Heats of Dissociation of the N2 Molecule and the NH Radical

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Heats of Dissociation of the N_2 Molecule and the NH Radical

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A comparison made between certain radicals and molecules would indicate that the heat of dissociation of nitrogen molecules ($D(N_2)$) is 9.764 ev and the heat of dissociation of NH radicals ($D(NH)$) into atoms is 3.74 ev.

THE heat of dissociation (D) of nitrogen molecules (N_2, $^1\Sigma_g^+$) into normal nitrogen atoms (^4S) is given by Herzberg[1] as 7.384 ev. However, Gaydon[2] discussed the interpretation of a predissociation phenomenon in the nitrogen spectrum made by Van der Ziel[3] and suggested that Van der Ziel's consideration is not necessarily unique and that the value 9.764 ev for the heat of dissociation of nitrogen molecules is not necessarily excluded. It is of interest to point out that the higher value goes very well with the heat of dissociation of carbon monoxide as given by Herzberg[1] ($D(CO) = 9.144$ ev) and by Hagstrum[4] ($D(CO) = 9.608$ ev). While the latter's argument for $D(CO) = 9.608$ ev rests on only one experimental value of the appearance potential of O^+ ions in CO gas, still his analysis of the band spectrum of carbon monoxide must be given weight. As far as the present discussion is concerned a choice need not be made between these two values.

The comparison made here refers to the fact that $N_2(^1\Sigma_g^+)$ and $CO(^1\Sigma^+)$ molecules are isoelectronic and that it has been known for a long time that many of their physical properties are very closely alike.[5]

While considerations based on such comparisons are to be made with circumspection, as has been pointed out by Herzberg,[6] it may be permissible in the present stage of knowledge concerning heats of dissociation to bring the attention to any evidence which may contribute in the choice to be made of various values under consideration at this time.

A further bit of indirect evidence for the higher value of $D(N_2, ^1\Sigma_g^+)$ can be gleaned from a study of the heats of dissociation of the first row hydride radicals (CH, NH, OH, FH). The force constants (k) of these diatomic molecules and their internuclear distances (R_e) are known.[7] In similar series it has been found by many investigators[8–13] that *the larger the internuclear*
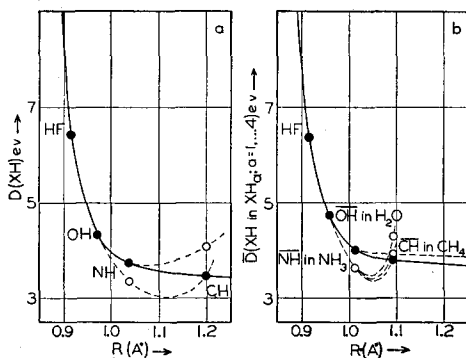

FIG. 1. Force constants of CH, NH, OH, and FH as radicals and in CH_4, NH_3, H_2O, and HF and the respective internuclear distances.

FIG. 2. Heats of dissociation of CH, NH, OH, and HF and average bond energies in CH_4, NH_3, H_2O, and HF and the respective internuclear distances.

[1] G. Herzberg, *Molecular Spectra and Molecular Structure, I. Diatomic Molecules* (Prentice-Hall, Inc., New York, 1939).
[2] A. G. Gaydon, Nature 153, 407 (1944).
[3] A. Van der Ziel, Physica 4, 373 (1937).
[4] H. D. Hagstrum, Phys. Rev. 72, 947 (1947).

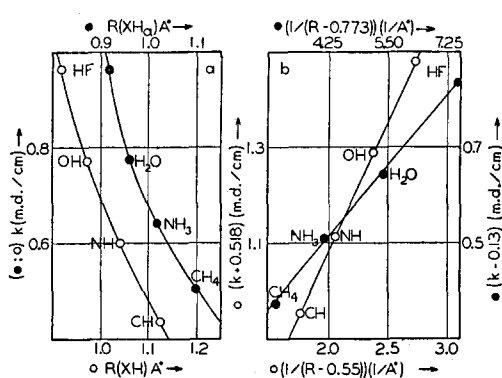[5] I. Langmuir, J. Am. Chem. Soc. 41, 868 (1919).
[6] See reference 1, p. 371.
[7] See reference 1, Table 36.
[8] R. M. Badger, J. Chem. Phys. 2, 128 (1934); 3, 710 (1935).

TABLE I. Force constants, heats of dissociation and internuclear distances (reference 1, Table 36).

		k(m.d./cm)		R_e (A)	D(ev)	
		(Expt.)	(Calc'd) Eq. 1		(Expt.)	(Calc'd) Eq. 2
CH	²Π_r	0.435	0.436	1.120	3.47	(3.47)
NH	³Σ⁻	0.600ᵃ	0.597	1.038	3.40(?)	3.74
OH	²Π_i	0.773	0.774	0.971	4.34ᵇ	(4.35)'
FH	¹Σ⁺	0.963	0.964	0.917	6.43ᶜ	(6.42)

ᵃ The frequency (ω_e ≈3300 cm⁻¹) is only approximately known (reference d).
ᵇ R. J. Dwyer and O. Oldenberg, J. Chem. Phys. 12, 351 (1944).
ᶜ D(F₂) ≈2.8 ev, reference 1.
ᵈ G. W. Funke, Zeits. f. Physik 96, 787 (1935).

distance (R_e) the smaller is the force constant. The relation is shown in Fig. 1a (Table I). It can be expressed empirically as

$$k = 0.544[1/(R_e - 0.550)] - 0.518 \qquad (1)$$

for the diatomic radicals (Fig. 1b). The force constants for the corresponding saturated molecules are also shown in Fig. 1a and as a straight line

$$k = 0.12[1/(R_e - 0.773)] + 0.13 \qquad (2)$$

in Fig. 1b.

Similarly, it has also been found[14-21] that the *heat of dissociation* (D) *of diatomic molecules is greater for smaller internuclear distances* in certain series of molecules and radicals. The case for the hydrides CH, NH, OH, and HF is shown in Fig. 2a and as a straight line

$$D = 0.12[1/(R_e - 0.884)] + 2.92 \qquad (2)$$

in Fig. 3 where, however, $D(NH) = 3.4$ ev has been omitted. This empirical relation is used to interpolate a value for $D(NH)$ of 3.74 ev. The value given by Bates[22] of 4.43 ev, and mentioned

⁹ C. H. Douglas Clark, Phil. Mag. 18, 459 (1934).
¹⁰ G. M. B. Sutherland, J. Chem. Phys. 8, 161 (1940).
¹¹ J. J. Fox and E. A. Martin, J. Chem. Soc. 180, 2106 (1938).
¹² R. Cherton, Bull. Soc. Chim. Belg. 52, 26 (1943).
¹³ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1940).
¹⁴ A. H. Skinner, Trans. Faraday Soc. 41, 645 (1945).
¹⁵ A. H. Long and A. D. Walsh, Trans. Faraday Soc. 43, 342 (1947).
¹⁶ A. H. Long and R. G. W. Norrish, Proc. Roy. Soc. A187, 337 (1946).
¹⁷ A. D. Walsh, Trans. Faraday Soc. 42, 52, 779 (1946); 43, 60 (1947).
¹⁸ H. D. Springall, Trans. Faraday Soc. 43, 177 (1947).
¹⁹ J. L. Kavanau, J. Chem. Phys. 12, 467 (1944); 15, 77 (1947).
²⁰ W. Gordy, J. Chem. Phys. 15, 81, 305 (1947).
²¹ W. J. Bernstein, J. Chem. Phys. 15, 284, 339, 688 (1947).
²² J. R. Bates, Zeits. f. physik. Chemie Bodenstein Festband 329 (1931).

TABLE II. Average bond energies of hydrides of first row elements.

	Q_f ev	Q_a ev	D̄(MH) ev	R_e^i A	k^i m.d./cm
CH₄	0.693ᵃ	15.07ᵈ	3.77	1.094	0.504
		15.54ᵉ	3.88		
		16.98ᶠ	4.25		
NH₃	0.476ᵇ	12.07ᵍ	4.02	1.014	0.642
		10.89ʰ	3.63		
OH₂	2.49ᶜ	9.47	4.73	0.958	0.776
FH	2.78ᵇ	6.43	6.43	0.9166	0.963

ᵃ E. J. Prosen, K. S. Pitzer, and F. D. Rossini, Bull. Nat. Bur. Stand. 34, 403 (1945).
ᵇ See reference 24.
ᶜ R. J. Dwyer and O. Oldenberg, J. Chem. Phys. 12, 351 (1944).
ᵈ Based on L(C) =5.424 ev.
ᵉ Based on L(C) =5.888 ev.
ᶠ Based on L(C) =7.334 ev.
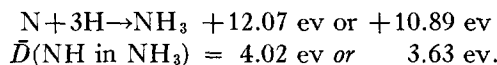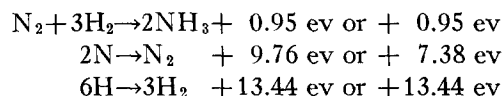ᵍ Based on D(N₂) =9.76 ev.
ʰ Based on D(N₂) =7.38 ev.
ⁱ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).

by Bichowsky and Rossini,[23] is only an upper limit. The value calculated by King[24] using Stehn's[25] formula also depends on an interpolation and may not deserve any more consideration than the value of 3.74 ev suggested here.

It is next of interest to compare this value with the average bond energy of NH in ammonia $(\bar{D}(NH \text{ in } NH_3))$. The calculation is made on the two assumptions: $D(N_2) = 9.76$ ev *or* $D(N_2) = 7.38$ ev:

$$N_2 + 3H_2 \rightarrow 2NH_3 + \ 0.95 \text{ ev or } + \ 0.95 \text{ ev}$$
$$2N \rightarrow N_2 \quad + \ 9.76 \text{ ev or } + \ 7.38 \text{ ev}$$
$$6H \rightarrow 3H_2 \quad +13.44 \text{ ev or } +13.44 \text{ ev}$$

$$N + 3H \rightarrow NH_3 \ +12.07 \text{ ev or } +10.89 \text{ ev}$$
$$\bar{D}(NH \text{ in } NH_3) = \ 4.02 \text{ ev } or \quad 3.63 \text{ ev.}$$

These two possible cases are now compared with the corresponding quantities $\bar{D}(CH \text{ in } CH_4)$,
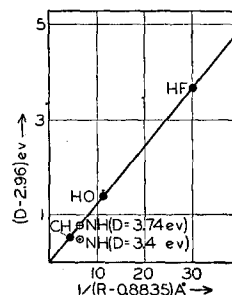

FIG. 3. Straight line relation between heats of dissociation and internuclear distance for CH, NH, OH, and HF.

²³ F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of the Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).
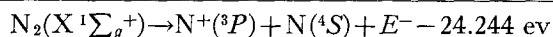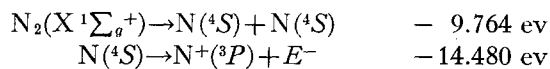²⁴ G. W. King, J. Chem. Phys. 6, 378 (1938).
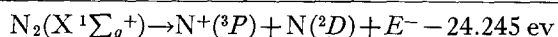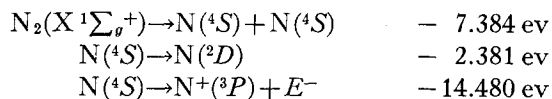²⁵ J. R. Stehn, J. Chem. Phys. 5, 186 (1937).

$\bar{D}$(OH in H_2O) and $\bar{D}$(HF in HF). As seen in Fig. 2b, the value $\bar{D}$(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 $\bar{D}$(NH in NH_3) based on $D(N_2)$ = 7.38 ev is *less than* D(NH, radical) (= 3.74 ev), whereas the corresponding distances are R(NH in NH_3) = 1.014A and R(NH, radical) = 1.038A. The higher value of 4.02 ev for $\bar{D}$(NH in NH_3) is therefore more acceptable.

With the higher value of $D(N_2)$ = 9.764 ev, the appearance potential of N^+ ions[4] will then refer to the reaction

$$N_2(X\,^1\textstyle\sum_g{}^+) \rightarrow N(^4S) + N(^4S) \qquad -\ 9.764\ \text{ev}$$
$$N(^4S) \rightarrow N^+(^3P) + E^- \qquad -14.480\ \text{ev}$$
$$\overline{}$$
$$N_2(X\,^1\textstyle\sum_g{}^+) \rightarrow N^+(^3P) + N(^4S) + E^- -24.244\ \text{ev}$$

rather than to

$$N_2(X\,^1\textstyle\sum_g{}^+) \rightarrow N(^4S) + N(^4S) \qquad -\ 7.384\ \text{ev}$$
$$N(^4S) \rightarrow N(^2D) \qquad -\ 2.381\ \text{ev}$$
$$N(^4S) \rightarrow N^+(^3P) + E^- \qquad -14.480\ \text{ev}$$
$$\overline{}$$
$$N_2(X\,^1\textstyle\sum_g{}^+) \rightarrow N^+(^3P) + N(^2D) + E^- -24.245\ \text{ev}$$

The only difference is the state of the nitrogen atom, which cannot be detected in a mass spectrograph. 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[26] which indicates that the high value of the heat of sublimation of carbon (L(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 $\bar{D}$(CH in CH_4) as shown in Fig. 2b.

Wahrhaftig[27] determined that the heat of dissociation of 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 $D(F_2)$, but the empirical value of D(NH) = 3.74 ev is not affected.

The comparison made here favors the higher value of the heat of dissociation of nitrogen ($D(N_2)$ = 9.764 ev) and either of the lower values of the heat of sublimation of carbon (L(C) = 5.424 or 5.888 ev).

[26] Unpublished results.
[27] A. L. Wahrhaftig, J. Chem. Phys. **10**, 248 (1942).

The Heat of Dissociation of Nitric Oxide

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The heat of dissociation of nitric oxide (D(NO)) is considered to be 6.49 ev on the basis of a comparison of the series CO, NO, O_2, OF, its band spectrum, and its photo-chemical dissociation. Appearance potentials of N^+, O^+, and O^- can be interpreted on this basis.

IF the heat of dissociation of nitrogen is 7.384 ev,[1] 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, Gaydon[2] discussed the possibility that the higher value of 9.764 ev for the heat of dissociation of N_2 is more acceptable. The following considerations lend support to this view.

[1] G. Herzberg, *Molecular Spectra and Molecular Structure I. Diatomic Molecules* (Prentice-Hall, Inc., New York, 1939).

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