

The Heat of Dissociation in Nitrogen

George Glockler

Citation: *The Journal of Chemical Physics* **18**, 1518 (1950); doi: 10.1063/1.1747534

View online: <http://dx.doi.org/10.1063/1.1747534>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/18/11?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Dissociation of nitrogen-oxygen complexes by rapid thermal anneal heat treatments](#)

J. Appl. Phys. **92**, 1238 (2002); 10.1063/1.1488242

[The dissociation of dense liquid nitrogen](#)

J. Chem. Phys. **86**, 7110 (1987); 10.1063/1.452360

[Induction Time for Nitrogen Dissociation](#)

J. Chem. Phys. **56**, 3172 (1972); 10.1063/1.1677661

[Dissociation of Nitrogen in Shock Waves](#)

J. Chem. Phys. **23**, 1366 (1955); 10.1063/1.1742301

[The Rate of Dissociation of Nitrogen Tetroxide](#)

J. Chem. Phys. **1**, 251 (1933); 10.1063/1.1749281



The above value of $D_0(\text{CO})$ has been used to construct the energy diagram of CO shown in Fig. 1. The distinctive feature is a repulsive state arising from $\text{C}(^3P) + \text{O}(^3P)$ at 89397 cm^{-1} or 11.08 eV and reaching about 89700 cm^{-1} or 11.12 eV at $r = 1.2 \text{ \AA}$. Toward smaller distances it rises and at 1.1 \AA it is about 93500 cm^{-1} or 11.60 eV . This repulsive level is supposed to predissociate $\text{C}^2\Sigma^+$ ($v=0, K=29$) at 93536 cm^{-1} , $\text{B}^2\Sigma^+$ ($v=0, K=38$) at 89700 cm^{-1} , $\text{B}^2\Sigma^+$ ($v=1, K=18$) at 89650 cm^{-1} , and $\text{b}^2\Sigma^+$ ($v=0, K=55$) at about this height. The vibration levels $v=1$ of $\text{C}^2\Sigma^+$ ($\sim 94008 \text{ cm}^{-1}$), $v=2$ of $\text{B}^2\Sigma^+$ ($\sim 90940 \text{ cm}^{-1}$) are affected by the crossing of this assumed repulsive state and no bands arising from them have been found as yet.⁷ The repulsive state may perhaps cause the effects observed, not only by predissociation but also by dissociating molecules possessing energies in this region by virtue of a greater transition probability. All other irregularities in the spectrum of CO are considered to be perturbations. $\text{A}'\Pi$ is an example.⁸ The state $\text{b}^2\Sigma^+$ ($v=2$) at about 88140 cm^{-1} is crossed by $\text{a}^3\Sigma^+$ at $r = 1.02 \text{ \AA}$ leading to strong perturbation which may be the reason for its absence at that point.⁸

It is suggested that this energy diagram can serve as a start to explain all perturbations and so-called predissociations of the CO molecule provided the simple Morse curves are replaced by others involving the rotational changes mentioned by Oldenberg.⁹

* Financial support was received from ONR under Contract N-8 onr 79400.

¹ Brewer, Gilles, and Jenkins, *J. Chem. Phys.* **16**, 797 (1948).

² Simpson, Thorn, and Winslow, AEC Argonne National Laboratory, Report of Chemistry Division ANL-4264 (1949).

³ A. L. Marshall and F. J. Norton, *J. Am. Chem. Soc.* **72**, 2166 (1950).

⁴ *Selected Values of Properties of Hydrocarbons* (National Bureau of Standards, Circular C461, 1947).

⁵ G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950).

⁶ A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (John Wiley and Sons, Inc., New York, 1947).

⁷ References 5 and 6 give all of the literature references used.

⁸ Reference 6, p. 186.

⁹ O. Oldenberg, *Zeits. f. Physik* **56**, 563 (1929).

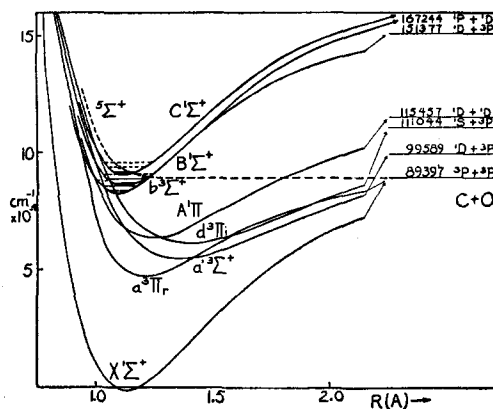


FIG. 1. Energy level diagram of nitrogen.

for CO] do not follow this rule. However, the term $\text{a}'(^1\Sigma_u^-)$ for N_2 can be calculated to be 66380 cm^{-1} from $\text{d}^3\Pi_u$ (62299.4) of CO. Gaydon estimates it to be around 65000 to 67000 cm^{-1} . Applying the rule to $D(\text{N}_2):D(\text{CO})$ with $D(\text{CO}) = 11.08 \text{ eV}$ yields $D(\text{N}_2) = 11.80 \text{ eV}$. This value has been used to construct an energy diagram for nitrogen (Fig. 1). It is supposed that a repulsive state starts from the $^4S + ^4S$ level (95206 cm^{-1}) and crosses $\text{C}^3\Pi_u$ just below 97946 cm^{-1} at the dissociation limit.^{2,3} The breaking-off points on account of predissociation in $v' = 1, 2, 3, 4$ at $K = 65, 55, 43$, and 28 lie on this repulsive curve at about $1.195, 1.223, 1.253$, and 1.281 \AA , respectively. These points were found from the work of Büttendörfer and Herzberg⁵ and sketching the probability functions of the oscillator onto the corresponding vibration levels. It may be that this proposed repulsive state has a greater transition probability than other states at about 11 eV and hence other states may not appear. The $\text{A}^3\Sigma_u^+$ -state perturbs $\text{B}^3\Pi_g$ ($v=12$) at 79385 and the $\text{a}'\Pi_u$ ($v=9$) at 84787 cm^{-1} . In Fig. 1 these crossings happen at 74000 and 98000 , respectively. It must be remembered that these simple Morse curves do not give quite the correct picture of the potential energy of the molecule. It is suggested that the value $D(\text{N}_2) = 11.8 \text{ eV}$ mentioned here deserves consideration and that this diagram can serve as basis for explaining all the perturbations and so-called predissociations of the nitrogen molecule. An early value of $D(\text{N}_2) = 11.5 \text{ eV}$ by Sponer⁶ was based on electron impact experiments and hence less accurate. The possibility that active nitrogen is really nitrogen atoms must again be considered.⁷

* Financial support was received from ONR under Contract N-8 onr 79400.

¹ K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (Verlag, Julius Springer, Berlin, 1931).

² G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950).

³ A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (John Wiley and Sons, Inc., New York, 1947).

⁴ Reference 3, p. 184.

⁵ G. Büttendörfer and G. Herzberg, *Ann. d. Physik* **21**, 577 (1935).

⁶ H. Sponer, *Zeits. f. Physik* **34**, 622 (1925).

⁷ R. J. Strutt, *Proc. Roy. Soc.* **85**, 219 (1911).

The Heat of Dissociation in Nitrogen

GEORGE GLOCKLER

Department of Chemistry and Chemical Engineering,
State University of Iowa,* Iowa City, Iowa

September 5, 1950

AN estimate of the heat of dissociation of nitrogen is made by comparing this molecule with the isoelectronic carbon monoxide. The force constants are $k(\text{N}_2) = 2.29$ and $k(\text{CO}) = 1.89$ megadynes/cm. The internuclear distances² are $R(\text{N}_2) = 1.095 \text{ \AA}$ and $R(\text{CO}) = 1.128 \text{ \AA}$. The currently discussed heats of dissociation^{2,3} are $D(\text{N}_2) = 9.764$ or 7.384 eV and $D(\text{CO}) = 9.61$ or 11.1 eV . The latter value fits the determinations of the heat of sublimation of carbon⁴ (preceding note). From a comparison of these properties one would expect that the heat of dissociation of nitrogen should also be greater than either of the above values. If the term values of N_2 are compared with the ones of CO arranged in order of magnitude,² then it is found that they stand in the ratio $1.0655:1$. The second highest terms [$\text{A}^3\Sigma_u^+$ (50206) for N_2 and $\text{a}^3\Pi_r$ (48688)