

# Potential energy curves for NO<sup>+</sup>

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In recent years, high-resolution photoelectron spectroscopy and *ab initio* calculations have considerably revised and enlarged the understanding of the electronic structure of the NO<sup>+</sup> ion. Based on these results, new potential energy curves for the electronic states of NO<sup>+</sup> below 24 eV have been constructed and are given here. RKR potentials were calculated from new molecular constants for the eight experimentally well-defined states. For the other states, the main features of the potentials were estimated from theoretical calculations and from isoelectronic analogies. A brief review is given of the information on which each potential energy curve is based.

## I. INTRODUCTION

In 1965, Gilmore<sup>1</sup> reported his now-classic potential energy curves for the electronic states of the N<sub>2</sub>, NO, and O<sub>2</sub> molecules and their ions. The potentials for the commonly excited states were constructed from a broad and solid base of optical-spectroscopic data. As a consequence, the main features of this set of potential curves are as accurate today as they were over a decade ago, despite the enormous amount of research that has since been directed toward understanding the structure of these molecules. However, because the set of potential curves were intended to reflect the full state of the knowledge at the time, the information on which some of the curves were based was necessarily tentative and speculative, as was carefully noted by the author. It is not surprising, therefore, that some of this information has now been superseded by new, and often different, data. Although the majority of such needed revisions in this set of potential curves are minor, the notable exception is the set for NO<sup>+</sup>.

The NO<sup>+</sup> ion has only grudgingly given up information about its structure. This is in sharp contrast to the isoelectronic molecules N<sub>2</sub> and CO, whose electronic states are quite well-known. The difference arises largely because N<sub>2</sub> and CO, being stable *neutral* molecules, can be studied by absorption spectroscopy, an approach not generally available for ions. Furthermore, only one NO<sup>+</sup> emission band system is known to any extent. Thus, the only structural data available to Gilmore<sup>1</sup> were from analyses of this band system, which was of limited vibrational extent, and from two Rydberg series that were believed to converge to other NO<sup>+</sup> electronic states.

Since that time, however, the advent of high-resolution and high-sensitivity photoelectron spectroscopy has provided a new valuable tool for elucidating the electronic structure of ions. Moreover, improved *ab initio* calculations are now available to aid in the assignment of electronic state designations to the observed locations. As a result of all of this, there have been numerous changes in the understanding of the NO<sup>+</sup> electronic structure since Gilmore's<sup>1</sup> potential curves and many of these changes are large even on the eV-sized scale of these curves. We present in Fig. 1 a revised

and extended set of NO<sup>+</sup> potential energy curves that are based on the best current experimental and theoretical knowledge of the structure of this ion.

## II. METHOD

The potential curves were constructed using the method of choice for such tasks, the Rydberg-Klein-Rees procedure,<sup>2</sup> which can yield numerical potentials whose eigenvalues generally reproduce the experimental energy levels to spectroscopic accuracy. The input data to the RKR procedure are vibrational energies,  $G_v$ , and rotational constants,  $B_v$ , which are commonly expressed in terms of the vibrational and rotational Dunham coefficients,<sup>3</sup>

$$G_v = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \dots \quad (1)$$

and

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2 + \dots, \quad (2)$$

respectively. For many of the experimentally well-known electronic states, we have determined new values for these coefficients from all of the measurements that are currently available and the results are given in Table I. The values are obtained in various ways depending on the extent of the information available for each state.

For the states that have rotational analyses, these coefficients are obtained from weighted least-squares fits<sup>4</sup> of Eqs. (1) and (2) to the band origins,  $\nu_0(v', v'')$ , and the rotational constants,  $B_v$ , respectively, both accurately provided by high-resolution optical spectroscopy. For NO<sup>+</sup>, such information is available only for three electronic states, because of the dearth of emission band systems in this ion. For the remaining NO<sup>+</sup> electronic states, the vibrational coefficients  $\omega_e$  and  $\omega_e x_e$  are obtained from a weighted fit of Eq. (1) to the vibrational band structures provided by photoelectron spectroscopy and by UV-absorption Rydberg-series spectroscopy, but the rotational structure is not resolved in such studies. To determine the corresponding rotational coefficients, we use the technique employed by Field,<sup>5</sup> who, in his earlier review of the NO<sup>+</sup> states, found that the well-known coefficients  $B_e$  and  $\omega_e$  of the  $(\pi 2p)^{-1}$  states (see Table I, footnote r) in the isoelec-

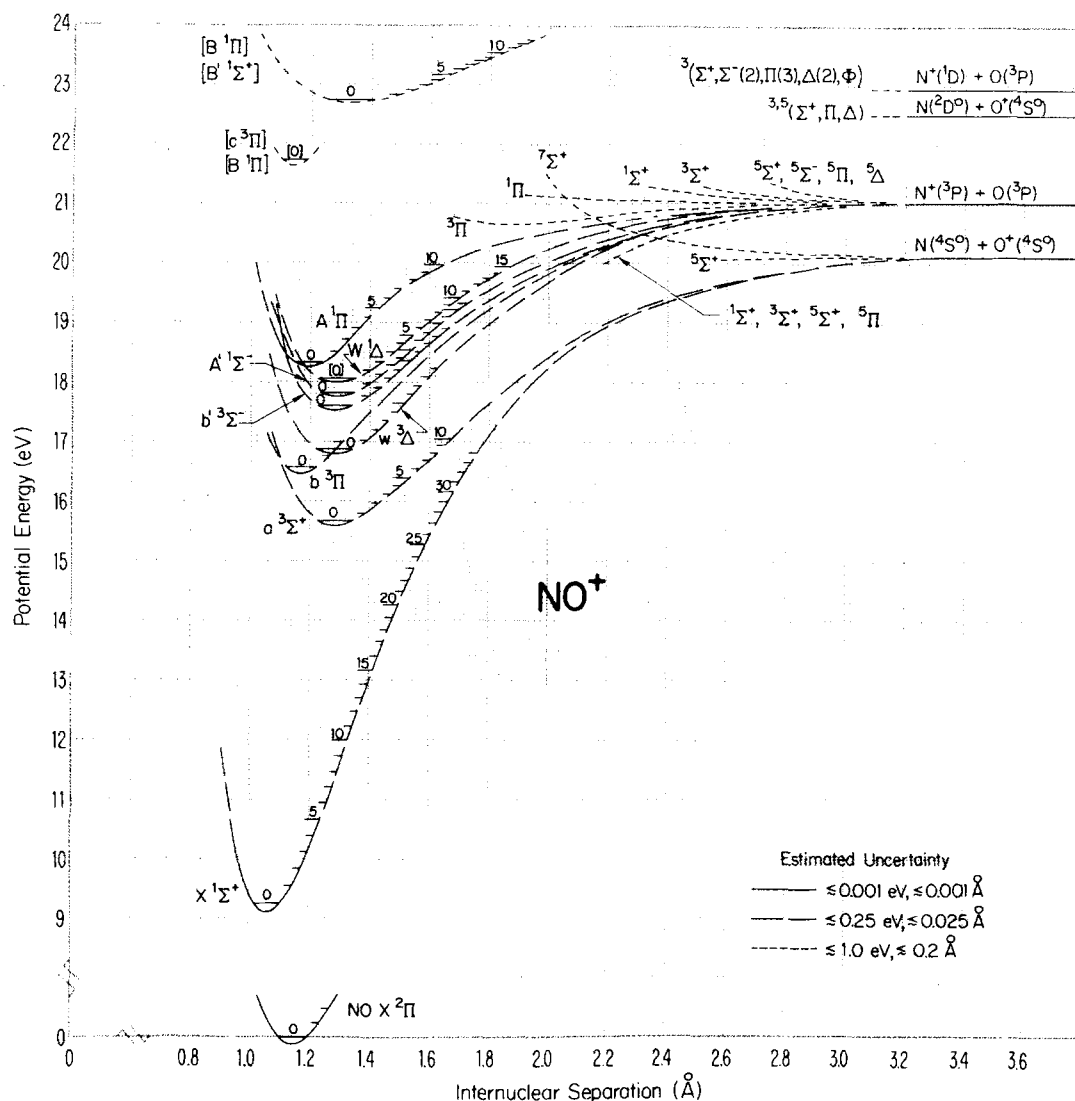


FIG. 1. NO<sup>+</sup> potential energy curves. Brackets denote uncertainty in identification.

tronic molecules N<sub>2</sub> and CO were related rather accurately by the expression<sup>8</sup>

$$B_e = 0.7459 + 4.825 \times 10^{-4} \omega_e, \quad (3)$$

where  $B_e$  and  $\omega_e$  are expressed in cm<sup>-1</sup>. The  $B_e$  values for most of the  $(\pi 2p)^{-1}$  states in NO<sup>+</sup> in Table I were interpolated from this relation. The corresponding values for  $\alpha_e$  were estimated from Pekeris expression (Ref. 3, p. 108)

$$\alpha_e = 6(\omega_e x_e B_e^3)^{1/2} / \omega_e - 6B_e^2 / \omega_e, \quad (4)$$

based on a Morse potential (Ref. 3, p. 101).<sup>8</sup> In the absence of rotational structure, the identification of the type of NO<sup>+</sup> electronic state that corresponds to the vibrational peaks observed in photoelectron spectroscopy has been an evolving process over the last decade.<sup>9</sup> The assignments in Table I are the currently accepted ones (Ref. 7, pp. 481–483), which are now well established, due largely to advances in molecular-orbital techniques.<sup>10</sup> In the state-by-state discussions below, a few details of these assignments are summarized for the states whose locations have changed considerably from those used by Gilmore.<sup>1</sup>

The RKR portions of the potentials in Fig. 1 are generally those below the uppermost indicated vibrational level. An extrapolation to the dissociation limit is made by smoothly splicing the Hulbert–Hirschfelder analytical potential (Ref. 3, p. 102) to the last several RKR potential pairs. The selection of the separated-atom limits to which the various electronic states dissociate is based on the Wigner–Witmer correlation rules (Ref. 3, p. 318), which specify the types of states that arise from various types of atomic states, and on the noncrossing rule (Ref. 3, p. 295), which assigns a state to the lowest separated-atom limit with which it can correlate. For the two lowest limits shown in Fig. 1, N(<sup>4</sup>S°)+O(<sup>4</sup>S°) and N(<sup>3</sup>P)+O(<sup>3</sup>P), all of the molecular states that can arise are given, although only small parts of some of the potential curves are shown due to lack of information. The states arising from the higher limits are only noted by type, for the same reason. Here,  $^{3,5}(\Sigma^+, \Pi, \dots)$  stands for  $^3\Sigma^+$ ,  $^5\Sigma^+$ ,  $^3\Pi$ ,  $^5\Pi$ , etc., and  $\Pi(2)$  implies two  $\Pi$  states. There are, of course, many other higher-lying separated-atom limits that are not shown, many of which are very close together. Only the limits less than 23.0 eV<sup>11</sup> are given in Fig. 1.

TABLE I. Molecular constants of the experimentally known electronic states of NO<sup>+</sup> below 24 eV.<sup>a</sup>

State	$T_{00}^b$ (NO X <sup>2</sup> Π reference)	$T_{00}^{*c}$ (NO <sup>+</sup> X <sup>1</sup> Σ <sup>+</sup> reference)	$T_e^{*d}$ (NO <sup>+</sup> X <sup>1</sup> Σ <sup>+</sup> reference)	$\omega_e$	$\omega_e x_e$	$\omega_e y_e$	$v_{\max}^e$	Degrees of freedom <sup>f</sup>
NO <sup>+</sup> { $[B^1\Pi]^g$ $[B'^1\Sigma^+]^g$	183 341(40)	108 620(40)	109 441(11)	729.56(3.80)	6.398(0.260)		13	11
{ $[c^3\Pi]^g$ $[B^1\Pi]^g$	175 260(40) <sup>h</sup>	100 539(40) <sup>h</sup>		[1900] <sup>g</sup>				
A <sup>1</sup> Π	147 804.92(0.60)	73 083.42(0.10)	73 471.83(0.08)	1601.927(0.140)	20.2075(670)	-0.268 33(880)	4 <sup>i</sup>	1
W <sup>1</sup> Δ	145 790(400) <sup>h</sup>	71 069(400) <sup>h</sup>	71 647(36) <sup>h</sup>	1217.74(10.00) <sup>h</sup>	11.587(0.690) <sup>h</sup>		9 <sup>h,i</sup>	5
A <sup>1</sup> Σ <sup>-</sup>	143 717(40)	68 996(40)	69 543.3(5.5)	1279.88(2.40)	13.206(0.210)		11	9
b <sup>1</sup> Σ <sup>-</sup>	141 952.65(40.00)	67 231.15(40.00)	67 776.52(13.00) <sup>k</sup>	1283.228(4.800) <sup>k</sup>	10.7689(0.4700) <sup>k</sup>		9	6
w <sup>3</sup> Δ	136 107.2(40.0)	61 385.7(40.0)	61 914.3(12.0) <sup>l</sup>	1316.89(5.40) <sup>l</sup>	10.834(0.600) <sup>l</sup>		9	9
b <sup>3</sup> Π	133 565(6) <sup>m</sup>	58 844(6)	59 177	1710 <sup>n</sup>	14.18 <sup>n</sup>		1 <sup>o</sup>	
a <sup>3</sup> Σ <sup>+</sup>	126 331(50)	51 609(50)	52 145.6(13.0)	1303.07(6.20)	15.158(0.590)		9 <sup>p</sup>	13
NO <sup>+</sup> X <sup>1</sup> Σ <sup>+</sup>	74 721.5(0.5) <sup>q</sup>	0	0	2376.721(0.110)	16.2553(180)	-0.015 620(920)	34	40
NO X <sup>2</sup> Π	0							

State	Configuration <sup>r</sup>	$D_0^s$	$r_e$ (Å)	$B_e$	$\alpha_e$	$\gamma_e$	$v_{\max}^c$	Degrees of freedom <sup>f</sup>
NO <sup>+</sup> { $[B^1\Pi]^g$ $[B'^1\Sigma^+]^g$	{ $(\sigma^*2s)^{-1}g$		[1.34] <sup>g</sup>	[1.27] <sup>g</sup>	[0.0165] <sup>g,t</sup>			
{ $[c^3\Pi]^g$ $[B^1\Pi]^g$	{ $(\sigma^*2s)^{-1}g$		[1.15] <sup>g</sup>					
A <sup>1</sup> Π	( $\sigma 2p$ ) <sup>-1</sup>	21 821(10)	1.193 88(37)	1.584 057(990)	0.022 194(940)	-0.000 457(180)	4	2
W <sup>1</sup> Δ	( $\pi 2p$ ) <sup>-1</sup>	23 836(400) <sup>h</sup>	1.301	1.333 <sup>u</sup>	0.0171 <sup>t</sup>			
A <sup>1</sup> Σ <sup>-</sup>	( $\pi 2p$ ) <sup>-1</sup>	25 909(50)	1.287	1.363 <sup>u</sup>	0.0184 <sup>t</sup>			
b <sup>1</sup> Σ <sup>-</sup>	( $\pi 2p$ ) <sup>-1</sup>	27 673(40)	1.2759(140)	1.386 85(3000) <sup>k</sup>	0.024 681(5500) <sup>k</sup>		9	6
w <sup>3</sup> Δ	( $\pi 2p$ ) <sup>-1</sup>	33 518(40)	1.279	1.381 <sup>u</sup>	0.0156 <sup>t</sup>			
b <sup>3</sup> Π	( $\sigma 2p$ ) <sup>-1</sup>	36 061(15)	1.1756 <sup>n</sup>	1.634 <sup>n</sup>	0.0184 <sup>n</sup>			
a <sup>3</sup> Σ <sup>+</sup>	( $\pi 2p$ ) <sup>-1</sup>	35 907(60)	1.281	1.375 <sup>n</sup>	0.0202 <sup>t</sup>			
NO <sup>+</sup> X <sup>1</sup> Σ <sup>+</sup>	( $\pi^*2p$ ) <sup>-1</sup>	87 516(10)	1.063 250(24)	1.997 194 5(890)	0.0187904 (690)		5	7
NO X <sup>2</sup> Π	0	52 400(10) <sup>v</sup>	1.150 787 70(10) <sup>w</sup>					

<sup>a</sup>All units are reciprocal centimeters, except where noted. The conversion to electron volts in Fig. 1 was made with 8065.479(21) cm<sup>-1</sup> = 1 eV (Ref. 11). Except for  $T_{00}$  and  $T_{00}^*$ , the numbers in parentheses represent the precision (one standard error) expressed in terms of the rightmost digits, e.g., 20.2075(670) = 20.2075 ± 0.0670.

<sup>b</sup> $T_{00}$  is the energy difference between the  $v=0$  level of the given state and the  $v=0$  level of the NO X<sup>2</sup>Π state (also see Ref. 12). The numbers in parentheses represent the estimated accuracy; the precision is usually much smaller.

<sup>c</sup> $T_{00}^*$  is the energy difference between the  $v=0$  level of the given state and the  $v=0$  level of the NO<sup>+</sup> X<sup>1</sup>Σ<sup>+</sup> state. The numbers in parentheses represent the estimated accuracy; the precision is usually much smaller.

<sup>d</sup> $T_e^*$  is the energy difference between the equilibrium energy corresponding to  $r_e$  and  $G(v=-\frac{1}{2})$  (Eq. 1) of the given state and that of the NO<sup>+</sup> X<sup>1</sup>Σ<sup>+</sup> state.

<sup>e</sup>Here  $v_{\max}$  is the uppermost vibrational level for which there exist reliable spectroscopic data and therefore represents the level beyond which the present coefficients will yield only an extrapolation (of unknown quality). If no level is given, the coefficients were inferred indirectly [Eqs. (3) and (4)] and their valid range is not well-defined. (See Refs. 6 and 8).

<sup>f</sup>This column lists the degrees of freedom (Ref. 4) of the least-squares fit with which the coefficients were determined. When blank, no least-squares fit was made.

<sup>g</sup>Brackets denote considerable uncertainty in identification or accuracy.

<sup>h</sup>The vibrational numbering is uncertain.

<sup>i</sup>Tanaka (Ref. 48) gives band heads of the A<sup>1</sup>Π-X<sup>1</sup>Σ<sup>+</sup> system up through  $v'=10$ .

<sup>j</sup>Edqvist *et al.* (Ref. 21) give approximate energies for  $v=10-15$ .

<sup>k</sup>See Ref. 47.

<sup>l</sup>See Ref. 46.

<sup>m</sup>Takezawa (Ref. 42). Also see Ref. 43.

<sup>n</sup>These values are those of Field (Ref. 5).

<sup>o</sup>Edqvist *et al.* (Ref. 21) gives an approximate energy for  $v=2$ .

<sup>p</sup>Edqvist *et al.* (Ref. 21) gives an approximate energy for  $v=10$ .

<sup>q</sup>Miescher (Ref. 15).

<sup>r</sup>This column denotes the orbital from which the electron is removed when NO X<sup>2</sup>Π is ionized to yield the given NO<sup>+</sup> state; e.g., ( $\pi 2p$ )<sup>-1</sup> denotes the configuration that exists after one  $\pi 2p$  electron is removed from NO. The molecular orbital configuration corresponding to the NO X<sup>2</sup>Π state is ( $\sigma 1s$ )<sup>2</sup> ( $\sigma^* 1s$ )<sup>2</sup> ( $\sigma 2s$ )<sup>2</sup> ( $\sigma^* 2s$ )<sup>2</sup> ( $\sigma 2p$ )<sup>2</sup> ( $\pi 2p$ )<sup>4</sup> ( $\pi^* 2p$ )<sup>1</sup>, where the bonding character of the last three orbitals are: ( $\sigma 2p$ ) nonbonding, ( $\pi 2p$ ) bonding, and ( $\pi^* 2p$ ) antibonding (Ref. 34). The ( $\pi^* 2p$ )<sup>-1</sup> configuration gives rise to a <sup>1</sup>Σ<sup>+</sup> NO<sup>+</sup> state, which is the ionic ground state. The six states—<sup>3</sup>Σ<sup>+</sup>, <sup>3</sup>Δ, <sup>3</sup>Σ<sup>-</sup>, <sup>1</sup>Σ<sup>-</sup>, <sup>1</sup>Δ, and <sup>1</sup>Σ<sup>+</sup>—of the ( $\pi 2p$ )<sup>-1</sup> configuration have all been identified, except for the <sup>1</sup>Σ<sup>+</sup> state. The <sup>3</sup>Π and <sup>1</sup>Π states of the ( $\sigma 2p$ )<sup>-1</sup> configuration have both been identified. However, the <sup>3</sup>Π and <sup>1</sup>Π states of the ( $\sigma^* 2s$ )<sup>-1</sup> configuration remain to be unambiguously assigned.

<sup>s</sup>The dissociation energy is referenced to the  $v=0$  level of the given state.

<sup>t</sup>These  $\alpha_e$  values were determined from Eq. (4). Also see Ref. 8.

<sup>u</sup>The  $B_e$  values were determined from Eq. (3). Also see Ref. 6.

<sup>v</sup>Dingle *et al.* (Ref. 13).

<sup>w</sup>K.-E. Hallin, J. W. C. Johns, D. W. Lepard, A. W. Mantz, D. L. Wall, and K. Narahari Rao, *J. Mol. Spectrosc.* 74, 26 (1979).

As indicated, the zero of potential energy in Fig. 1 is the zeroth vibrational level of the ground electronic state of the neutral molecule, NO  $X^2\Pi$  ( $v=0$ ).<sup>12</sup> The energies of the separated-atom limits relative to this reference are the sum of the dissociation energy of the NO  $X^2\Pi$  state<sup>13</sup> and the appropriate atomic energy levels.<sup>14</sup>

The indicated vibrational levels of the potentials in Fig. 1 are those that have been observed experimentally. The accuracies of each vary, of course, because of the different experimental techniques used. However, all of these levels have been placed to better than 0.01 eV, which is about the thickness of the line indicating the level in Fig. 1. In a few cases, the vibrational quantum numbers assigned to the levels are uncertain by a few units. Brackets are placed about these quantum numbers to denote this uncertainty.

Although related in most cases, the accuracy of the potential curve is separate from that of the experimentally placed vibrational levels and is given in the key in the lower right-hand corner of Fig. 1. The most accurate parts of the curves are denoted by a solid line, which corresponds to an RKR portion constructed from expansion coefficients. The large-dashed lines represent less-accurate Hulbert-Hirschfelder extensions. The small-dashed lines are used to denote the states for which there is little or no direct experimental information about the shape of the potential curve. The repulsive or attractive nature of these states have been estimated from theory or by isoelectronic analogy. Frequently in Fig. 1, the small-dashed line is merely a schematic representation of two or more states that are all estimated to have repulsive or attractive tendencies. Brackets about the molecular term symbol, e.g., [ $c^3\Pi$ ], denote that the identity of the state that is experimentally known to be at that location is uncertain.

All of the above accuracy indicators should, of course, influence the way in which these potential curves are used.

### III. RESULTS

#### A. NO<sup>+</sup> $1\Sigma^+$

The location of the zeroth vibrational level of the ground electronic state of NO<sup>+</sup> is established by the very accurate ionization potential obtained recently by Miescher<sup>15</sup> from a detailed optical study of Rydberg series converging to that level. The potential in Fig. 1 is based on data from various sources. The accurate RKR part is established by the high-resolution optical studies of the  $A^1\Pi-X^1\Sigma^+$  bands by Alberti and Douglas<sup>16</sup> and by Miescher,<sup>17</sup> the latter having been reanalyzed by Field.<sup>5</sup> In these investigations, rotational constants and vibrational energies were determined for the vibrational levels  $v=0-5$  of the  $X^1\Sigma^+$  state. For the higher vibrational levels, a remarkable situation occurs. In their NO photoelectron spectrum between 9 and 17 eV, Natalis *et al.*<sup>18,19</sup> found a long progression of peaks that could be assigned to the vibrational levels  $v=0-34$  of the NO<sup>+</sup>  $X^1\Sigma^+$  state. The peaks corresponding to the lower levels are the result of direct ionization, agree-

ing well with the earlier photoelectron spectra of Edqvist *et al.*<sup>20,21</sup> but the higher ones are attributed to autoionization via a superexcited NO  $^2\Sigma^+$  state. The vibrational coefficients in Table I were determined from a correlated (Ref. 4, pp. 43-48) least-squares fit to the  $\Delta G_v$  data from all of these sources.<sup>5,16,21,22</sup> The rotational coefficients were determined from the  $B_v$  values furnished by the emission studies.<sup>5,16</sup> Since these values were limited to levels less than  $v=5$ , only the lower part of the potential curve has RKR accuracy, as indicated in Fig. 1.

#### B. NO<sup>+</sup> $a^3\Sigma^+$

The potential energy of the first excited state of NO<sup>+</sup> has been somewhat controversial. Its location now at 15.7 eV is 1.5 eV higher than that believed ten years ago,<sup>1</sup> which is the largest such revision required by Fig. 1. The earlier location was based primarily on the assignment of the  $a^3\Sigma^+$  state as the upper state of the  $\alpha$  Rydberg series observed<sup>23,24</sup> converging to 14.2 eV in the UV absorption spectrum of NO. The existence of a state at this energy appeared to gain support from early photoionization<sup>25</sup> and photoelectron<sup>26,27</sup> studies. Furthermore the assignment of this limit to the  $a^3\Sigma^+$  state seemed reasonable on the basis of early *ab initio* calculations<sup>28</sup> that placed this state at 15.0 eV, which was closer to the 14.2 eV location than to any other experimental location that was clearly identified at the time. However, other contemporary photoelectron investigations<sup>29-31</sup> failed to find a state at this energy and Penning-electron<sup>32</sup> and kinetic charge-transfer<sup>33</sup> studies supported these negative results. Furthermore, it was recognized<sup>33</sup> that the NO  $a^3\Sigma^+$  state arises from the removal of an electron from a bonding orbital,<sup>34</sup>  $\pi 2p$  (see Table I). The resulting large change in  $r_e$  from that of the NO  $X^2\Pi$  state should cause the  $a^3\Sigma^+$ -state photoionization spectrum to have considerable bandlike structure, which would more resemble the broad feature observed<sup>29</sup> at 15.7 eV rather than the relatively sharp structureless feature at 14.2 eV. Huber<sup>35</sup> reappraised the evidence for the  $\alpha$  Rydberg series and concluded that the five-to-seven broad, diffuse, and irregular bands were not, in fact, a Rydberg series at all.<sup>36</sup> The matter was settled by the high-resolution and high-sensitivity photoelectron spectroscopy of Edqvist *et al.*<sup>20,21</sup> who demonstrated that *no* NO<sup>+</sup> state exists at 14.2 eV and whose data established the present understanding of all of the excited NO<sup>+</sup> states below 18 eV.<sup>37</sup> These data have been confirmed by later high-resolution photoelectron studies.<sup>18,38</sup> The vibrational coefficients for the  $a^3\Sigma^+$  state are based on the photoelectron data of Edqvist *et al.*<sup>21</sup> ( $v=1-8$ ) and Natalis<sup>22</sup> ( $v=0-9$ ) and the rotational coefficients follow from Eqs. (3) and (4).

#### C. NO<sup>+</sup> $b^3\Pi$

The  $\beta$  Rydberg series<sup>23,24</sup> had long established the existence of an NO<sup>+</sup> state at 16.6 eV. Moreover, a sharp feature appeared at this energy in the early photoelectron spectra<sup>26,27,29,31</sup> of NO. However, this location has seen assignments of  $^3\Pi$ ,<sup>35</sup>  $^3\Sigma^-$ ,<sup>26,27</sup> and  $^3\Delta$  states.<sup>1</sup> The difficulty in this assignment was due to several

complications, but most notably to (a) the above-mentioned misassignment of the  $a^3\Sigma^+$  state to 14.2 eV, (b) the appearance of a statelike feature at 15.7 eV in the early photoelectron spectra,<sup>26,27,29,30</sup> and (c) the initial theoretical estimates<sup>28</sup> that the ordering of the NO<sup>+</sup> excited states with increasing energy was  $^3\Sigma^+$ ,  $^3\Delta$ , and  $^3\Pi$ . Now, high-resolution photoelectron spectroscopy<sup>20,21</sup> has shown that a state does *not* exist at 14.2 eV and more recent theoretical calculations<sup>10,39,40</sup> predict an ordering of  $^3\Sigma^+$ ,  $^3\Pi$ , and  $^3\Delta$ . Furthermore, the modest vibrational development observed<sup>20,21</sup> is consistent with the removal of the nonbonding electron  $\sigma 2p$  that leads to the  $^3\Pi$  state, rather than the bonding  $\pi 2p$  electron, since this implies little change in  $r_e$  and hence a concentration of intensity in the first few peaks. Therefore, the two lowest-energy observed features have been assigned to the  $a^3\Sigma^+$  state at 15.7 eV, as described above, and to the  $b^3\Pi$  state at 16.5 eV.

Photoelectron spectroscopy<sup>21</sup> furnishes the energies of only the  $v=0, 1,$  and  $2$  vibrational levels and the peak associated with  $v=2$  is too weak to be usable. Field<sup>5</sup> based his  $\omega_e$  value on the values for  $\Delta G_{1/2}$  from the photoelectron data<sup>21</sup> and from beam emission data<sup>41</sup> for two weak  $b^3\Pi-X^1\Sigma^+$  bands and on the average of the  $\omega_e x_e$  values of the analogous states of N<sub>2</sub> and CO. The rotational coefficient  $B_e$  was estimated by interpolation of the ratios  $r_e(^1\Pi)/r_e(^3\Pi)$  for CO and N<sub>2</sub> and the value for  $\alpha_e$  obtained from an isoelectronic average. These values cannot be improved upon at the present and are used here in Table I. However, Takezawa,<sup>42</sup> in his recent extension of the  $\beta$  Rydberg series, has provided a considerably improved value of  $T_{00}$  for the NO<sup>+</sup>  $b^3\Pi$  state.<sup>43</sup>

#### D. NO<sup>+</sup> $w^3\Delta$

In contrast to the states discussed above, no state had been suspected at the energy where the  $w^3\Delta$  state is now known to occur.<sup>44</sup> Edqvist *et al.*<sup>20,21</sup> resolved the complex features of the photoelectron spectrum between 16.5 and 18.5 eV and reported energies for the  $v=0-9$  levels of the  $w^3\Delta$  state. The vibrational coefficients in Table I are based on a correlated (Ref. 4, pp. 43-48) least-squares fit to these  $\Delta G_{v+1/2}$  values and the limits of the Rydberg series that Takezawa<sup>42</sup> found converging to the  $v=3$  and  $4$  levels of this state.<sup>46</sup> The rotational coefficients follow from Eqs. (3) and (4).

#### E. NO<sup>+</sup> $b'^3\Sigma^-$

Like the  $w^3\Delta$  state, the  $b'^3\Sigma^-$  state was first located by photoelectron spectroscopy.<sup>20,21</sup> The observed progression for  $v=0-9$  was strongly overlapped by other peaks (see Fig. 1 of Ref. 20), hence the vibrational energies are relatively uncertain. In contrast, some of the rotational constants are known relatively well. This fortuitous circumstance arises because of a near resonance between some of the  $b'^3\Sigma^-$  ( $v=5, 9$ ) and  $A^1\Pi$  ( $v=0, 3$ ) rotational levels, thereby producing perturbations in the lines of the  $A^1\Pi-X^1\Sigma^+$  bands, which have been examined in high resolution.<sup>16,17</sup> Field's<sup>5</sup> analysis of the  $b'(v=5)-A(v=0)$  perturbations gave values for the rotational constant  $B_e$  of the  $b'^3\Sigma^-$  state and

the energy separation of the  $v=0$  and  $v=5$  levels of the  $A^1\Pi$  and  $b'^3\Sigma^-$  states, respectively. The later analysis by Alberti and Douglas<sup>16</sup> of the  $b'(v=9)-A(v=3)$  perturbation gave a value for the energy of the  $J=22$  level of the  $F_2$  component of the  $b'^3\Sigma^-$  state. The vibrational and rotational constants in Table I were determined from a simultaneous correlated (Ref. 4, pp. 43-48) fit to the photoelectron  $\Delta G_{v+1/2}$  data and the energies and rotational constants from the emission and perturbation studies.<sup>47</sup> As indicated in Fig. 1, only the potential in the vicinity of  $v=5$ , where the rotational constants are well-defined, have RKR accuracy.

#### F. NO<sup>+</sup> $A'^1\Sigma^-$

Edqvist *et al.*<sup>20,21</sup> resolved the levels  $v=0-11$  in their photoelectron spectra of the  $A'^1\Sigma^-$  state. The vibrational coefficients in Table I are from a fit to these data,<sup>21</sup> the rotational coefficients following from Eqs. (3) and (4). It is interesting to note that simple molecular orbital arguments<sup>10</sup> predict that the  $A'^1\Sigma^-$  and the  $b'^3\Sigma^-$  states should have the same energy. Indeed, as shown in Table I, experiment has found that the zeroth vibrational level of these two states lie within 1800 cm<sup>-1</sup> of each other.

#### G. NO<sup>+</sup> $W^1\Delta$

The  $W^1\Delta$  state forms a long progression in the NO photoelectron spectrum<sup>20,21</sup> between 18.4 and 19.5 eV. However, the first bands are strongly overlapped; hence, the vibrational numbering is still uncertain. The vibrational assignment is supported somewhat by Field's<sup>5</sup> favorable comparison of Franck-Condon factors to the photoelectron peak heights,<sup>20,21</sup> which suggests that the assignment is unlikely to be in error by more  $\pm 1$  unit. The vibrational and rotational coefficients in Table I are from a weighted fit to these data<sup>21</sup> and Eqs. (3) and (4), respectively. In Fig. 1, the zeroth vibrational level designation is given in brackets to warn that the vibrational numbering of the  $W^1\Delta$  state is uncertain.

#### H. NO<sup>+</sup> $A^1\Pi$

The existence of an NO<sup>+</sup> electronic state at 18.3 eV has been long known from Tanaka's<sup>23</sup> far-UV  $\gamma$  Rydberg series. Later, this state could be assigned as a  $^1\Pi$  when it was recognized<sup>48,49</sup> that the band system discovered by Baer and Miescher<sup>50</sup> was an NO<sup>+</sup>  $^1\Pi-X^1\Sigma^+$  transition. Miescher's<sup>17</sup> high-resolution study of the rotational structure of these bands showed that the  $r_e$  of the  $A^1\Pi$  states was equal to that of the NOX<sup>2</sup> $\Pi$  state; thus, it has been well-established that this state is the  $^1\Pi$  state of the  $(\sigma 2p)^{-1}$  configuration (see Table I). For many years,<sup>1,5</sup> this high-resolution study provided the only detailed  $A^1\Pi$ -state information, which was limited to the vibrational levels  $v=0$  and  $1$ . Recently, however, Alberti and Douglas<sup>16</sup> extended this system through  $v=4$ . The vibrational and rotational coefficients in Table I are based on a fit to these data. Tanaka<sup>48</sup> has extended the band heads of the  $A^1\Pi-X^1\Sigma^+$  system in low resolution up through  $v=10$ . The location of the higher vibrational levels of the  $A^1\Pi$  potential in Fig. 1 are based on these band heads ( $\pm 0.01$  eV), but, as indicated, the

internuclear separation at which these levels occur are more uncertain than those corresponding to the lower levels because of the lack of rotational constants.

### I. NO<sup>+</sup> 5Σ<sup>+</sup>

Only indirect evidence is available for the NO<sup>+</sup> 5Σ<sup>+</sup> state. For the isoelectronic molecule N<sub>2</sub>, Carroll<sup>51</sup> has estimated a slightly bound (0.14 eV) potential based on its role in the predissociation of the *a* 1Π<sub>g</sub> and *B* 3Π<sub>g</sub> states and in the recombination of N(<sup>4</sup>S) atoms. Gilmore<sup>1</sup> used these results to construct his N<sub>2</sub> 5Σ<sub>g</sub><sup>+</sup> potential curve, but added a small (0.05 eV) maximum. Michels<sup>52</sup> found only a repulsive curve in his full CI calculations, but recently Krauss and Newmann<sup>53</sup> reported MC-SCF calculations of the N<sub>2</sub> 5Σ<sub>g</sub><sup>+</sup> potential that was slightly bound (0.10 eV) and had a small maximum (0.11 eV). Some information about this NO<sup>+</sup> state can be gleaned from the data of Govers and Schopman,<sup>54</sup> who have observed O<sup>+</sup> fragments from the N(<sup>4</sup>S<sup>o</sup>) + O(<sup>4</sup>S<sup>o</sup>) dissociation limits with kinetic energies as low as 0.037 ± 0.003 eV that presumably arise from a predissociation of high-lying vibrational levels (*v* ≈ 26) of the *w*<sup>3</sup>Δ state by the 5Σ<sup>+</sup> state. These data suggest a rather flat 5Σ<sup>+</sup> potential curve with essentially no maximum. This is consistent with the expectation that the ion-induced dipole attraction present in NO<sup>+</sup> would defeat the tendency to form a small barrier that occurs in N<sub>2</sub>. The short, weakly attractive portion of the 5Σ<sup>+</sup>-state potential in Fig. 1 is based on these considerations, but, as the small-dashed construction warns, the shape is quite uncertain. (See note added in proof.)

### J. NO<sup>+</sup> 7Σ<sup>+</sup>

Gilmore<sup>1</sup> based his repulsive NO<sup>+</sup> 7Σ<sup>+</sup> potential curve on the N<sub>2</sub> 7Σ<sup>+</sup> curve, which had been determined from early valence-bond calculations. The NO<sup>+</sup> 7Σ<sup>+</sup> potential in Fig. 1 is also taken from N<sub>2</sub> *ab initio* calculations, namely, those of Michels,<sup>52</sup> who also finds a strongly repulsive curve.

### K. NO<sup>+</sup>[*c* 3Π] and/or [*B* 1Π]

In comparison with the bound states discussed above, the knowledge of the NO<sup>+</sup> states above 20 eV is very poor. There is, however, ample experimental evidence that NO<sup>+</sup> states do occur in the 20–23 eV range, but their assignments are quite uncertain. Early photoelectron studies<sup>30,31,55</sup> revealed an NO<sup>+</sup> ionization potential at 21.7 eV, in the vicinity of where the 3Π and 1Π states of the (σ\*2s)<sup>-1</sup> configuration were expected (Table I). Furthermore, photoionization studies<sup>30,56–58</sup> have shown the existence of a predissociating state near this energy.

The high-resolution photoelectron spectrum of Edqvist *et al.*<sup>20,21</sup> shows a sharp intense feature beginning at 21.722 eV and with a short unresolved tail toward higher energies, which could possibly be deconvoluted into two sets of rather irregularly spaced peaks with different intensity patterns. This possibly two-component feature was assigned to the NO *c* 3Π and *B* 1Π states of the (σ\*2s)<sup>-1</sup> configuration, which were assumed to lie very close together. However, Lefebvre-Brion<sup>59</sup> has

considered the effects of the mixing of electron configurations on these states and finds that the *B* 1Π state is considerably more influenced by mixing than the *c* 3Π state, which should considerably broaden the former relative to the latter. The calculated 1Π, 3Π splittings (1Π–3Π ≈ 1.9 eV), intensity ratios (3Π/1Π ≈ 4.4), and relative shapes suggested the assignment of the feature at 21.7 eV to only the *c* 3Π state and the assignment of a weaker and broader feature seen by Edqvist *et al.*<sup>20,21</sup> at higher energy (discussed below) to the *B* 1Π state.

In the extreme ultraviolet, Narayama and Price<sup>60</sup> found Rydberg series<sup>61</sup> converging to the 21.7 eV limit. No evidence was found that indicated two closely spaced limits and, on the basis of Lefebvre-Brion's<sup>59</sup> calculations and other considerations, it was concluded that only the *c* 3Π state occurred at this limit. By analogy with N<sub>2</sub> and O<sub>2</sub>, the *c* 3Π state potential was estimated to have an equilibrium structure similar to that of the NO *X* 2Π state, but with the high levels (i.e., the "tail" found by Edqvist *et al.*<sup>20,21</sup>) perhaps perturbed by another state.<sup>62</sup> This *r<sub>e</sub>* estimate is close to those made by Lefebvre-Brion<sup>59</sup> and Edqvist *et al.*<sup>20</sup> Sasanuma *et al.*<sup>63</sup> have recently examined the same Rydberg series. With regard to the question of whether one or two electronic states exist at the convergence limit, they concluded that either the energy levels of the *c* 3Π and *B* 1Π states were coincident within 0.02 eV or the Rydberg series converging to the *B* 1Π states are considerably weaker.

The CI calculations of Thulstrup *et al.*<sup>39,40</sup> are suggestive, but are not of sufficient accuracy at these energies to resolve the question of the identity of the feature at 21.7 eV. Three 3Π and perhaps one 1Π bound states are found in the 20–23 eV region. The lowest 3Π, an indication of which is given in Fig. 1, is found to have two minima (not shown), the smaller-*r<sub>e</sub>* minimum lying at higher energies. If this second minimum is indeed the *c* 3Π state, Thulstrup *et al.*<sup>40</sup> point out that one could perhaps think of the double minima as being responsible for the observed irregularities in the 21.7 eV feature.

In view of the above uncertainties, the potential curve of the [*c* 3Π] and/or [*B* 1Π] state(s) is placed at *r<sub>e</sub>* ≈ *r<sub>e</sub>*(NO *X* 2Π) and with *v* = 0[?] at 21.72 eV, which are the only features that seem very weakly established at the present.

### L. NO<sup>+</sup>[*B* 1Π] or [*B*' 1Σ<sup>+</sup>]

Although not as well-documented as the above-mentioned feature at 21.7 eV, the existence of an NO<sup>+</sup> state near 23 eV has been known for some while from photoelectron spectroscopy,<sup>30,55</sup> photodissociative ionization,<sup>64</sup> and collision-induced spectroscopy,<sup>57</sup> but its assignment has been even more uncertain. The photoelectron spectrum of Edqvist *et al.*<sup>20,21</sup> shows 14 well-resolved peaks beginning at 22.7 eV. The energies of the rather closely spaced peaks yield the relatively small *ω<sub>e</sub>* and *ω<sub>e</sub>x<sub>e</sub>* values listed in Table I, which imply a broad shallow potential curve. These investigators considered that this state was analogous to the *b*' 1Σ<sup>+</sup> state of N<sub>2</sub>, which has the same characteristics, and assigned the feature at 22.7 eV to the *B*' 1Σ<sup>+</sup> state of NO<sup>+</sup>. However,

for the reasons given above, Lefebvre-Brion<sup>59</sup> suggests that this feature may be the  $B^1\Pi$  state of the  $(\sigma^*2s)^{-1}$  configuration, having been modified by strong configuration interaction such that the  $r_e$  value was much larger than its companion  $c^3\Pi$  state. The calculations of Thulstrup *et al.*<sup>39,40</sup> cannot be used to resolve this question.

The NO<sup>+</sup> [ $B^1\Pi$ ] or [ $B'^1\Sigma^+$ ] potential in Fig. 1 is based on the photoelectron  $\omega_e$  and  $\omega_e x_e$  values and an  $r_e$  value that is midway between that calculated by Lefebvre-Brion,<sup>59</sup> 1.23 Å, and that suggested by Edqvist *et al.*,<sup>20</sup> 1.44 Å, from the  $N_2b'^1\Sigma_u^+$  state. This midway value is close to that proposed by Natalis *et al.*,<sup>19</sup> 1.385 Å, on the basis of their study of the preionizing  $2^2\Sigma^+$  state, which they consider as a member of the Rydberg series converging to the feature at 23 eV (interpreted as the  $B'^1\Sigma^+$  state). The  $\alpha_e$  value in Table I was estimated from Eq. (4). In spite of the well-resolved and extensive vibrational development, the shape of this potential is still uncertain, as the short-dashed lines indicate, and the identity of the state is quite uncertain.

#### M. Other NO<sup>+</sup> bound states

No indications of other NO<sup>+</sup> states above the 22.7 eV feature have been observed experimentally until energies greater than 28 eV are reached.<sup>30,55,64,65</sup> However, there are some *predicted* bound states that are relevant to Fig. 1. For the  $N^*(^3P)+O(^3P)$  limit, the CI calculations of Thulstrup *et al.*<sup>39,40</sup> suggest that the  $1^1\Sigma^+$  and  $3^1\Sigma^+$  states are bound, as indicated in Fig. 1, with minima at 18.7 eV, 1.56 Å and 20.3 eV, 1.70 Å, respectively (not shown). Grouped schematically with these two states in Fig. 1 are  $5^1\Sigma^+$  and  $5^1\Pi$  states that the CI calculations of O'Neil and Schaefer<sup>66</sup> for CO suggest, by isoelectronic analogy, are also bound for NO<sup>+</sup>. (Thulstrup and co-workers did not report on quintet states.) The  $3^1\Pi$  and  $1^1\Pi$  states shown in part in Fig. 1 are estimated by Thulstrup *et al.*<sup>39,40</sup> to have double minima. The  $3^1\Pi$  state was discussed above in connection with the 21.7 eV feature and these investigators speculate that the  $1^1\Pi$  state may be associated with the 22.7 eV feature in the same fashion, although the shapes of the estimated potentials in Fig. 1 make this seem somewhat unlikely. O'Neil and Schaefer's<sup>66</sup> CO calculations also give these  $3^1\Pi$  and  $1^1\Pi$  states as bound. The  $1^1\Sigma^+$  state shown nearby in Fig. 1 was reported to be bound by Thulstrup *et al.*<sup>39,40</sup> and purely repulsive by O'Neil and Schaefer<sup>66</sup> for CO. As Thulstrup and co-workers emphasize, it is not clear how reliable their NO<sup>+</sup> predictions are at energies above 20 eV and, correspondingly, it is not clear how far one can stretch isoelectronic analogies.

Thulstrup *et al.*<sup>39,40</sup> predict the locations of a few other triplet bound states below 20 eV, but ones that do not dissociate to the  $N^*(^3P)+O(^3P)$  limit. (None of these are shown in Fig. 1). The lowest lying of these is a  $3^1\Delta$  state with a minimum at 19.0 eV, 1.63 Å.

#### N. Other NO<sup>+</sup> repulsive states

By analogy to O'Neil and Schaefer's<sup>66</sup> calculations for CO, the  $3^1\Sigma^+$ ,  $5^1\Sigma^+$ ,  $5^1\Pi$ , and  $5^1\Delta$  states arising from the  $N^*(^3P)+O(^3P)$  limit are indicated as repulsive. Thul-

strup *et al.*<sup>39,40</sup> did not report on any purely repulsive states.

#### IV SUMMARY

Because of a wealth of new information, the understanding of the electronic structure of NO<sup>+</sup> has changed considerably from that summarized by Gilmore<sup>1</sup> in 1965. The indicated energy levels and potential curves of the eight NO<sup>+</sup> electronic states below 20 eV in Fig. 1 are now well-characterized on the scale of this figure. The location of these states agrees with that expected from theory and corresponds state by state with those of the well-known isoelectronic molecules N<sub>2</sub> and CO, as well as other ten-valence-electron diatomic molecules.<sup>67,68</sup>

Two bound NO<sup>+</sup> electronic states are known experimentally to lie in the range 20–24 eV, but they have not yet been unequivocally identified as to electronic type. The bound or repulsive tendencies of the other electronic states that arise from the lowest two separated-atom limits can be estimated from *ab initio* calculations for NO<sup>+</sup> or by isoelectronic analogies with N<sub>2</sub> and CO.

A full-sized print of Fig. 1 and corresponding Franck-Condon factors for the ionizing and NO<sup>+</sup> dipole-allowed transitions are available by request from D. L. A.

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*Note added in proof:* For the  $5^1\Sigma^+$  state dissociating to the  $N(^4S^o)+O(^4S^o)$  limit, the recent calculations of Michels<sup>69</sup> yield a bound potential with a minimum at 18.2 eV and 1.63 Å. This study also found the  $1^1\Sigma^+$ ,  $5^1\Sigma^+$ , and  $5^1\Pi$  states of the next higher limit to be significantly bound (~1 eV), as indicated in Fig. 1.

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- ( $\pi 2p$ )<sup>-1</sup> states of N<sub>2</sub> and CO compiled by Huber and Herzberg (Ref. 7). They differ only slightly from the coefficients given by Field. The precision of a predicted  $B_e$  value corresponding to an  $\omega_e$  of 1290 cm<sup>-1</sup>, which is typical for NO<sup>+</sup> ( $\pi 2p$ )<sup>-1</sup> states, is  $\pm 0.0014$  cm<sup>-1</sup> (one standard error). The accuracy is difficult to assess, but a comparison of the  $B_e$  value for the NO<sup>+</sup>  $b' \ ^3\Sigma^-$  state determined with Eq. (3) to that in Table I, which was determined in a different way, suggests that the accuracy could be about 0.02 cm<sup>-1</sup>.
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- <sup>43</sup>Takezawa (Ref. 42) considers that this  $T_{00}$  value refers to the lowest multiplet component ( $\Omega=0$ ) of the  $b \ ^3\Pi$  state; this is based on the assumption that the magnitude of the spin-orbit splitting constant of this state is similar to that of the corresponding states of N<sub>2</sub> and CO, i. e.,  $A \approx 40$  cm<sup>-1</sup>. However, Lefebvre-Brion's SCF calculation (private communication, 1978) yields a value  $A(\text{NO}^+ \ b \ ^3\Pi) = 72$  cm<sup>-1</sup>, which implies that the  $T_{00}$  value refers to either the  $\Omega=0$  or  $\Omega=1$  component.
- <sup>44</sup>Gilmore (Ref. 1) did assign a state at 17.0 eV, but this was based on a reported (Ref. 45) NO<sup>+</sup> band at 4380 Å that was identified as a  $^3\Pi - a \ ^3\Sigma^+$  transition and the location of the  $a \ ^3\Sigma^+$  at 14.22 eV, the latter of which has been revised.
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- <sup>47</sup>As above (Ref. 46), the standard errors alone of the  $T_e, \omega_e, \omega_e x_e, B_e,$  and  $\alpha_e$  values of the NO<sup>+</sup>  $b' \ ^3\Sigma^-$  state in Table I cannot directly show the precision gained from the perturbation analyses. The standard errors on the  $T_v$  and  $B_v$  values predicted from the coefficients in Table I are 7, 2, 0.03, 4, and 11 cm<sup>-1</sup> and 0.02, 0.01, 0.001, 0.01, and 0.02 cm<sup>-1</sup>, respectively, for  $v=1, 3, 5, 7,$  and 9. A further perturbation analysis (Ref. 5) of the existing emission data (Ref. 16) could yield further improvements in the coefficients for the NO<sup>+</sup>  $b' \ ^3\Sigma^-$  state.
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