

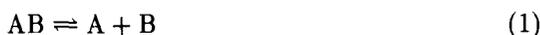
Dissociation Energies and Partition Functions of Small Molecules

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1 Introduction

For a simple dissociation equilibrium



the equilibrium constant K_p at temperature T can be written in terms of partial pressures p or densities n in the form given by Equation 6 of Tatum (1966)

$$K_p(T) = \frac{p_A p_B}{p_{AB}} = kT \frac{n_A n_B}{n_{AB}} = \left(\frac{2\pi m kT}{h^2} \right)^{\frac{3}{2}} kT \frac{Q_A Q_B}{Q_{AB}} e^{-D_0/kT} \quad (2)$$

where m is the reduced mass of AB, k the Boltzmann constant, h the Planck constant, Q_A , Q_B , Q_{AB} the internal partition functions of the species, and D_0 ¹ the dissociation energy of AB. This equation derives from a more general expression of $K_p(T)$ for a chemical reaction that is demonstrated in all physical-chemistry textbooks treating statistical thermodynamics (see for example Atkins 1990). Partition functions are weighted Boltzmann factors

$$Q = \sum_n g_n e^{-\epsilon_n/kT} \quad (3)$$

¹ The dissociation energy D_0 invoked throughout the paper refers to the energy difference between the zero point energies (ZPE) of the products of dissociation and the molecule. This is the microscopic (molecular) definition of the dissociation energy which is measured spectroscopically. The macroscopic (molar) definition uses the notations D_0^0 or D_0° , with the subscript referring to the temperature $T = 0$ K and the superscript to the standard state. Indeed, dissociation energies determined thermochemically are calculated from standard enthalpies of formation at 0 K (see Equation 6 and others in the text, where we have dropped the superscript for clarity). The two definitions give identical values. They differ from the dissociation energy labelled D_e as often found in theoretical work which, for a diatomic molecule, is the energy difference between the separated ground-state atoms and the minimum of its potential energy curve.

with ϵ_n corresponding to the energy of the eigenstates of degeneracy g_n . Provided all the eigenvalues are known, Q values can be calculated exactly. Derivations and calculations of the partition functions can be found in textbooks or in reviews relating to astrophysics. The monographs of Tatum (1966) and Sauval & Tatum (1984) which include calculations of partition functions and equilibrium constants for 300 diatomic molecules of astrophysical interest are particularly relevant. Approximations such as the so-called high temperature approximation for the rotational partition function and the Morse potential for the vibrational partition function have been used to yield simple analytical expressions that only depend on the temperature. Nevertheless, comparison with the extensive calculations obtained by direct summation over calculated eigenstates reveals no striking difference. For example, the CN partition function computed between 1000 and 8500 K in that manner by Jørgensen & Larsson (1990) differs at most by 4 % from the values of Sauval & Tatum (1984).

While the knowledge of accurate molecular partition functions is essential to compute equilibrium constants, this requirement is not strictly necessary for abundance analyses of atomic species derived from molecular opacities. Indeed, the absorption coefficient, κ_{vJ} , of a molecular line in a medium in thermodynamic equilibrium at temperature T relative to a particular quantum state vJ of energy ϵ_{vJ} is

$$\kappa_{vJ} \propto n_{AB(v,J)} f_{vJ} = \frac{n_{AB} (2J + 1) e^{-\epsilon_{vJ}/kT}}{Q_{AB}} f_{vJ} \quad (4)$$

where f_{vJ} is the line oscillator strength. It follows that the molecular partition function cancels out when combining Equation (2) and (4):

$$\kappa_{vJ} \propto \frac{n_A n_B}{Q_A Q_B} \left(\frac{2\pi mkT}{h^2} \right)^{-\frac{3}{2}} (2J + 1) e^{-\epsilon_{vJ}/kT} e^{+D_0/kT} f_{vJ} . \quad (5)$$

However, when the product $n_A n_B$ is extracted from a calculated equilibrium constant, care should be taken to use the same partition functions that were entered in the calculation of the equilibrium constant. Sauval & Tatum (1984) have stressed the importance of giving a set of both equilibrium constants and partition functions to avoid inconsistent comparisons.

The dissociation energy always remains a critical factor in the calculation of equilibrium constants or in the evaluation of abundances from molecular opacities. Consider again the example of CN: an uncertainty of 0.3 eV in the dissociation energy results in a variation of the equilibrium constant by a factor of 2 for the solar photosphere, and even more for cooler objects, when turning from the lower to the upper bound ($D_0 = 7.6$ to 7.9 eV, as found in many references).

2 Current Status of the Knowledge of Dissociation Energies

It is not self evident that any value of a dissociation energy quoted with low error limits should be taken for granted, even when it is found in a review or a

database considered as being authoritative on the subject. Compilations, once they have been recognized, have the tendency to last too many years before they are finally considered as obsolete. Quoted values can disagree, and when establishing comparisons, it is not at all clear that the best value should be in the more recently published review.

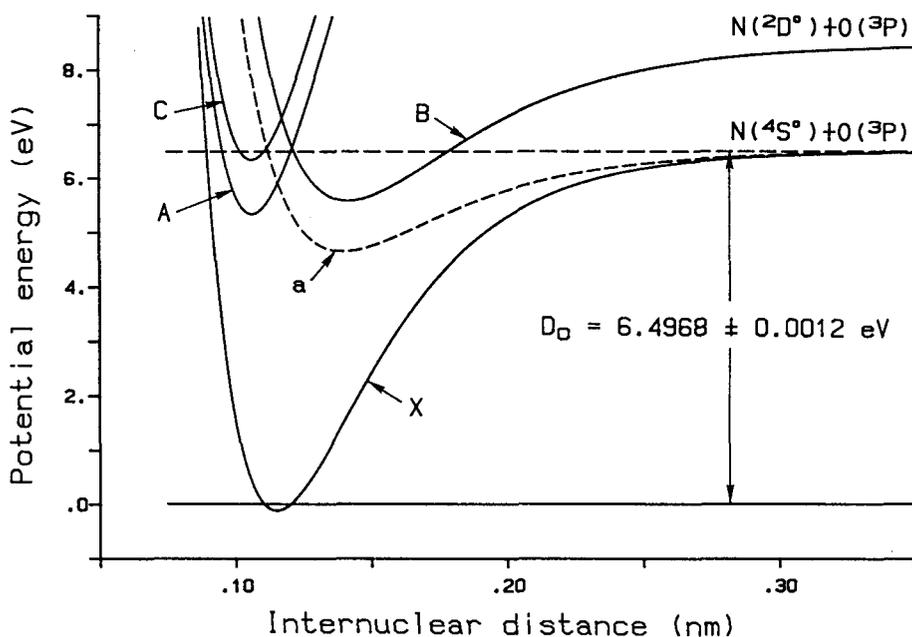


Fig. 1. Potential energy curves of some low-lying states of NO: $X^2\Pi_r$, $a^4\Pi_i$, $A^2\Sigma^+$, $B^2\Pi_r$ and $C^2\Pi_r$.

The example of the NO molecule can be taken to illustrate briefly the latter point. Following the last complete revision of the JANAF tables (Chase et al. 1985), the quoted standard enthalpies of formation of NO, N and O at 0 K are respectively $\Delta_f H_0(\text{NO}) = 0.9305 \pm 0.0018 \text{ eV}$ per molecule ($89.775 \pm 0.17 \text{ kJ mole}^{-1}$), $\Delta_f H_0(\text{N}) = 4.8797 \pm 0.0010 \text{ eV}$ ($470.82 \pm 0.10 \text{ kJ mole}^{-1}$) and $\Delta_f H_0(\text{O}) = 2.5578 \pm 0.0010 \text{ eV}$ ($246.79 \pm 0.10 \text{ kJ mole}^{-1}$). Since

$$D_0(\text{NO}) = \Delta_f H_0(\text{N}) + \Delta_f H_0(\text{O}) - \Delta_f H_0(\text{NO}) \quad (6)$$

the $D_0(\text{NO})$ value can be deduced to be $6.5071 \pm 0.0038 \text{ eV}$, which is not consistent with the value given in the compilation of constants of diatomic molecules provided by Huber & Herzberg (1979): $D_0(\text{NO}) = 6.4968 \pm 0.0012 \text{ eV}$. Yet, the value selected by Huber & Herzberg is based on papers by Callear & Pilling (1970) and Dingle et al. (1975) that could have been considered in the 1985 JANAF tables. Indeed, these authors established that only a very few rotational

levels of the $C^2\Pi_r$ Rydberg state, predissociated by the interaction with the $a^4\Pi_i$ state, lie below the dissociation limit (Fig. 1). Direct spectroscopic evidence had been found by Dingle et al. by inverse predissociation in the two body recombination reaction of N and O atoms. This process populates $C^2\Pi_r$ rovibrational levels situated above the dissociation limit. Consequently, observation of the $C^2\Pi_r \rightarrow A^2\Sigma^+$ infrared bands reveals a break-off in the rotational structure (sudden drop in intensity) for levels below the dissociation limit, which yields precisely the dissociation energy, confirmed in subsequent papers.

Another current source of difficulty is to establish the complete path of the determination, as a value of a dissociation energy given in a paper is in general dependent on previous determinations of dissociation energies or standard enthalpies of formation at 0 K of other molecules. For example $D_0(C_2-H)$ can be deduced as follows:

$$D_0(C_2H-H) = \Delta_f H_0(C_2H) + \Delta_f H_0(H) - \Delta_f H_0(C_2H_2) \quad (7)$$

$$D_0(C_2-H) = \Delta_f H_0(C_2) + \Delta_f H_0(H) - \Delta_f H_0(C_2H) \quad (8)$$

$$D_0(C_2) = 2\Delta_f H_0(C) - \Delta_f H_0(C_2) \quad (9)$$

Hence, eliminating $\Delta_f H_0(C_2H)$ and $\Delta_f H_0(C_2)$ yields:

$$D_0(C_2-H) = 2\Delta_f H_0(C) - D_0(C_2) + 2\Delta_f H_0(H) - \Delta_f H_0(C_2H_2) - D_0(C_2H-H) \quad (10)$$

The result is that the certainty of $D_0(C_2-H)$ calculated concomitantly from the measurement of $D_0(C_2H-H) = 5.69 \pm 0.03$ eV (131.3 ± 0.7 kcal mole⁻¹) by Ervin et al. (1991), also depends on the certainty of four other values. Ervin et al. have retained three JANAF values: $\Delta_f H_0(C) = 7.371 \pm 0.005$ eV (711.19 ± 0.46 kJ mole⁻¹), $\Delta_f H_0(H) = 2.23906 \pm 0.00006$ eV (216.035 ± 0.006 kJ mole⁻¹), $D_0(C_2) = 6.11 \pm 0.11$ eV (140.95 ± 2.5 kcal mole⁻¹), with enlarged uncertainty for the latter value, and discarded the fourth: $\Delta_f H_0(C_2H_2) = 2.443 \pm 0.008$ eV (235.755 ± 0.79 kJ mole⁻¹), replaced by 2.371 ± 0.007 eV (54.68 ± 0.17 kcal mole⁻¹) from Pedley et al. (1986), which results in $D_0(C_2-H) = 5.04 \pm 0.11$ eV (116.3 ± 2.6 kcal mole⁻¹). Following the same scheme but using their own measurement of $D_0(C_2)$: 6.30 ± 0.02 eV (145.2 ± 0.5 kcal mole⁻¹), Urdahl et al. (1991) have taken the four other values from Ervin et al. to deduce $D_0(C_2-H) = 4.86 \pm 0.04$ eV (112.0 ± 0.8 kcal mole⁻¹).

Dissociation energy values can be classified according to the methods of their determination. The best known values are those obtained directly by spectroscopy for molecules showing a predissociative behaviour, such as NO as discussed above, or a convergence limit in a progression of bands in the absorption spectrum, such as the one found in the Schumann-Runge ($B^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$) transition of O₂: this has set a value of $D_0(O_2) = 5.1156 \pm 0.0019$ eV (41260 ± 15 cm⁻¹) (Brix & Herzberg 1954). A high level of accuracy is found for these experiments and the absolute uncertainty can be as low as 0.1 meV. These dissociation energies can be considered as reference values, which constitute the frame of the complex body of enthalpies of formation at 0 K. Fortunately, a reasonable

number of dissociation energies enter in this category, which includes the dissociation energies of the diatomic permanent gases and also a few diatomic radicals such as OH. Such methods have not been successful with strongly bonded radicals because they require tunable vacuum-ultraviolet (vuv, below 200 nm) light so far only provided by conventional light sources. For such light sources, the density of species required is too high to be provided by the methods available for generation of radicals in the laboratory. Nonetheless, the availability of new pulsed laser sources, truly tunable over wide wavelength ranges in the vuv, will certainly set up for more determinations of this type in the near future.

Beside the values determined by the spectroscopic methods mentioned above, the accuracy of the others should always appear questionable. In the following it is not our intention to review all the field but rather to indicate trends of what we believe the best and most promising methods could be.

3 Determinations of Dissociation Energies by Ab Initio Methods

Ab initio methods have considerably improved in recent years, although they have not yet reached the accuracy of the best experimental determinations. The results of the Gaussian-2 theory deserve to our opinion special attention. In the first paper of the series devoted to this theory, Curtiss et al. (1991) have given an impressive list of 133 calculated total atomisation energies, i.e. the rupture of all chemical bonds (ΣD_0), including 67 diatomics and 33 triatomics and the rest being molecules with 4 to 8 atoms. The average value of the absolute deviation compared to the experimental values taken for a very large majority from JANAF (1985) or from Huber & Herzberg (1979) is found not to exceed 0.05 eV for a selected set of 53 molecules. The disagreement exceeds 0.2 eV for only 15 molecules, but most of the experimental values concerned can only be considered as roughly known dissociation energies or preliminary estimations not supported by convincing determinations. In fact, the major failure of the theory pointed out by the authors themselves, has been encountered for SO₂ with $(\Sigma D_0)_{\text{theory}} = 10.79 \text{ eV}$ (248.9 kcal mole⁻¹) compared to $(\Sigma D_0)_{\text{exp.}} = 11.013 \pm 0.007 \text{ eV}$ (1062.61 ± 0.66 kJ mole⁻¹) as derived from JANAF tables.

Variations in the Gaussian-2 theory have also been presented with calculations performed at higher or lower levels of treatment of the correlation energy (Curtiss et al. 1992, 1993). No great changes in accuracy have been pointed out in these studies which reveal the validity of the assumptions made in the initial treatment and the versatility of the method to treat small and large systems as well.

The Gaussian-2 method thus appears of good reliability. It can furnish a useful basis when a dissociation energy is unknown, and in case of gross disagreement with the experimental value, a situation which holds for MgO: $(D_0)_{\text{exp.}} = 3.53 \text{ eV}$ (cited as "quite uncertain" by Huber & Herzberg) and $(D_0)_{\text{theory}} = 2.57 \text{ eV}$ (59.2 kcal mole⁻¹), the theoretical value should be preferred.

4 Determinations of Dissociation Energies from Product Internal Energy Release of Chemical Reactions

4.1 Method

The method is based on the observation of nascent products from gas phase reactions produced under well defined conditions. It uses an atom-exchange reaction of type



The energetics of each independent reactive event are determined by applying the energy conservation law (Fig. 2)

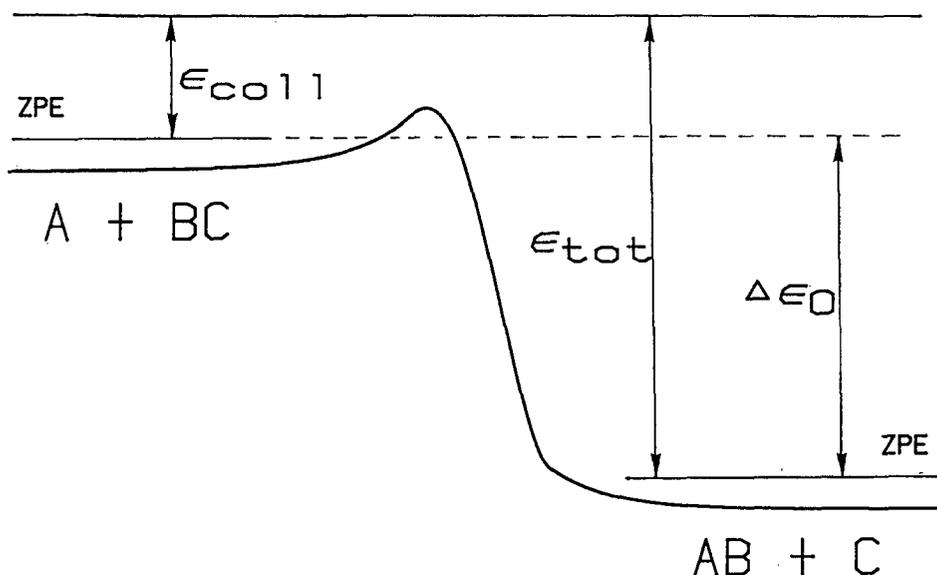


Fig. 2. Schematic representation of the potential energy along the reaction path, for an exoergic process.

$$\epsilon_{\text{tot}} = \epsilon_{\text{tr}} + \epsilon_i(A) + \epsilon_i(BC) - \Delta\epsilon_0 = \epsilon'_{\text{tr}} + \epsilon'_i(AB) + \epsilon'_i(C) \quad (12)$$

where ϵ_{tot} is the total energy available to the reaction products. The left side of Equation (12) refers to reactants: ϵ_{tr} is their relative translational energy (or kinetic energy of relative motion in the centre-of-mass frame) and the ϵ_i s stand for their internal energies. The right side of Equation (12) refers to the products of the reaction with ϵ'_{tr} defining their relative translational energy (also known as recoil energy) and the ϵ'_i their respective internal energies. The sum

$$\epsilon_{\text{coll}} = \epsilon_{\text{tr}} + \epsilon_i(A) + \epsilon_i(BC) \quad (13)$$

is also defined as the collision energy. The reaction energy

$$\Delta\epsilon_0 = D_0(\text{BC}) - D_0(\text{AB}) \quad (14)$$

is the difference between ZPE of products and reactants and obviously corresponds to the difference of the dissociation energies of BC and AB bonds.

In a typical experiment, one observes the energy release into the AB product to determine the highest energy level of AB populated by the reaction. This determination can be achieved by detecting chemiluminescence if the reaction directly produces AB in an excited radiative state. The spontaneous emission is then dispersed through a monochromator, giving information on the population densities of the upper electronic state of the transition observed. However, more detailed information can be obtained using laser-induced fluorescence (LIF): in that case, the absorption spectrum of AB is explored while scanning laser wavelength; furthermore, an extremely high signal-to-noise ratio can be achieved by collecting all (i.e. not dispersed) fluorescence photons emitted, at right angles of the laser beam. The latter method yields population densities in the lower electronic state of the transition probed.

Once the highest value of the AB internal energy has been found, it can be equated to the total energy ϵ_{tot} with the assumptions that these AB fragments of highest internal energy have recoiled from companion C fragments produced (i) without internal energy and (ii) with a relative translational energy that can be neglected (i.e. setting $\epsilon'_i(\text{C})$ and ϵ'_{tr} to zero in Equation (12)). These two assumptions, the validity of which is discussed and illustrated later on, allow the reaction energy to be evaluated from the knowledge of the collision energy. $D_0(\text{AB})$ can thus also be calculated provided $D_0(\text{BC})$ is accurately known.

The collision energy spread $\delta\epsilon_{\text{coll}}$ plays an essential role in the determination of a sharp population limit. The simplest operating conditions, achieved when performing the experiment in a cell at low pressure, are those that yield the largest collision energy spread. Better definition of the collision energy is achieved either in a beam-gas experiment where a beam of A atoms, generally with a Maxwell distribution of velocities, is scattered by AB molecules in a low pressure cell, or in a crossed molecular beam experiment. Finally, the best that can be done is to use crossed, supersonic molecular beams because these beams have high velocity resolution and give highly efficient cooling of the internal degrees of freedom ($\epsilon_i = 0$). Thus, the collision energy is well defined and almost equal to the reactant relative translational energy calculated from measured reactant velocities v_A and v_{BC} :

$$\epsilon_{\text{tr}} = \frac{1}{2} \mu (v_A^2 + v_{\text{BC}}^2 - 2v_A v_{\text{BC}} \cos \alpha) \quad (15)$$

Here, μ stands for the reactant reduced mass, and α for crossing angle of the two molecular beam axes. It is important to operate with collimated beams in order to keep the dispersion in translational energy arising from collisions with velocity vectors at angles around the mean value α as low as possible.

4.2 Application of the Method in a Crossed Beam Experiment

The instrument used for these experiments combines techniques of pulsed, crossed, supersonic molecular beams, LIF detection and atom generation by laser vaporization. The experimental conditions obtained with this instrument (Costes et al. 1987 and 1989) are particularly relevant for an accurate determination of dissociation energies by the method examined in the following.

Determination of the excitation limit. The excitation limit is determined by analysing the experimental spectra. This is achieved by generating synthetic spectra including the spectroscopy of the transition of interest (for instance, $B^2\Sigma^+ \leftrightarrow X^2\Sigma^+$ for AlO produced by the reaction $\text{Al} + \text{O}_2$), transition probabilities, apparatus function and rovibrational population distributions. The following distribution function, derived from the information-theoretic approach to the analysis of state-to-state reaction dynamics (Bernstein 1982) has been introduced to model the rotational populations:

$$P(v, J) = P^o(v, J) e^{-\beta_r \phi(J)} \quad (16)$$

The first term represents the prior expectation and the exponential term the deviance to the prior defining the reduced surprisal parameter, β_r ; the $\phi(J)$ function reads

$$\phi(J) = \frac{F(J)}{\epsilon_{\text{tot}} - \epsilon'_1(C) - G(v)} \quad (17)$$

where $G(v)$ and $F(J)$ stand for vibrational and rotational energies of the diatomic fragment, AB, for corresponding vibrational and rotational quantum numbers v and J .

Taking a statistical distribution as the prior expectation yields:

$$P^o(v, J) \propto (2J + 1) \{\epsilon_{\text{tot}} - \epsilon'_1(C) - G(v) - F(J)\}^{1/2} \quad (18)$$

In the fitting procedure, the surprisal parameter, β_r , the energy available to the products, ϵ_{tot} , and the respective weights of the vibrational levels are adjusted to give a close match to the experimental spectra.

When the distribution is close to statistical (i.e. $\beta_r \rightarrow 0$), the rotational population sharply falls off in the vicinity of the excitation limit, which thus allows for a clear observation of this limit. In this very favourable case, the rotational distribution function is only slightly affected by the β_r value. The spectrum can thus be fitted with a single parameter (apart from the vibrational populations): the energy available to products, ϵ_{tot} .

This case is exemplified by the LIF spectra of AlO (from $\text{Al} + \text{O}_2$ reaction), as shown in Fig. 3. Only the part of the spectra in the region of the excitation limit is displayed. Synthetic spectra computed with extreme values of $\epsilon_{\text{tot}} = 0.213$ to 0.243 eV are also displayed. Among the different features, the (1-0)P(53) line appears to be clearly underestimated at $\epsilon_{\text{tot}} = 0.213$ eV (Fig. 3-b), and overestimated at $\epsilon_{\text{tot}} = 0.243$ eV (Fig. 3-c). The best fit is obtained when a ϵ_{tot} value of 0.228 eV is introduced into the calculation.

In this example, it is noteworthy that a variation of ± 15 meV significantly alters the spectrum appearance, thus emphasizing the sensitivity of the method.

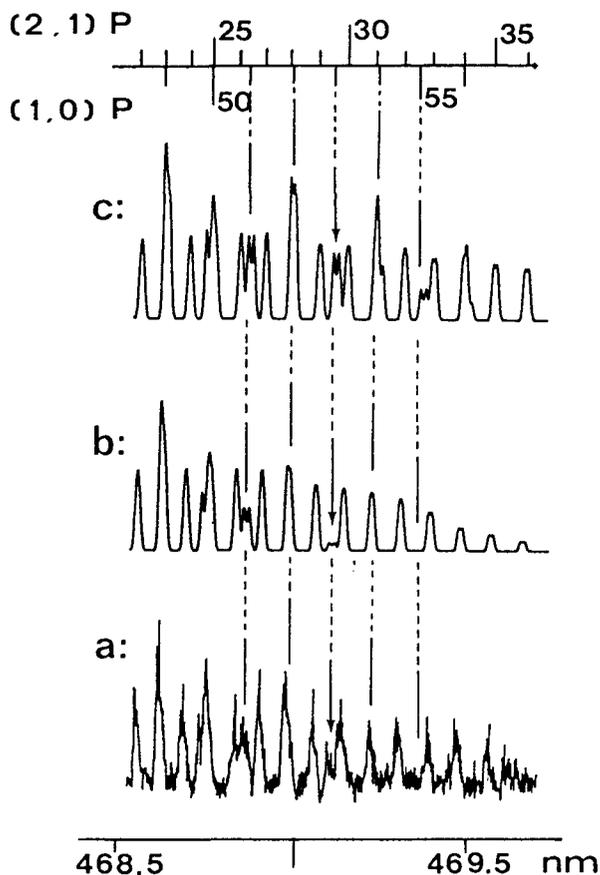


Fig. 3. Part of the LIF spectrum of $\text{AlO}(B^2\Sigma^+ \leftrightarrow X^2\Sigma^+, \Delta v = 1)$ from the $\text{Al} + \text{O}_2 \rightarrow \text{AlO} + \text{O}$ reaction at $\epsilon_{\text{tr}} = 0.083 \text{ eV}$: (a) experimental, (b) calculated for $\epsilon_{\text{tot}} = 0.213 \text{ eV}$ and (c) calculated for $\epsilon_{\text{tot}} = 0.243 \text{ eV}$; rotational line labelling refers to the N quantum number (total angular momentum apart from spin), with $J = N \pm \frac{1}{2}$ for a doublet state.

Determination of the reactant translational energy. The reactant relative translational energy is determined, using Equation (15), by measuring the reactant beam velocities. The dispersion results from several uncertainties: the error on the velocity measurement of both beams, which does not exceed 5 % in the worst case, the velocity spread around the mean values, which ranges between 10 and 20 % full-width at half-maximum, and the effect of collisions at angles different from the mean value $\alpha = 90^\circ$.

Determination of the reactant and companion-fragment internal energies. Reactants are cooled down within the supersonic expansion. Consequently, only the lowest levels of the ground-state manifold of the BC molecule are signif-

icantly populated, with residual internal energy not exceeding a few meV. The situation for the atom beam is less favourable, because the cooling processes have to start from the very high energy imparted to the atoms in the laser-generated plasma. In particular, if the ground state is a multiplet, all spin-orbit components can be significantly populated: in the case of aluminium atoms, for instance, both spin-orbit levels of the ground state, $^2P_{1/2}$ and $^2P_{3/2}$ ($\epsilon = 14$ meV), are almost equally populated. This is taken into account in the fitting procedure. In the case of carbon atoms, where the respective weights of individual spin-orbit components cannot be measured by LIF, because the absorption lines lie too far in the vuv, the spin-orbit energy is introduced by broadening the uncertainty domain by the value of the energy of the highest excited component ($\epsilon(^3P_2) = 5.4$ meV).

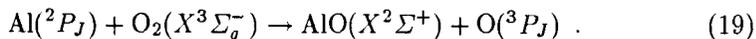
The companion fragment can be produced in any internal state. Unfortunately, it is out of reach to determine its internal energy distributions for each internal state of the first outcome. The following cases have been considered:

(i) 3-atom case: the companion fragment (second outcome) is an atom; a statistical distribution over spin-orbit terms is assumed; the rotational distribution function of the diatomic product (first outcome) is then computed as a linear combination of individual distribution functions calculated with an internal energy and a statistical weight corresponding to each spin-orbit energy of the outcoming atom; the procedure is repeated for each spin-orbit component of the incoming atom;

(ii) 4-atom case: the second outcome now is a diatom as in the example reported here ($\text{Si} + \text{N}_2\text{O} \rightarrow \text{SiN} + \text{NO}$). Without measurement of the recoil energy, it becomes generally not possible to fit the experimental spectra with a single distribution function. However, this restriction no longer holds when the data can be fitted to a completely statistical distribution, as found for the endoergic $\text{Si} + \text{N}_2\text{O}$ reaction at collision energies close to the reaction threshold. Such a statistical distribution is computed by direct summation over the number of states of the second diatom outcome that can be populated by the reaction at a given total energy, for each state of the first outcome, assuming all states equiprobable.

4.3 Results: Determination of Dissociation Energies of AlO, CN and SiN

$D_0(\text{AlO})$. The dissociation energy of AlO has been derived from the crossed-beam study (Costes et al. 1987) of the reaction:



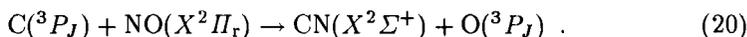
As illustrated above, the excitation limit, and hence the reaction energy $\Delta\epsilon_0 = 0.145 \pm 0.030$ eV is derived from the analysis of LIF spectra of the AlO product. This combined with the O_2 dissociation energy $D_0(\text{O}_2) = 5.1156 \pm 0.002$ eV gives the AlO dissociation energy $D_0(\text{AlO}) = 5.26 \pm 0.03$ eV.

This reaction was first studied by Dagdigian et al. (1975) in a beam-gas arrangement using an effusive Al source. They deduced a value of the AlO dissociation energy $D_0(\text{AlO}) = 5.27 \pm 0.04$ eV. This result was confirmed by Pasternack

& Dagdigian (1977), again in a beam-gas study but with a velocity selected, effusive Al source: $D_0(\text{AlO}) = 5.27 \pm 0.02 \text{ eV}$.

Our result is in excellent agreement since the value of the AlO dissociation energy is found within the uncertainty range of these two previous studies (note that the JANAF value is based – among others – on the determination of Pasternack & Dagdigian 1977).

$D_0(\text{CN})$. The dissociation energy of CN has been derived from the crossed-beam study (Costes et al. 1990) of the reaction:



The same method as for AlO was used. The exoergicity of the reaction, $\Delta\epsilon_0 = -1.27 \pm 0.05 \text{ eV}$ is deduced from the determination of the excitation limit of the CN product. Introducing the value of the NO dissociation energy (6.4968 eV) recommended in the compilation of Huber & Herzberg (1979) yields $D_0(\text{CN}) = 7.77 \pm 0.05 \text{ eV}$.

A first group of experimental determinations of $D_0(\text{CN})$ in the last twenty years has used spectroscopic measurements on $\text{CN}(B^2\Sigma^+ \leftrightarrow X^2\Sigma^+)$ violet transitions for laboratory sources: Arnold & Nicholls (1973): $7.89 \pm 0.13 \text{ eV}$, Engleman and Rouse (1975): $7.66 \pm 0.05 \text{ eV}$, Colket (1984): $7.92 \pm 0.07 \text{ eV}$, or ($A^2\Pi_1 \leftrightarrow X^2\Sigma^+$) red transitions in the solar spectrum: Sinha & Tripathi (1986): $7.71 \pm 0.05 \text{ eV}$. All these determinations which are based on the use of Equation (5) with three parameters to work with (the source temperature, the band oscillator strength of the transition analysed and the CN dissociation energy) cannot be considered as very accurate. Only the shock-tube experiments of Arnold and Nicholls, performed at three very different temperatures, could yield both the band oscillator strength and the dissociation energy. Furthermore, the uncertainties quoted reflect more a deviation from an assumed fit, except the one given by Arnold and Nicholls, than a value including possible systematic errors.

A second group of determinations has used the laser photofragmentation of the cyanogen molecule, $(\text{NC-CN}) \rightarrow \text{CN} + \text{CN}$. This type of experiment directly yields $D_0(\text{NC-CN})$: $5.83 \pm 0.04 \text{ eV}$ ($47000 \pm 300 \text{ cm}^{-1}$, Eres et al. 1984), $5.84 \pm 0.04 \text{ eV}$ ($47100 \pm 300 \text{ cm}^{-1}$, Wannemacher et al. 1990), $5.84 \pm 0.02 \text{ eV}$ (Huang et al. 1992). It also yields indirectly $\Delta_f H_0(\text{CN})$

$$2\Delta_f H_0(\text{CN}) = D_0(\text{NC-CN}) + \Delta_f H_0(\text{NC-CN}) \quad (21)$$

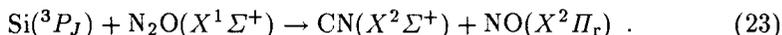
and $D_0(\text{CN})$

$$D_0(\text{CN}) = \Delta_f H_0(\text{C}) + \Delta_f H_0(\text{N}) - \Delta_f H_0(\text{CN}) \quad (22)$$

$\Delta_f H_0(\text{N}) = \frac{1}{2} D_0(\text{N}_2)$ is a reference value, already cited, and $\Delta_f H_0(\text{C}) = 711.19 \pm 0.46 \text{ kJ mole}^{-1}$ can reasonably be considered likewise. Thus, the confidence on the value of $D_0(\text{CN})$ obtained: $7.75 \pm 0.04 \text{ eV}$, $7.74 \pm 0.04 \text{ eV}$ and $7.74 \pm 0.03 \text{ eV}$ depends mostly on the confidence on the third standard enthalpy of formation at 0 K: $\Delta_f H_0(\text{NC-CN}) = 307.219 \pm 1.8 \text{ kJ mole}^{-1}$ following JANAF.

There has been also a number of theoretical determinations. Only the more recent studies will be considered here. Bauschlicher et al. (1988) used the multireference configuration interaction (MRCI) method, with an extended basis set of atomic orbitals: the pure calculation yielded $D_0(\text{CN}) = 7.53 \text{ eV}$, which was rescaled to $D_0(\text{CN}) = 7.65 \text{ eV}$, by comparison with the experimental $D_0(\text{N}_2)$ value and the computed one using the same basis set. Bauschlicher et al. estimated the accuracy of their determination to be within 0.06 eV . The result of the Gaussian-2 theory (Curtiss et al. (1991): $D_0(\text{CN}) = 7.63 \text{ eV}$ ($176.0 \text{ kcal mole}^{-1}$)) falls into this interval. We have taken great care in our own work to check for all possible systematic errors. Our D_0 value of $7.77 \pm 0.05 \text{ eV}$ could only suffer from two of these: (i) an error on $D_0(\text{NO})$ and (ii) the failure of the $\text{C} + \text{NO}$ reaction to populate the $\text{CN}(X^2\Sigma^+)$ manifold up to the total energy available to reaction products, which could only be checked by measuring the recoil energy distribution. The former appears very unlikely and if the latter was occurring, it would lead to a lower limit of $D_0(\text{CN})$, increasing the difference with the ab initio results. Finally, it should be noted that the D_0 values derived from the photodissociation of $(\text{NC} - \text{CN})$ can also be influenced by these two types of possible systematic errors.

$D_0(\text{SiN})$. The dissociation energy of SiN has been derived from the determination of the excitation limit of SiN produced in a crossed-beam experiment (Naulin et al. 1993) by the reaction:



An experimental value of $0.25 \pm 0.13 \text{ eV}$ has been found for the reaction energy, which can be expressed as:

$$\Delta\epsilon_0 = D_0(\text{N-NO}) - D_0(\text{SiN}) . \quad (24)$$

The N-NO dissociation energy can be derived from dissociation energies of the diatomics N_2 , O_2 and NO , already cited as reference values, and standard formation enthalpy of N_2O at 0 K ($85.48 \pm 0.4 \text{ kJ mole}^{-1}$ following JANAF):

$$D_0(\text{N-NO}) = D_0(\text{N}_2) + \frac{1}{2}D_0(\text{O}_2) - D_0(\text{NO}) - \Delta_f H_0(\text{N}_2\text{O}) = 4.93 \pm 0.01 \text{ eV} \quad (25)$$

Introducing the obtained values for $D_0(\text{N-NO})$ and $\Delta\epsilon_0$ in Equation (24) yields: $D_0(\text{SiN}) = 4.68 \pm 0.14 \text{ eV}$. This experimental value is substantially different from the imprecise JANAF value $D_0(\text{SiN}) = 5.64 \pm 0.65 \text{ eV}$ ($130 \pm 15 \text{ kcal mole}^{-1}$) but is in good agreement with the theoretical determination of Curtiss et al. (1991): $D_0(\text{SiN}) = 4.58 \text{ eV}$ ($105.6 \text{ kcal mole}^{-1}$). It is again important to note that if the reaction fails to populate the highest energetically accessible levels of SiN, the present determination would be an underestimate. Since the theoretical $D_0(\text{SiN})$ value already lies close to the lower limit of the experimental determination, a higher experimental value would significantly depart from the theoretical prediction. Given the accuracy and consistency of the Gaussian-2 method for a huge number of species, such a discrepancy for SiN seems unlikely.

5 Determinations of Dissociation Energies from Product Energy Release of Laser-Photofragmentation Reactions

For a photodissociation reaction induced by the absorption of n laser-light photons of energy $h\nu$:



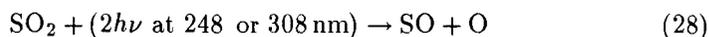
The total energy shared by the photofragments is written, similarly to Equation (12):

$$\epsilon_{\text{tot}} = n h \nu + \epsilon_i(ABC) - D_0(AB - C) = \epsilon'_{\text{tr}} + \epsilon'_i(AB) + \epsilon'_i(C) . \quad (27)$$

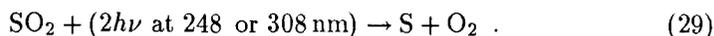
Different experiments can be used. The main difference between these and the method described in section 4 is that even a rather simple experiment performed with two pulsed lasers, by photolyzing the molecule in a cell at low pressure and probing the nascent AB photofragments, can furnish fairly accurate results. This is because the spread in relative translational energy, which is always difficult to fight in reactive scattering experiments, is now replaced by the bandwidth of the photolyzing laser. In the worst case, an excimer laser delivers the high flux of necessary photons at most useful lines of 193 nm, 248 nm and 308 nm with a bandwidth of 150 cm^{-1} . Double dye laser outputs which furnish the opportunity to scan through the absorption spectrum can be emitted in less than 1 cm^{-1} at wavelengths approaching 200 nm. Furthermore, if cooling of the internal energy of the sample is achieved by using a molecular beam, the total energy can be incomparably well defined.

As in section 4, the validity of the measurement is dependent on the same kind of assumptions if only $\epsilon'_i(AB)$, but not ϵ'_{tr} , is probed. However, a high flux of photoproducts along with a perfect timing of the experiment allow for using more powerful techniques like photofragment translational spectroscopy (PTS). The photofragment, after leaving the photolysing zone in the molecular beam and travelling without suffering collisions through a time-of-flight (TOF) tube, is then detected by mass spectrometry or by laser techniques such as resonance-enhanced-multiphoton ionisation (REMPI). The vibrational and even the rotational structure can be apparent in the TOF spectrum, and the threshold in the translational energy spectrum reveals the value of ϵ_{tot} and thus $D_0(AB-C)$.

These PTS techniques have been for example used in the photodissociation of SO_2 by Effenhauser et al. (1990) who have detected the SO and S photofragments from reactions



and



All observed kinetic thresholds of the various pathways leading to the different electronic states energetically accessible were compatible with $D_0(\text{SO}-\text{O}) = 5.628 \text{ eV}$ (543 kJ mole^{-1}) and $\Delta\epsilon_0 = 5.897 \text{ eV}$ (569 kJ mole^{-1}) for the $\text{SO}_2 \rightarrow \text{S} + \text{O}_2$ reaction. Using $D_0(\text{O}_2) = 5.1156 \pm 0.0019 \text{ eV}$ it can also be

deduced that the total atomisation energy is $\Sigma D_0 = 11.013$ eV and that $D_0(\text{SO}) = 5.385$ eV. Using the JANAF values for $\Delta_f H_0(\text{S}) = 274.73 \pm 0.25$ kJ mole⁻¹, $\Delta_f H_0(\text{SO}_2) = -294.299 \pm 0.21$ kJ mole⁻¹, $\Delta_f H_0(\text{SO}) = 5.03 \pm 1.3$ kJ mole⁻¹ and $\Delta_f H_0(\text{O}) = \frac{1}{2} D_0(\text{O}_2)$ (mentioned above) yields the following values: $D_0(\text{SO-O}) = 5.660 \pm 0.017$ eV (546.12 ± 1.61 kJ mole⁻¹), slightly overestimated, $\Sigma D_0 = 11.013 \pm 0.007$ eV (1062.61 ± 0.66 kJ mole⁻¹), in perfect agreement, and $D_0(\text{SO}) = 5.353 \pm 0.015$ eV (516.49 ± 1.65 kJ mole⁻¹), subsequently slightly underestimated by the same amount as found in $D_0(\text{SO-O})$.

Sophisticated laser techniques including production of vuv radiation at the Lyman-alpha wavelength, 121.6 nm, and coupled with H atom PTS experiments have been recently used in the laser photodissociation of HCN by Morley et al. (1992). The HCN dissociation energy obtained, $D_0(\text{H-CN}) = 5.423 \pm 0.019$ eV (43740 ± 150 cm⁻¹) reduces the uncertainty compared to the JANAF value 5.36 ± 0.19 eV (517.3 ± 18.4 kJ mole⁻¹) based on $\Delta_f H_0(\text{H}) = 216.035 \pm 0.006$ kJ mole⁻¹, $\Delta_f H_0(\text{CN}) = 436.8 \pm 10$ kJ mole⁻¹ and $\Delta_f H_0(\text{HCN}) = 135.53 \pm 8.4$ kJ mole⁻¹.

6 Conclusion

Abundance analyses of atomic species derived from molecular opacities are more sensitive to the values of dissociation energies than to partition functions that are introduced into the calculations. Some of the worse cases, such as the dissociation energy of CN, now appear to be resolved. Most dissociation energies will be determined with high accuracy in the near future, by the extensive use of laser-based methods employing tunable vuv light.

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