Lawrence Berkeley National Laboratory

Title
DISSOCIATION ENERGIES FROM INVERSE PREDISSOCIATION.

Permalink
https://escholarship.org/uc/item/0m36h2m5

Author
Phillips, Leon F.

Publication Date
1968-04-01

University of California

Ernest O. Lawrence
Radiation Laboratory

DISSOCIATION ENERGIES FROM INVERSE PREDISSOCIATION

Leon F. Phillips

April 1968

Berkeley, California

DISCLAIMER

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

DISSOCIATION ENERGIES FROM INVERSE PREDISSOCIATION

Leon F. Phillips

April 1968

DISSOCIATION ENERGIES FROM INVERSE PREDISSOCIATION

Leon F. Phillips[*]

Inorganic Materials Research Division, Lawrence Radiation Laboratory,
University of California, Berkeley, California

The use of predissociations in electronic spectra to fix limits for dissociation energies has been very common,[1,2] but although the principle of determining similar limits from observations of inverse predissociation in chemiluminescence has been known for a long time,[2] relatively few values of dissociation energy have actually been found by this means. It is the purpose of the present note to consider the conditions that must be fulfilled before one can be reasonably certain that an observed emission spectrum is the result of an inverse predissociation, and also to discuss observations in the literature which, when interpreted in terms of inverse predissociation, in a few cases give rise to distinct improvements in the precision of listed dissociation energies.

Measurements of the intensity of chemiluminescence arising from atom and radical recombination reactions in the presence of various added gases[3] show that when the emission is in the form of discrete bands the excitation process is normally a termolecular reaction of the type

$$X + Y + M \rightarrow XY^* + M \qquad (1)$$
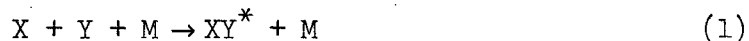
Here X and Y are ground-state species, at least one of which is an atom or radical, and M is an "inert" third body. If the excited product XY^* is in a state which does not correlate with ground-state X and Y at

---

infinite internuclear distance then an inverse predissociation, or

"preassociation," type of mechanism must be considered. It should be

realized, however, that the process (1) differs from a true inverse

predissociation because of the intervention of the third body M, so that,

for example, normal selection rules governing predissociation will not

necessarily apply. The following criteria are suggested as a basis for

deciding whether a particular chemiluminescent emission from a species

XY is the result of preassociation:

1.   The emission spectrum should originate from a state of XY that

does not correlate with ground-state X and Y.

2.   The intensity of the emission should depend kinetically on the

product of the concentrations of X and Y.

3.   There should be available a repulsive or slightly attractive po-

tential energy curve, derived from ground-state X and Y, to cross the

excited state from which the radiation originates at an energy level

close to the dissociation limit. This is not as strict a requirement

as it is for predissociation, since in the presence of the third body

M it is likely that the course of any potential energy curve is appre-

ciably different from what it is for the isolated molecule.

4.   The upper state of the observed transition should show evidence

of predissociation. This also should not be a stringent requirement

because of the probable relaxing effect of the third body on selection

rules for predissociation.

5.   In general we can conclude that whereas the onset of predissociation

indicates an upper limit for the dissociation energy of the X-Y bond, the

onset of preassociation indicates a lower limit for this dissociation energy.

Thus where both processes are observed to occur these energy limits should practically coincide, and in any case a preassociation limit should never occur at a higher energy than the dissociation limit as found by any other reliable means, unless it is to be presumed that excited atoms are involved. Only in high temperature systems such as burner flames, where the value of RT is typically around 4 kcal per mole, should there be significant overlap of predissociation and pre-association limits.

Table I lists a number of representative examples of diatomic radicals and molecules for which an observed chemiluminescence might be attributed to preassociation. We consider them individually as follows:

N_2: This is to be regarded as the classic example of preassociation, all of the above criteria being satisfied. The relationship between the predissociation in the B-state of N_2 and the Lewis-Rayleigh after-glow of active nitrogen is thoroughly discussed elsewhere.[4]

OH: The predissociation at v = 2 and in upper rotational levels of v = 1 in the A-state was first observed by Gaydon and Wolfhard.[5] Gaydon[6] suggested that the inverse process should contribute signi-ficantly to the population of electronically excited OH in flame gases. Tiktin, Spindler and Schiff[7] showed that the intensity of OH chemi-luminescence from a double discharge-flow system containing O and H atoms is proportional to the product of the concentrations of the two atoms, and examined the population of rotational levels resulting from the recombination process.

NO: The predissociation in the δ-bands of NO is well established.[8] It results from crossing of the C-state with a repulsive $^4\Pi$ state derived from ground-state atoms. The preassociation is discussed by Young and Sharpless,[9] who observed several systems of bands, some arising from electronic levels considerably below the dissociation limit.

NH: The possibility that NH emission from a system containing N and H atoms was due to preassociation was first raised by Guenebaut, Pannetier and Goudmand.[10] Their suggestion was criticised by Mannella,[11] on the grounds that the $^5\Sigma^-$ state would be expected to rise too steeply to cross the A-state near the dissociation limit, but as pointed out above this objection may not be valid in the presence of a third body. The alternative excitation mechanism proposed by Mannella involved the A-state of N_2 as a reactant, and must be rejected in the light of recent experiments which show that the concentration of A-state molecules in active nitrogen is extremely low.[12] If the preassociation mechanism is accepted, as seems reasonable, then the dissociation energy of NH must be considered to lie very close to the limit at 94 kcal.

CuH, TlH and AlH: Emission spectra with intensity proportional to [Cu][H] and [Tl][H] were reported by Bulewicz and Sugden for hydrogen/air flames containing traces of cupric and thallous salts respectively.[13,14] The emission was originally believed to be due to thermal excitation of hydride molecules formed through the equilibria

$$Cu + H + M \rightleftharpoons CuH + M \qquad (2)$$

$$Tl + H + M \rightleftharpoons TlH + M \qquad (3)$$

but later work[15] has shown that a mechanism based on reaction (1) is much more likely. The predissociation limits are as given by Gaydon[1]

and Herzberg,[2] who also discuss similar conclusions for AlH. In the case of AlH the reported coincidence of predissociation and pro-association limits leads to a value of 70.5 kcal for the dissociation energy, with some uncertainty due to the high temperature of the source.

CN and CO: The observations of chemiluminescence were made by Savadatti and Broida,[16] who mixed carbon vapour, containing a small percentage of atomic carbon, with atomic H, N, and O. They proposed that the C_2 emission they observed was produced as a result of the reaction of an excited metastable C_3 with atomic oxygen or nitrogen. According to Ballik and Ramsay[17] the $A^3\Pi_g$ state from which the bands originated can be populated directly by collision of ground-state atoms, so a pre-association mechanism is not required. Carbon atoms would be expected to be much more plentiful in the flame with N or O atoms than in pure carbon vapour; however, it is notable that no CH emission was observed from a mixture of carbon vapour with atomic hydrogen. The predissociation limit for CO is given by Douglas and Møller.[18]

IO, BrO and ClO: Emission bands arising from states of these molecules that do not correlate with ground-state atoms are observed from burner flames containing traces of the appropriate halogen.[19-21] For IO and BrO it has been shown that the intensity is proportional to the product of the concentrations of atomic oxygen and atomic halogen.[22,23] Quite precise values of dissociation energy, based on convergence limits of these band systems, are available for ClO and BrO,[24] and a less precise estimate based on a ground-state Birge-Sponer extrapolation is avail-able for IO.[1,25] For IO the preassociation limit leads to a satis-factory value for the dissociation energy provided it is

assumed that $^2P_{1/2}$ iodine atoms are involved. For BrO the presumed

lower limit appears to be at least 10 kcal too high, even after $^2P_{1/2}$

bromine atoms are invoked, while for ClO the limit obtained is so high

that a preassociation mechanism is ruled out. Of the three halogens

only iodine is present in the flame almost entirely in the form of free

atoms.[26] For chlorine the thermal excitation of equilibrium amounts of

ground-state ClO could be sufficient to account for the observed bands;

this process might also account for a part of the BrO emission.

NBr, NCl and NF: For NBr Milton, Dunford and Douglas originally proposed

a preassociation mechanism for population of the observed excited state;[27]

their listed dissociation energy represents a compromise between the

preassociation limit and a Birge-Sponer extrapolation. For NCl and NF

the chemiluminescence was observed from discharged mixtures which are

reasonably certain to have contained both atomic species, but the light

emission was very weak and was certainly not observed right up to the

dissociation limit in either case. The D° values for NCl and NF given

in the last column of Table I represent linear Birge-Sponer extrapola-

tions based on the ground-state data obtained in these studies,[27,28]

and are expected to be too high.

It is anticipated that the above discussion should serve to indicate

the need for further work to fill in some of the gaps in Table I, and to

extend the table to include other small molecules and radicals.

ACKNOWLEDGEMENTS

Table I.

Molecule	Transition	Crossing State	Kinetics	Preassociation Limit	Predissociation Limit	Listed D_o
N_2	$B^3\Pi_g - A^3\Sigma_u^+$	$^5\Sigma_g^+$	$[N]^2$	225	225	225.1 (Ref. 1)
OH	$A^2\Sigma^+ - X^2\Pi$	$^2\Sigma^-$	[O][H]	101.3	110	101.5 (Ref. 1)
NO	$C^2\Pi - X^2\Pi$	$^4\Pi$	[N][O]	149.5	149.5	150 (Ref. 1)
NH	$A^3\Pi - X^3\Sigma$	$^5\Sigma^-$	--	94	--	85±10 (Ref. 1)
CuH	$^1\Sigma - X^1\Sigma$	--	[Cu][H]	66.5	66.5	64±11 (Ref. 1)
TℓH	B-A	--	[Tℓ][H]	50	50	46±4 (Ref. 1)
AℓH	$^1\Pi - X^1\Sigma^+$	--	--	70.5	70.5	67±5 (Ref. 1)
CN	$B^2\Sigma - X^2\Sigma$	--	--	160	--	187±7 (Ref. 1)
CO	$b^3\Sigma^+ - a^3\Pi$	--	--	240	256	256.1 (Ref. 1)
IO	$A^2\Pi - X^2\Pi$		[I][O]	46	63	44±4 (Ref. 1)
BrO	$A^2\Pi - X^2\Pi$	--	[Br][O]	71	81	55 (Ref.24)
CℓO	$A^2\Pi - X^2\Pi$	--	--	92	97	63.5 (Ref.24)
NBr	$b^1\Sigma^+ - X^3\Sigma^-$	$^3\Pi, ^5\Pi$ or $^5\Sigma^-$	--	63.4	--	67±5 (Ref.27)
NCℓ	$b^1\Sigma^+ - X^3\Sigma^-$	$^3\Pi, ^5\Pi$ or $^5\Sigma^-$	--	54	--	96 (LBX)
NF	$b^1\Sigma^+ - X^3\Sigma^-$	$^3\Pi, ^5\Pi$ or $^5\Sigma^-$	--	61	--	103 (LBX)

REFERENCES

1. A. G. Gaydon, Dissociation Energies, Second edition (Chapman and Hall, London, 1953).

2. G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules, Second Edition (D. Van Nostrand, New Jersey, 1950).

3. See, for example, M. A. A. Clyne and B. A. Thrush, Disc. Farad. Soc. 33, 139 (1962).

4. K. R. Jennings and J. W. Linnett, Quart. Rev. Chem. Soc. (London) 12, 116 (1958).

5. A. G. Gaydon and H. C. Wolfhard, Proc. Roy. Soc. (London) A208, 63 (1951).

6. A. G. Gaydon, The Spectroscopy of Flames (Chapman and Hall, London, 1957), p. 75.

7. G. B. Spindler, S. Tiktin, and H. I. Schiff, Nature 214, 1006 (1967); Disc. Farad. Soc. (Molecular Dynamics of Chemical Reactions), 1967 in press.

8. P. J. Flory and H. L. Johnstone, J. Chem. Phys. 14, 212 (1946).

9. R. A. Young and R. L. Sharpless, J. Chem. Phys. 39, 1071 (1963), and Disc. Farad. Soc. 33, 228 (1962).

10. H. Guenebaut, A. Pannetier and P. Goudmand, Comptes Rendus Acad. Sci. (Paris) 251, 1480 (1960).

11. G. G. Mannella, J. Chem. Phys. 36, 1079 (1962).

12. R. A. Young, Can. J. Chem. 44, 1171 (1966).

13. E. M. Bulewicz and T. M. Sugden, Trans. Farad. Soc. 52, 1475 (1956).

14. E. M. Bulewicz and T. M. Sugden, Trans. Farad. Soc. 53, 830 (1957).

15. R. W. Reid and T. M. Sugden, Disc. Farad. Soc. 33, 213 (1962).

16. M. I. Savadatti and H. P. Broida, J. Chem. Phys. 45, 2390 (1966).

17. E. A. Ballik and D. A. Ramsay, Astrophys. J. 137, 84 (1963).

18. A. E. Douglas and C. K. Møller, Can. J. Phys. 33, 125 (1955).

19. E. H. Coleman, A. G. Gaydon and W. M. Vaidya, Nature 162, 108 (1948).

20. E. H. Coleman and A. G. Gaydon, Disc. Farad. Soc. 2, 166 (1947).

21. A. Pannetier and A. G. Gaydon, Nature 161, 242 (1948).

22. L. F. Phillips and T. M. Sugden, Trans. Farad. Soc. 57, 921 (1961).

23. M. J. McEwan and L. F. Phillips, Combustion and Flame 11, 63 (1967).

24. R. A. Durie and D. A. Ramsay, Can. J. Phys. 36, 35 (1958).

25. R. A. Durie, F. Legay and D. A. Ramsay, Can. J. Phys. 38, 444 (1960).

26. M. J. McEwan, (Ph.D. Dissertation), University of Canterbury, 1965.

27. E. R. V. Milton, H. B. Dunford and A. E. Douglas, J. Chem. Phys. 35, 1202 (1961).

28. R. Colin and W. E. Jones, Can. J. Phys. 45, 301 (1967).

29. A. E. Douglas and W. E. Jones, Can. J. Phys. 44, 2251 (1966).