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 calculations¹⁷ using the Ar- 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 available¹⁸ 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 ${}^2\Pi$ molecule¹³ 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.¹⁹

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†Present address: Department of Chemistry, University of Chicago, Chicago, Illinois 60637.

‡Present address: Department of Chemistry, California Institute of Technology, Pasadena, California 91109.

§Also Adjunct Professor of Chemistry, Brigham Young University.

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