

## The Heat of Dissociation of Nitric Oxide

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Citation: [The Journal of Chemical Physics](#) **16**, 604 (1948); doi: 10.1063/1.1746954

View online: <http://dx.doi.org/10.1063/1.1746954>

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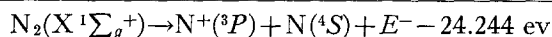
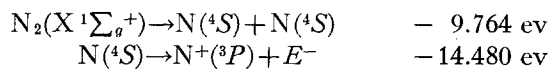
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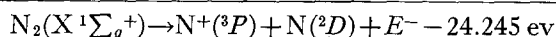
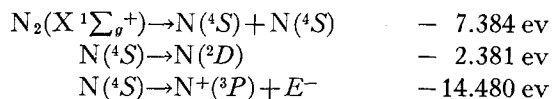
$\bar{D}(\text{OH in H}_2\text{O})$  and  $\bar{D}(\text{HF in HF})$ . As seen in Fig. 2b, the value  $\bar{D}(\text{NH in NH}_3)=4.02$  ev fits into this series. The needed information is collected in Table II. The heat of formation from atoms ( $Q_a$ ) divided by the number of bonds gives the average bond energy ( $\bar{D}$ ).

The lower value of 3.63 ev of  $\bar{D}(\text{NH in NH}_3)$  based on  $D(\text{N}_2)=7.38$  ev is less than  $D(\text{NH, radical}) (=3.74$  ev), whereas the corresponding distances are  $R(\text{NH in NH}_3)=1.014\text{\AA}$  and  $R(\text{NH, radical})=1.038\text{\AA}$ . The higher value of 4.02 ev for  $\bar{D}(\text{NH in NH}_3)$  is therefore more acceptable.

With the higher value of  $D(\text{N}_2)=9.764$  ev, the appearance potential of  $\text{N}^+$  ions<sup>4</sup> will then refer to the reaction



rather than to



The only difference is the state of the nitrogen atom, which cannot be detected in a mass spec-

trograph. Hence no conflict is apparent with these impact experiments. The effect on the heat of dissociation of NO will be discussed at a later date.

The values for the carbon-hydrogen bond energies have been taken from a study<sup>26</sup> which indicates that the high value of the heat of sublimation of carbon ( $L(\text{C})=7.334$  ev) is not acceptable, since the CH bond energy for the free radical would have to be 4.08 ev rather than the spectroscopic value of 3.47 ev (Table I). It is seen that this high value does not fit at all into the sequence of Fig. 2a nor does the average bond energy  $\bar{D}(\text{CH in CH}_4)$  as shown in Fig. 2b.

Wahrhaftig<sup>27</sup> determined that the heat of dissociation of  $\text{F}_2$  should be somewhat less than the usually accepted value (2.8 ev). It has no great influence on the interpolation made here (Fig. 2). The constants of Eqs. (1) and (2) are slightly changed for a smaller value of  $D(\text{F}_2)$ , but the empirical value of  $D(\text{NH})=3.74$  ev is not affected.

The comparison made here favors the higher value of the heat of dissociation of nitrogen ( $D(\text{N}_2)=9.764$  ev) and either of the lower values of the heat of sublimation of carbon ( $L(\text{C})=5.424$  or  $5.888$  ev).

<sup>26</sup> Unpublished results.

<sup>27</sup> A. L. Wahrhaftig, J. Chem. Phys. **10**, 248 (1942).

## The Heat of Dissociation of Nitric Oxide

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(Received February 16, 1948)

The heat of dissociation of nitric oxide ( $D(\text{NO})$ ) is considered to be 6.49 ev on the basis of a comparison of the series CO, NO,  $\text{O}_2$ , OF, its band spectrum, and its photo-chemical dissociation. Appearance potentials of  $\text{N}^+$ ,  $\text{O}^+$ , and  $\text{O}^-$  can be interpreted on this basis.

IF the heat of dissociation of nitrogen is 7.384 ev,<sup>1</sup> then the heat of dissociation of nitric oxide must be 5.30 ev since the heat of dissociation of oxygen is known to be 5.082 ev. However,

<sup>1</sup> G. Herzberg, *Molecular Spectra and Molecular Structure I. Diatomic Molecules* (Prentice-Hall, Inc., New York, 1939).

Gaydon<sup>2</sup> discussed the possibility that the higher value of 9.764 ev for the heat of dissociation of  $\text{N}_2$  is more acceptable. The following considerations lend support to this view.

<sup>2</sup> A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (John Wiley and Sons, Inc., New York, 1947).

## SERIES COMPARISON

If the heats of dissociation of the oxides of the first row elements C, N, O, F are compared (Fig. 1 and Table I), it is seen that the relation between dissociation energy ( $D$ ) and internuclear distance ( $R$ ) shows the same trend as does the similar relation between force constant ( $k$ ) and internuclear distance. Such comparisons have been made by other writers,<sup>3</sup> and they appear to have validity if the series of structures to be studied is chosen properly. In the present case the four elements belong to the first group of the periodic table, and their oxides are all diatomic molecules, with the exception of the OF radical, where the necessary information was obtained from fluorine monoxide, to be discussed below. The relation between force constants and internuclear distances follows the rule that a large force constant goes with a relatively small internuclear distance, even though the electron structures are disposed in a variety of ways.

Since the heat of dissociation of carbon monoxide is still in question,<sup>2,4</sup> two values have been included in Table I. However, the main point of the present argument is not affected. It is seen from Fig. 1 that *the lower value of 5.30 ev of the heat of dissociation of NO does not fit into this series*. If the attempt is made to include it, then a curve is obtained which is quite different

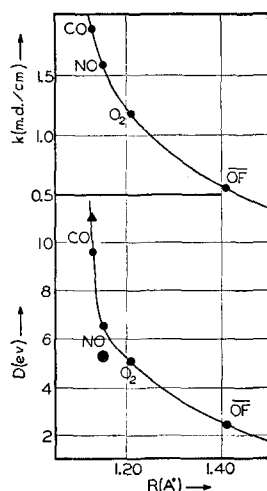


FIG. 1. Force constants and dissociation energies of CO, NO, O<sub>2</sub>, and OF.

<sup>3</sup> For literature references see G. Glockler, J. Chem. Phys. 16, 602 (1948).

<sup>4</sup> H. D. Hagstrum, Phys. Rev. 72, 947 (1947).

TABLE I. Force constants ( $k$ ), dissociation energies ( $D$ ), and internuclear distances ( $R$ ) (reference 1, Table 36).

		$k$ (m.d./cm)	$R$ Å	$D$ (ev)			
				a	b	c	d
N <sub>2</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	2.286	1.095	7.384	7.384	9.764	9.764
CO	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	1.89	1.1284	11.054	9.608	11.054	9.608
NO	<sup>2</sup> Π <sub>g</sub> <sup>-</sup>	1.59	1.150	5.30	5.30	6.49	6.49
O <sub>2</sub>	<sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	1.18	1.2076	5.082	5.082	5.082	5.082
OF	(OF <sub>2</sub> )	0.56	1.41 ± .05	2.45	2.45	2.45	2.45*

a  $D$ (N<sub>2</sub>) = 7.384 ev;  $L$ (C) = 7.334 ev.

b  $D$ (N<sub>2</sub>) = 7.384 ev;  $L$ (C) = 5.888 ev.

c  $D$ (N<sub>2</sub>) = 9.764 ev;  $L$ (C) = 7.334 ev.

d  $D$ (N<sub>2</sub>) = 9.764 ev;  $L$ (C) = 5.888 ev.

\* See text.

from the corresponding  $k$ — $R$  curve. This finding is used for the assertion that the higher figure of  $D$ (NO) (=6.49 ev) is the correct value. The heat of dissociation of the OF radical was estimated to be 2.45 ev from the compound OF<sub>2</sub>, using the heat of formation ( $Q_f$ ) given by Bichowsky and Rossini.<sup>5</sup> The heat of dissociation of F<sub>2</sub> was taken as 2.6 ev.<sup>6</sup> Had the higher current value (2.8 ev)<sup>1</sup> been employed, then the average bond energy ( $\bar{D}$ (OF)) would have been 2.55 ev with no effect on the trend of the curve in the important region. The breaking of the first OF bond in OF<sub>2</sub> may, however, be quite different from the bond energy of the remaining OF radical. A study of similar cases (water, ozone) indicates that  $D$ (OF) would hardly be greater than about 3.5 ev and that  $R$ (OF) would not differ very much from  $R$ (OF in O<sub>2</sub>F). In order

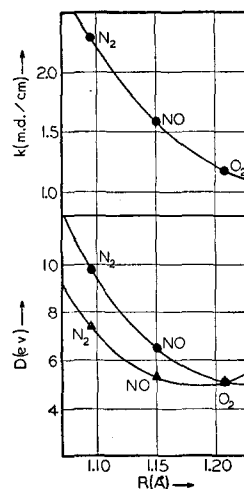


FIG. 2. Force constants and dissociation energies of N<sub>2</sub>, NO, and O<sub>2</sub>.

<sup>5</sup> F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of the Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

<sup>6</sup> A. L. Wahrhaftig, J. Chem. Phys. 10, 248 (1942).



sociation have been in question for so many years,<sup>2</sup> it seems appropriate to discuss any and all lines of argument which might help in settling the values of these important constants. It is believed that these *series comparisons* can be used as additional lines of argument to assist in determining magnitudes of force constants, internuclear distances, or bond energies.

### BAND SPECTRUM

The higher value of  $D(\text{NO})$  must fit into the energy level scheme of the molecule. In this connection it is of interest to point out that Herzberg and Mundie<sup>9</sup> make the suggestion that the  $\epsilon$ -bands of NO are really a continuation of the  $\gamma$ -bands, as can be seen from their table of intervals. They base their remarks on the absorption spectra of Leifson<sup>10</sup> and derive a pre-dissociation limit between 51088 and 53271  $\text{cm}^{-1}$  (6.33 and 6.60 eV). Hence  $D(\text{NO})$  must be equal to or less than these values. There is quite a remarkable change in intensity of these bands at  $v'=4$ . It may be supposed that some of the so-called  $\gamma$ -bands ( $v'=4$  to 7) are stronger than expected because some of them overlap certain  $\beta$ -bands, enhancing their appearance on the photographic plate. The band at 1877.2 Å (53271  $\text{cm}^{-1}$ ) could be  $\gamma(4',0'')$  (53375  $\text{cm}^{-1}$ ) and  $\beta(8',0'')$  (53254  $\text{cm}^{-1}$ ) and  $\beta(10',1'')$  (53216

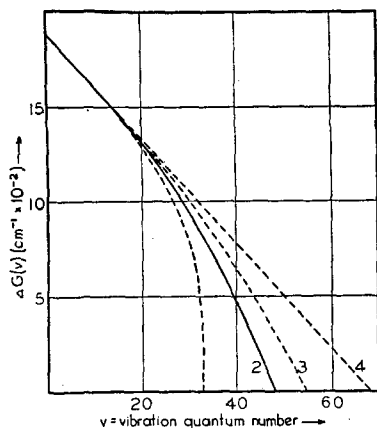


FIG. 4. Heat of dissociation of NO. 1.  $D(\text{NO})=5.30$  eV based on  $D(\text{N}_2)=7.384$  eV. 2.  $D(\text{NO})=6.49$  eV based on  $D(\text{N}_2)=9.764$  eV. 3.  $D(\text{NO})=7.02$  eV after Jenkins, Barton, and Mulliken (reference 10). 4.  $D(\text{NO})=7.92$  eV after Birge and Spomer (reference 18).

<sup>9</sup> G. Herzberg and L. G. Mundie, J. Chem. Phys. 8, 263 (1940).

<sup>10</sup> S. W. Leifson, Astrophys. J. 63, 73 (1926).

TABLE IV. Delta-bands of nitric oxide.

	Band origins <sup>a-c</sup> ( $v',0''$ ) $\text{cm}^{-1}$	Band centers <sup>d</sup> $\text{cm}^{-1}$	Intensity observed F.C.	Reference below
0'	52287	52340	8	0
1'		54669	10	5
2'		57035	6	10
3'		59168	4	8
4'		61686	2	8

<sup>a</sup> A. G. Gaydon, Proc. Phys. Soc. London 56, 90 (1944); P. Migeotte and B. Rosen, Bull. Soc. Roy. Sci. Liège 14, 49 (1945); H. P. Knauss, Phys. Rev. 32, 417 (1928).

<sup>b</sup> W. Jevons, Band Spectra of Diatomic Molecules (University Press, Cambridge, England, 1932).

<sup>c</sup> R. Schmid, Zeits. f. Physik 59, 42 (1930); 64, 279 (1930).

<sup>d</sup> S. W. Leifson, Astrophys. J. 63, 73 (1926).

<sup>e</sup>  $\beta(7,0)$  at 1911.4 Å or 52318  $\text{cm}^{-1}$  is located here.

<sup>f</sup>  $\beta(12,0)$  at 1757.2 Å or 56907  $\text{cm}^{-1}$  is located here.

<sup>g</sup> Broad band.

$\text{cm}^{-1}$ ). However, Gaydon<sup>11</sup> and Migeotte and Rosen<sup>12</sup> have shown that the  $\epsilon$ -bands are really a band system apart from the  $\gamma$ -bands and  $\gamma(4',0'')$  is really  $\epsilon(0',0'')$ , etc.

The band at 1799.6 Å (55568  $\text{cm}^{-1}$ ), however, is very likely only  $\epsilon(1',0'')$  since other bands are about 400  $\text{cm}^{-1}$  distant. The band at 1729.7 Å (53813  $\text{cm}^{-1}$ ) can be  $\epsilon(2',0'')$  (57795  $\text{cm}^{-1}$ ) and  $\beta(13',0'')$  (57799  $\text{cm}^{-1}$ ). The band at 1666.6 Å

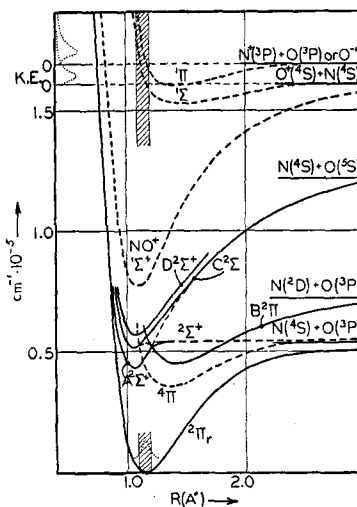


FIG. 5. Potential energy curves for NO and  $\text{NO}^+$ .  $\text{N}(^4\text{S}) + \text{O}(^3\text{P}) = 52380$   $\text{cm}^{-1}$  or 6.49 eV;  $\text{N}(^2\text{D}) + \text{O}(^3\text{P}) = 71590$   $\text{cm}^{-1}$  or 8.88 eV;  $\text{N}(^4\text{S}) + \text{O}(^5\text{S}) = 126150$   $\text{cm}^{-1}$  or 15.64 eV;  $\text{O}^+(^4\text{S}) + \text{N}(^4\text{S}) = 161640$   $\text{cm}^{-1}$  or 20.04 eV;  $\text{N}^+(^3\text{P}) + \text{O}(^3\text{P})$  or  $\text{O}^* = 169140$   $\text{cm}^{-1}$  or 20.97 eV.

<sup>11</sup> A. G. Gaydon, Proc. Phys. Soc. London 56, 90, 160 (1944).

<sup>12</sup> P. Migeotte and B. Rosen, Bull. Soc. Roy. Sci. Liège 14, 49 (1945).

(60000  $\text{cm}^{-1}$ ) can be  $\gamma(3',0'')$  (59955  $\text{cm}^{-1}$ ) and no overlapping occurs. The band at 1957.4A (51088  $\text{cm}^{-1}$ ) is clear of  $\beta(6',0'')$  (51373  $\text{cm}^{-1}$ ) and of  $\beta(8',1'')$  (51376  $\text{cm}^{-1}$ ) by about 290  $\text{cm}^{-1}$ . Hence considerable overlapping can be responsible for the actual intensity distribution of many bands on Leifson's photograph.

The details can best be seen in Tables II-IV. The band origins of the  $\beta$ -bands were calculated from an equation given by Jenkins, Barton, and Mulliken.<sup>13</sup> The similar quantities for the  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -bands were obtained from Gaydon.<sup>11</sup> It should be noted that Knauss<sup>14</sup> recognized the band  $\delta(0',0'')$  on Leifson's photograph. The difference between his value for the band head (1915.7A) and Leifson's measurement (1910A) he ascribes to the fact that the latter's values were all for the middle of the bands. This latter fact must be kept in mind when comparison is made between calculated values and experimental absorption bands. Rough guesses of intensities based on visual inspection of Leifson's photographs<sup>10</sup> and a crude use of the Franck-Condon principle are given in columns 9 and 10 of his Tables II-IV. The principle is not applicable in a simple manner in the present case as has been mentioned by Kaplan<sup>15</sup> and Barton, Jenkins, and Mulliken.<sup>16</sup>

These considerations and the work of Gaydon<sup>11</sup> suggest that an upper  $^2\Sigma^+$  state (from  $\text{N}(^6\text{S}) + \text{O}(^3\text{P})$  at 6.49 ev) might cross the region near  $\delta(1',0'') = 54700 \text{ cm}^{-1}$  at 1.15A. However, the non-crossing rule would have to be violated three times ( $A^2\Sigma^+$ ,  $C^2\Sigma$ ,  $D^2\Sigma^+$ ). It is therefore necessary to consider another scheme, shown in Fig. 3. Here  $A^2\Sigma^+$  is perturbed by a flat  $^2\Sigma^+$  state as above, so that  $\gamma(4',0'')$  does not exist. These two states form  $C^2\Sigma$ . The  $D^2\Sigma^+$  state lies above and is not affected. The non-crossing rule is not violated.  $A^2\Sigma^+$  may have a maximum at about 1.2A. Two interesting facts are noticeable in this connection.  $\beta(10',0'')$  is not mentioned by Leifson at all and certainly cannot be seen on the published photograph. This level seems greatly perturbed. Similarly,  $\beta(11',0'')$  differs

considerably from the calculated value. On the other hand,  $\beta(9',0'')$  is very strong in comparison. Hence these three levels appear perturbed by the presence of a repulsive state. This point may be cited in favor of the crossing of the  $^2\Sigma^+$  state at  $\delta(1',0'')$ , as mentioned above. However, the main consideration, namely, that the higher value of  $D(\text{NO}) = 6.49 \text{ ev}$ , favored by Gaydon,<sup>2</sup> can be fitted into an energy diagram, seems acceptable. It is obvious that not all the points at issue have been resolved.

#### PHOTO-CHEMICAL DISSOCIATION

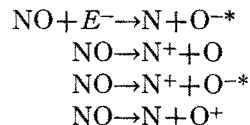
Flory and Johnston<sup>17</sup> state that they have observed photo-chemical dissociation at 1830A. However, this wave-length need not be taken too literally since spark sources usually have quite a continuous distribution in wave-length of radiation emitted.

#### BIRGE-SPONER EXTRAPOLATION

It is always of interest in a study of this kind to see how a suggested value for a heat of dissociation compares with the well-known Birge-Sponer extrapolation.<sup>18</sup> The usual plot is indicated in Fig. 4. It should be noted that the use of the equation of the origins of the  $\beta$ -bands given by Jenkins, Barton, and Mulliken<sup>13</sup> gives a value for  $D(\text{NO})$  nearer to the presently suggested figure than the usually accepted one.

#### APPEARANCE POTENTIALS

Hagstrum and Tate<sup>19</sup> studied the ionization and dissociation processes in nitric oxide. In their interpretation of these collision processes they used  $D(\text{NO}) = 5.30 \text{ ev}$ . Gaydon<sup>2</sup> already remarks that the larger value of 6.49 ev can be reconciled with the impact experiments. A detailed study (based on Fig. 5) of the processes



indicates that merely different amounts of kinetic energy of the resulting products need be assumed in order to bring the experiments into line with the high value of  $D(\text{NO}) = 6.49 \text{ ev}$ .

<sup>13</sup> F. A. Jenkins, H. A. Barton, and R. E. Mulliken, *Phys. Rev.* **30**, 150 (1927).

<sup>14</sup> H. P. Knauss, *Phys. Rev.* **32**, 417 (1928).

<sup>15</sup> J. Kaplan, *Phys. Rev.* **37**, 1406 (1931).

<sup>16</sup> H. A. Barton, F. A. Jenkins, and R. S. Mulliken, *Phys. Rev.* **30**, 175 (1927).

<sup>17</sup> P. J. Flory and H. L. Johnston, *J. Am. Chem. Soc.* **57**, 2641 (1935).

<sup>18</sup> R. T. Birge and H. Sponer, *Phys. Rev.* **28**, 259 (1926).

<sup>19</sup> H. D. Hagstrum and J. T. Tate, *Phys. Rev.* **59**, 354 (1941).