

A calculation of the electron detachment energy of NO_2^-

Earl Andersen* and Jack Simons†

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112
(Received 18 November 1976)

The equations-of-motion (EOM) method was used to calculate the detachment energy of NO_2^- , including correlation and relaxation effects. Enough of the SCF-level potential energy surface of NO_2^- was calculated to compute the thermodynamic electron affinity of NO_2 . The 2A_1 potential surface of NO_2 was obtained by adding the computed vertical detachment energy to the potential surface of NO_2^- at the corresponding geometry where the highest occupied molecular orbital was of a_1 symmetry. The calculated vertical detachment energy of NO_2^- at its equilibrium geometry was 2.66 eV. Using the calculated potential energy surfaces and the reported values for the vibrational energy differences between NO_2 and NO_2^- , the thermodynamic electron affinity of NO_2 was calculated to be 2.25 eV, which compares very well with Lineberger's experimental value of 2.36 ± 0.1 eV.

I. INTRODUCTION

Of the chain reactions that decompose ozone, the only stable odd electron series is NO_x (NO , NO_2). In 1973, the contribution of the NO_x system to the removal of odd oxygen (O , O_3) from the atmosphere was reported to be 60%–74%.¹ This is then the most important natural process for removing odd oxygen. The chain reaction that has been presented depends on free radical characteristics:



The net result of this chain is $2\text{O}_3 \rightarrow 3\text{O}_2$. Another reaction which is known to take place



combines with the reaction given in Eq. (3) to yield the destruction of two odd oxygen species.

With the addition of an electron to NO_2 , a stable anion is formed. This anion is generally considered quite unreactive and predicted to be an end product in the negative ion atmospheric chemistry.² The electron detachment energy (DE) of NO_2^- is thus an important quantity. Until recently, the experimental measurements of this property were not consistent,³ although the experimental values for the detachment energy have now clustered around 2.3 to 2.4 eV.^{4,5}

One of the problems which hinders the experimental determination of the adiabatic DE is the small Franck-Condon factor (0.003)⁵ for the (000–000) transition. Although the anion and neutral bond lengths are similar (2.3356 bohr,⁶ NO_2^- ; 2.256 bohr,⁷ NO_2), there is a large difference in the bond angle (115.4° ,⁶ NO_2^- ; 134.1° ,⁷ NO_2). The measurement of the adiabatic photodetachment energy required a laser with adequate intensity (to overcome the small Franck-Condon factor) and a narrow enough bandwidth.⁵ Thus, the need for accompanying theoretical study is apparent.

The equations-of-motion (EOM) method has been used successfully by us for obtaining electron affinities for diatomics which are in good agreement with experi-

ment.^{8–12} To date, results on only one polyatomic system have been reported, in which the quality of agreement with experiment was not as good as had been obtained in the earlier diatomic molecule work.¹³ The fact that the detachment energy of NO_2^- has recently been accurately determined experimentally and that this energy is an important quantity to know combine to make it clear that NO_2^- presents a good case for the application of the EOM method.

II. CALCULATIONS

The EOM technique for directly calculating vertical ionization potentials using SCF orbital energies and two-electron integrals has been developed¹⁴ and implemented^{10–13} in recent years. It is used here to consider the detachment of an electron from NO_2^- . The SCF wavefunctions employed in the present work were obtained using the POLYATOM labels and integral programs and the RHF part of Goddard's GVB program which had been adapted for the Wright Patterson Air Force Base CDC Cyber-74 computer by R. J. Blint. The starting basis set was Dunning's¹⁵ $[4s\ 2p]$ contraction of Huzinaga's¹⁶ $[9s\ 5p]$ for both nitrogen and oxygen. The DE was then maximized (to optimize the anion's energy) by adding diffuse s and p basis functions with orbital exponents equal to 1/4 the value of the smallest exponent of corresponding orbitals in the starting basis. Once the DE failed to increase with further addition of basis functions, a three point parabola fit of DE vs orbital exponent was used to maximize the DE for those basis functions which contributed most significantly. This optimization of the basis set was performed at the experimentally determined equilibrium conformation of NO_2^- ($R_3 = 2.3356$ bohr and $\theta_e = 115.4^\circ$). Because the NO_2 state of interest in this calculation was the 2A_1 state (the reported lowest state), the important diffuse basis functions added to the oxygens and to the central nitrogen were of a_1 symmetry (i.e., the molecule lies in the x, y plane where the C_2 symmetry axis coincides with the y axis). The final resulting optimized basis set is shown in Table I. This basis set was used without further optimization to calculate the NO_2^- and NO_2 potential energy surfaces.

Although the SCF calculations were performed with

TABLE I. NO_2^- basis set.

Center	Type	Exponent	Coefficient
N	S	5909.44	0.002004
		887.451	0.015310
		204.749	0.074293
		59.8376	0.253364
		19.9981	0.600576
		2.686	0.245111
		7.1927	1.0
		0.700	1.0
		0.2133	1.0
		0.0854	1.0
	$P(X, Y, Z)$	26.786	0.018257
		5.9564	0.116407
		1.7074	0.390111
		0.5314	0.637221
		0.1654	1.0
		0.0413	1.0
		O	S
1175.82	0.015436		
273.188	0.073771		
81.1696	0.247606		
27.1836	0.611832		
3.4136	0.241205		
9.5322	1.0		
0.9398	1.0		
0.2846	1.0		
$P(X, Y)$	35.1832		
	7.9040		0.124189
	2.3051		0.394727
	0.7171		0.627375
	0.2137		1.0
	0.0527		1.0
	$P(Z)$		35.1832
7.9040			0.124189
2.3051			0.394727
0.7171			0.627375
0.2137			1.0

38 contracted Gaussian basis functions, the version of our EOM program used in this work could treat a maximum of 20 molecular orbitals. Hence, only integrals over the lowest 20 molecular orbitals were computed; this simply involves using a 20×38 matrix in the one- and two-electron integral transformation step. We did carry out tests to see the changes in the resulting DE for different selections of the "chosen" 20 functions; variations of less than 10% were observed for reasonable selections of the 20 chosen molecular orbitals. Because the use of the lowest (energy) 20 SCF orbitals gave the large DE, this set of orbitals was used for all of the calculations.

The resultant electronic configuration of NO_2^- for most molecular geometries was

TABLE II. Results of some calculations for NO_2^- .

	Pfeiffer and Allen ⁶	Bonaccorsi <i>et al.</i> ¹⁸	This work
R_{NO} (bohr)	2.3356	2.33	2.39
θ_{ONO} (deg)	115.4	115	118
E_{total} (hartree)	-203.9551	-203.9859	-204.0427

$$1b_2^2 1a_1^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 5a_1^2 3b_2^2 1b_1^2 4b_2^2 1a_2^2 6a_1^2.$$

However, calculations performed at a bond angle of 105° and bond lengths of 2.3356 and 2.40 a.u. gave a highest occupied molecular orbital (HOMO) of a_2 symmetry; at a bond angle of 95° , a HOMO of b_2 symmetry; and for all other geometries a HOMO of a_1 symmetry.

III. RESULTS AND DISCUSSION

A. Potential surfaces for NO_2^- and NO_2

An SCF-level potential surface was calculated using the basis set discussed above for NO_2^- . A survey of the literature for *ab initio* calculations on NO_2^- resulted in meager success. Two semiempirical calculations have been reported.¹⁷ All previous *ab initio* calculations^{6,18} have been performed only at the experimental geometry of NaNO_2 ($R_e = 2.3356$ bohr and $\theta_e = 115.4^\circ$) or only as functions of the angle. Previously, the best total SCF energy obtained for NO_2^- was -203.9859 hartree (see Table II).¹⁸ The above geometry and energy values compare well with results of our work, which yield a bond length of 2.39 bohr, a bond angle of 118° , and an energy of -204.0427 hartree, each of which we obtained by parabolic fits to our calculated data. Although all of our calculations were performed with C_{2v} symmetry constraints, we have explored both variation in bond length and angle, the results of which can be seen in Figs. 1 (variation of bond length) and 2 (variation of bond angle).

To obtain a potential surface for the 2A_1 state of NO_2 , the calculated EOM detachment energy was added to the NO_2^- SCF energy at each geometry:

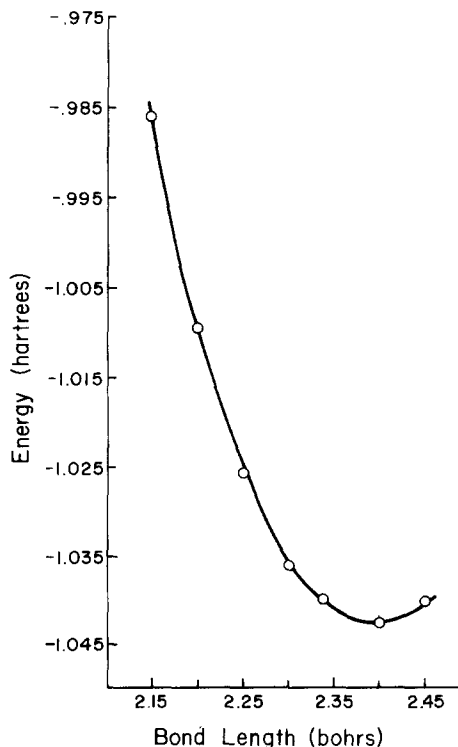


FIG. 1. The calculated NO_2^- potential energy curve at an ONO angle of 118.2° . We have added 203. hartree to each energy.

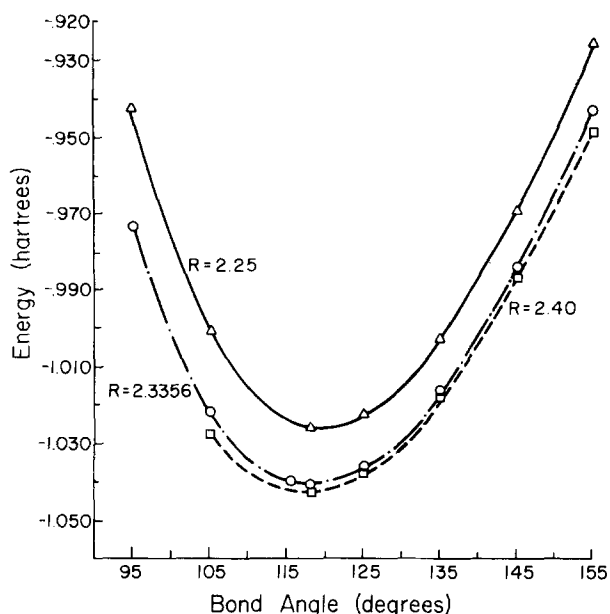


FIG. 2. These calculated potential subsurfaces for NO₂⁻ as a function bond angle. We have added 203. hartree to each energy.

$$E_{\text{NO}_2}(r, \theta) = E_{\text{NO}_2^-}(r, \theta) + E_{v.d.}, \quad (5)$$

where $E_{\text{NO}_2}(r, \theta)$ and $E_{\text{NO}_2^-}(r, \theta)$ are the total energies of NO₂ and NO₂⁻, respectively, as functions of bond length and bond angle, and $E_{v.d.}$ is the vertical detachment energy. This NO₂ surface is used, in combination with our computed NO₂⁻ surface, to calculate the thermodynamic electron affinity of NO₂. A surface produced by using the SCF energy of NO₂⁻ in Eq. (5) should be, at best, SCF-level quality because it is distorted by the correlation and relaxation energies contained in $E_{v.d.}$ which are not contained in $E_{\text{NO}_2^-}(r, \theta)$. Thus, our computed thermodynamic DE may not be as accurate as our (directly) calculated vertical DE.

The NO₂ surface obtained from Eq. (5) is compared to other SCF-level surfaces in Table III (also see Fig. 3); the comparison provides some evidence that our surface for NO₂ is comparable in accuracy to SCF surfaces, at least near the minimum-energy configuration. The NO₂ geometry obtained in our work is 2.29 bohr for the bond length and 134° for the bond angle. The total energy of NO₂ was calculated to be -203.9609 hartree. Most of the other calculations have been performed at the experimental geometry ($R_e = 2.2552$ bohr and $\theta_e = 134.1^\circ$). The lowest reported SCF energy was the estimated value by Gillispie²⁵ (-204.07 hartree).

TABLE III. Results of some SCF calculation for NO₂ (²A₁).

	Fink ¹⁹	Gangi <i>et al.</i> ²⁰	Del Bene ²¹	Brundle <i>et al.</i> ²²	Schaefer <i>et al.</i> ²³	Hay ²⁴	Gillispie <i>et al.</i> ²⁵	This work
R_{NO} (bohr)	2.25	2.25	2.34	2.25	2.2552	2.2552	2.25	2.29
θ_{ONO} (deg)	137	134.25	132	134	134.1	134.1	134	134
E_{total} (hartree)	-203.907	203.6930	Not given	-203.9318	-204.0679	-203.94702	-204.07 (estimated)	-203.9609

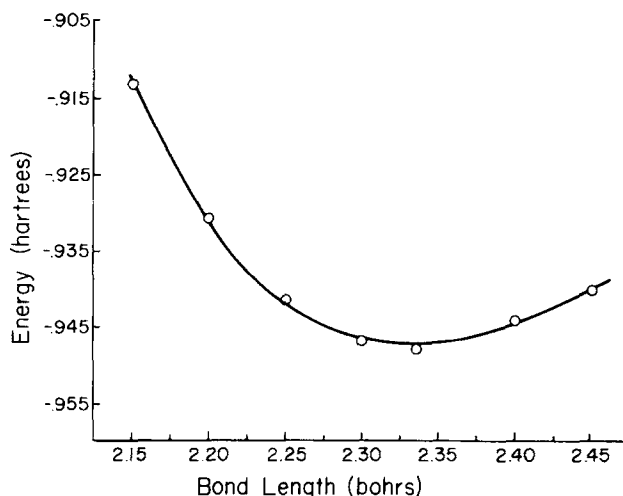


FIG. 3. The calculated potential energy curve for NO₂ obtained using Eq. (5) at an ONO angle of 118.2°. We have added 203 hartree to each energy.

The ²A₁ state NO₂ was found to be the lowest state at 105°; however, the ²B₂ state became the lowest state at 95°. This angle does not agree well with the recent work of Davidson,²⁶ who (using a C_s symmetry) obtained a crossing point of 114° for the ²B₂ and ²A₁ states. However, the vertical DE and thermodynamic DE reported here should still be good because the equilibrium angles of NO₂ and NO₂⁻ (118° and 134°) are in a region where the ²A₁ state of NO₂ is the lowest state.

B. Detachment energy of NO₂⁻

The calculated EOM-level detachment energy at the equilibrium geometry of NO₂⁻ is 2.66 eV. This value is extrapolated from data points computed around this geometry, and does not include any consideration of vibrational levels. Our calculated vertical electron affinity for NO₂ is 1.43 eV (again without consideration of vibrational levels). As can be seen from Figs. 2 and 4, the overlap of the anion and neutral (000-000) levels is not large, which is in agreement with Lineberger *et al.*,⁵ who reported a Franck-Condon factor of 0.003. The thermodynamic electron affinity determined using

$$E.A.(\text{thermo}) = E_{\text{NO}_2}(R_e, \theta_e)$$

$$- E_{\text{NO}_2^-}(R_e^-, \theta_e^-) + \frac{h}{2} \left(\sum_i \nu_i^{\text{NO}_2} - \sum_i \nu_i^{\text{NO}_2^-} \right), \quad (6)$$

in which experimentally determined vibrational fre-

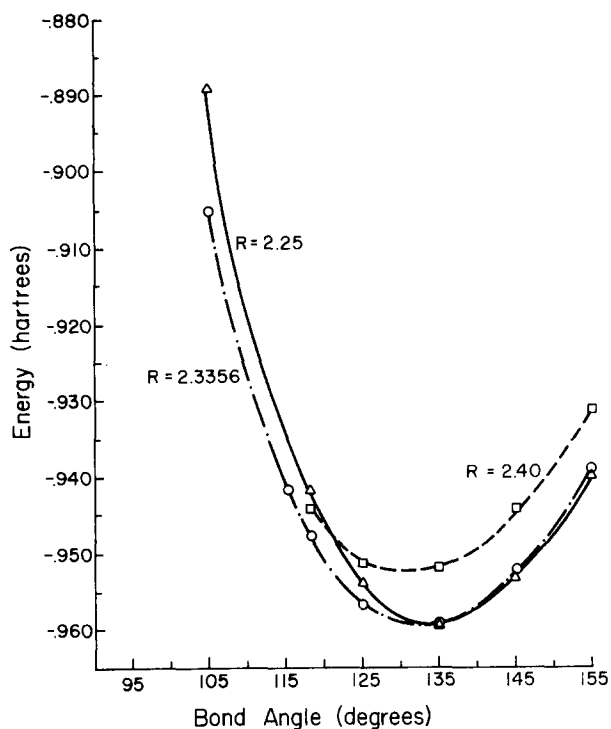


FIG. 4. The calculated potential subsurface for NO_2 calculated using Eq. (5), as a function of bond angle. We have added 203 hartree to each energy.

quencies^{27,28} are employed, is calculated to be 2.25 eV (the bottom of potential well to bottom of potential well value is 2.23 eV), which is in remarkable agreement with the experimental values (2.36 ± 0.10^5 and $2.28 \pm 0.1 \text{ eV}^4$).

IV. CONCLUSION

Because C_{2v} rather than C_s symmetry was used in our calculations, all of the spectroscopic parameters could not be obtained from our potential surfaces. Thus, the quality of the potential surfaces may be judged only by comparison with the SCF-level surfaces reported in the literature and by their ability to yield good thermodynamic and vertical DE's. Our computed value for the thermodynamic DE of NO_2^- agrees to within 5% with the experimental values when vibrational considerations are taken into account. This indicates that the EOM results for polyatomics can be as good as they have been for diatomics, which was not the case in our earlier calculations for NH_2^- . Only by obtaining more results for polyatomics will we be able to answer the question of the general quality of the EOM results.

V. ACKNOWLEDGMENTS

We wish to acknowledge support from the U.S. Army Research Office (DAAG-29-74-G-022). We also would like to thank Dick Blint and Darrell Hopper.

*University of Utah Graduate Research Fellow. Present address: Department of Chemistry, University of Notre Dame, Notre Dame, IN 46556.

†Alfred P. Sloan Fellow 1973–1977, Camille and Henry Dreyfus Fellow.

¹H. S. Johnston, *Acta Astron.* **1**, 135 (1974).

²F. C. Fehsenfeld and E. E. Ferguson, *J. Chem. Phys.* **61**, 3181 (1974).

³See W. A. Chupka, J. Berkowitz, and D. Gutman, *J. Chem. Phys.* **55**, 2733 (1971).

⁴B. M. Hughes, C. Lifschitz, and T. O. Tiernan, *J. Chem. Phys.* **59**, 3162 (1973).

⁵E. Herbst, T. A. Patterson, and W. C. Lineberger, *J. Chem. Phys.* **61**, 1300 (1974).

⁶G. V. Pfeiffer and L. C. Allen, *J. Chem. Phys.* **51**, 190 (1969).

⁷G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1966), p. 602.

⁸W. D. Smith, T. T. Chen, and J. Simons, *J. Chem. Phys.* **61**, 2670 (1974).

⁹T. T. Chen, W. D. Smith, and J. Simons, *Chem. Phys. Lett.* **26**, 296 (1974).

¹⁰K. M. Griffing and J. Simons, *J. Chem. Phys.* **62**, 535 (1975).

¹¹J. Kenney and J. Simons, *J. Chem. Phys.* **62**, 592 (1975).

¹²K. M. Griffing and J. Simons, *J. Chem. Phys.* **64**, 3610 (1976).

¹³E. Andersen and J. Simons, *J. Chem. Phys.* **65**, 5393 (1976).

¹⁴J. Simons and W. D. Smith, *J. Chem. Phys.* **58**, 4899 (1973).

¹⁵T. H. Dunning, Jr., *J. Chem. Phys.* **53**, 2823 (1970).

¹⁶S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).

¹⁷K. L. McEwen, *J. Chem. Phys.* **34**, 547 (1961); H. J. Maria, D. Larson, M. E. McCarville, and S. P. McGlynn, *Acc. Chem. Res.* **3**, 368 (1970).

¹⁸R. Bonaccorsi, C. Petrongolo, E. Scrocco, and J. Tomasi, *J. Chem. Phys.* **48**, 1497 (1968).

¹⁹W. H. Fink, *J. Chem. Phys.* **54**, 2911 (1971).

²⁰L. Burnelle, A. M. May, and R. A. Gangi, *J. Chem. Phys.* **49**, 561 (1968).

²¹J. E. DelBene, *J. Chem. Phys.* **54**, 3487 (1971).

²²C. R. Brundle, D. Neumann, W. C. Price, D. Evans, A. W. Potts, and D. G. Streets, *J. Chem. Phys.* **53**, 705 (1970).

²³H. F. Schaefer, III and S. J. Rothenberg, *J. Chem. Phys.* **54**, 1473 (1971).

²⁴P. J. Hay, *J. Chem. Phys.* **58**, 4706 (1973).

²⁵G. D. Gillispie, A. U. Khan, A. C. Wahl, R. P. Hosteny, and M. Krauss, *J. Chem. Phys.* **63**, 3425 (1975).

²⁶C. F. Jackels and E. R. Davidson, *J. Chem. Phys.* **64**, 2906 (1976).

²⁷Vibrational frequencies were taken from NO_2^- (aqueous) data. R. E. Weston, Jr. and T. F. Brodasky, *J. Chem. Phys.* **27**, 683 (1957).

²⁸E. T. Arakawa and A. H. Nielsen, *J. Mol. Spectrosc.* **2**, 413 (1958).