

- [4] R. W. Field, R. S. Bradford, H. P. Broida, and D. O. Harris, *J. chem. Physics* 57, 2209 (1972).
 [5] K. Sakurai, S. E. Johnson, and H. P. Broida, *J. chem. Physics* 52, 1625 (1970).
 [6] S. E. Johnson, *J. chem. Physics* 56, 149 (1972); and S. E. Johnson, Ph. D. thesis, University of California, Santa Barbara 1972.
 [7] J. Hoelt, F. J. Lovas, E. Tiemann, and T. Törring, *Z. Naturforsch.* 25a, 1750 (1970).
 [8] A. Dienes, E. P. Ippen, and C. V. Shank, *IEEE J. Quantum Elect.* QE-8, 388 (1972).
 [8] H. W. Kogelnik, E. P. Ippen, A. Dienes, and C. V. Shank, *IEEE J. Quantum Elect.* QF-8, 373 (1972).
 [10] M. Hercher and H. P. Pike, *Optics Commun.* 3, 65 (1971).
 [11] S. E. Johnson, G. A. Capelle, and H. P. Broida, *J. chem. Physics* 56, 663 (1972).
 [12] G. A. Capelle, R. S. Bradford, and H. P. Broida, *Chem. Physics Letters* 21, 418 (1973).
 [13] R. S. Bradford (private communication).
 [14] R. W. Field (private communication).
 [15] J. West (private communication).
 [16] P. C. Mahanti, *Proc. Phys. Soc.* 46, 51 (1934).
 [17] A. Lagerqvist, E. Lind, and R. F. Varrow, *Proc. Phys. Soc.* 63A, 1132 (1950).
 [18] I. Kovács and A. Lagerqvist, *Arkiv Fysik* 2, 411 (1950).
 [19] A. Schultz, H. W. Cruse, and R. N. Zare, *J. chem. Physics* 57, 1354 (1972).
 [20] R. W. Field, " π Perturbations in CaO, SrO, and BaO", *J. chem. Physics* in press.

E 2759

Fluorescence of Free Radicals: A Method for Determining Dissociation Energy Limits

By Richard N. Zare

Department of Chemistry, Columbia University, New York, New York 10027, U.S.A.

Atom- und Molekularstrahlen / Fluoreszenz / Freie Radikale / Lumineszenz / Thermodynamik

In an elementary gas-phase atom-transfer reaction, $A + BC \rightarrow AB + C$, a lower bound to the dissociation energy of the AB molecule can be deduced from a knowledge of the dissociation energy of the BC molecule and from the knowledge of the highest internal state of the AB product that is populated by the reactive collision process. This latter information may be obtained spectroscopically either from detection of AB chemiluminescence or from detection of the AB product through laser-induced fluorescence. These two methods are illustrated for the elementary reactions $Al + O_3$ and $Al + O_2$, from which lower bounds are derived for $D_0^0(AlO)$ of 5.13 ± 0.06 eV and 5.23 ± 0.04 eV, respectively.

In einer elementaren Atomübertragungsreaktion in der Gasphase ($A + BC \rightarrow AB + C$) läßt sich eine untere Grenze für die Dissoziationsenergie des Moleküls AB ableiten aus der Kenntnis der Dissoziationsenergie des Moleküls BC und des obersten inneren Zustandes des Produkts AB, der bei dem reaktiven Zusammenstoß besetzt wird. Letztere Information kann man auf spektroskopischem Wege entweder über den Nachweis der Chemilumineszenz von AB oder dessen laser-angeregten Fluoreszenz erhalten. Diese zwei Methoden werden für die Elementarreaktionen $Al + O_3$ und $Al + O_2$ beschrieben, woraus die unteren Grenzen für $D_0^0(AlO)$ mit $5,13 \pm 0,06$ eV bzw. $5,23 \pm 0,04$ eV abgeleitet werden.

I. Introduction

The dissociation energy $D_0^0(AB)$ of a diatomic molecule AB is the energy required to separate the AB molecule in the lowest vibrational-rotational level of its ground electronic state into its constituent atoms A and B. Values of $D_0^0(AB)$ may be deduced rather directly from spectroscopic studies of the AB molecule [1, 2], most commonly through band convergence limits, extrapolation of such convergence limits, long-wavelength-limits of absorption continua, and pre-dissociation limits (breaking-off in rotational structure). The dissociation energy of $D_0^0(AB)$ is closely related to the heat of reaction ΔH for the gas-phase process



Here ΔH is a temperature-dependent thermodynamic quantity which involves the average thermal energies (internal and translational) of the reactants, A and B, and the products, AB, at a temperature T . However, as T approaches 0°K, ΔH becomes identical to $D_0^0(AB)$. It is this equality that provides one of the fundamental links between spectroscopic studies and thermodynamic calculations, which are at the heart of chemistry.

Despite the importance of dissociation energies, the detailed application of spectroscopic data to their determination has been rather uncertain in a number of important cases. This failure is particularly apparent for molecules that are transient high-temperature species with deep potential wells, such as many free radicals of interest. In these molecules, often, only the lowest-lying vibrational levels are known, and spectroscopically derived dissociation energies based on long band-convergence extrapolations are suspect. Moreover, because of the reactive nature of these species, thermodynamically derived dissociation energies, based on a concatenation of other uncertain bond energy values, heats of vaporization, etc., or based on uncertain assumptions that thermodynamic equilibrium has been obtained, are also often unconvincing.

We describe here a new method of determining dissociation energies through the spectroscopic study of elementary bimolecular exchange reactions [3, 4]. Here the reaction



is carried out under single-collision conditions using molecular beam techniques. The heat of reaction is derived, or more precisely, an upper bound to ΔH is determined by

measuring the internal energy of the products through spectroscopic means involving either their visible chemiluminescence or their laser-induced fluorescence. The value or limit to the value of ΔH_T is then extrapolated to $T = 0^\circ\text{K}$, where ΔH_0 corresponds to the energy difference $D_0^0(\text{AB}) - D_0^0(\text{BC})$. If the dissociation energy of BC is known previously, then an estimate for $D_0^0(\text{AB})$ may be obtained. Thus in this procedure we derive the heats of elementary reactions using spectroscopic means based on fluorescence, either natural or induced, of the products. We illustrate this procedure by deriving bounds on the dissociation energy of the free radical, aluminum monoxide (AlO). First the chemiluminescent reaction $\text{Al} + \text{O}_3$, previously reported by Gole and Zare [5], is discussed. Then, the unpublished preliminary results of the laser-induced fluorescence study of $\text{Al} + \text{O}_2$ obtained by H. W. Cruse and P. J. Dagdigian of this laboratory are presented.

II. Determination of a Lower Bound to $D_0^0(\text{AlO})$ from the Elementary Reaction $\text{Al} + \text{O}_3$

Most chemical reactions do not yield electronically excited products. However, for those that do, an analysis of the chemiluminescent emission provides an excellent means of establishing bounds on the internal energy of the products. In practice, however, chemiluminescent studies often suffer from the occurrence of multiple secondary reactions that obscure the luminescence produced by a given reaction. To overcome this problem, we have constructed a molecular beam apparatus [3–5], called Labstar, in which metal atoms from a differentially-pumped oven source chamber traverse a scattering chamber where they intersect a poorly-defined beam of reactant molecules. At low reactant pressures, the configuration approaches crossed molecular beams, while at higher pressures the setup is that of a scattering chamber filled with reactant gas. The chemiluminescence is detected with a one-meter Interactive Technology Czerny-Turner spectrometer which views the reaction through a part in the scattering chamber.

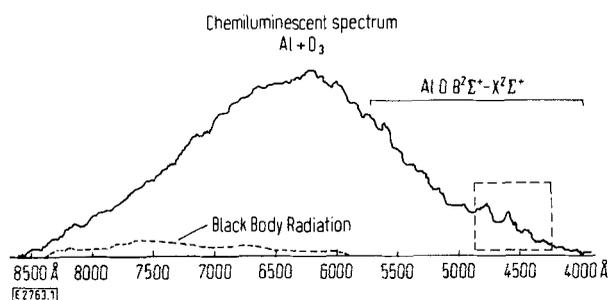


Fig. 1

Chemiluminescent spectrum for the reaction of Al with O_3 . Black-body radiation from the oven is indicated by dotted lines in the figure. The portion of the spectrum enclosed by the dashed lines is shown at higher resolution in Fig. 2

Fig. 1 shows a rapid scan scan (500 Å/min) of the chemiluminescence accompanying the reaction $\text{Al} + \text{O}_3$ when a thermal beam of aluminum atoms ($\approx 1700^\circ\text{K}$) intersects an uncollimated thermal beam of ozone molecules ($\approx 300^\circ\text{K}$). The chemiluminescence spectrum consists of (1) the $\text{AlO } B^2\Sigma^+ -$

$X^2\Sigma^+$ blue-green band system and (2) a more intense but less structured emission continuum which appears to be from a polyatomic aluminum oxide, most likely AlO_2^* . Fig. 2 shows

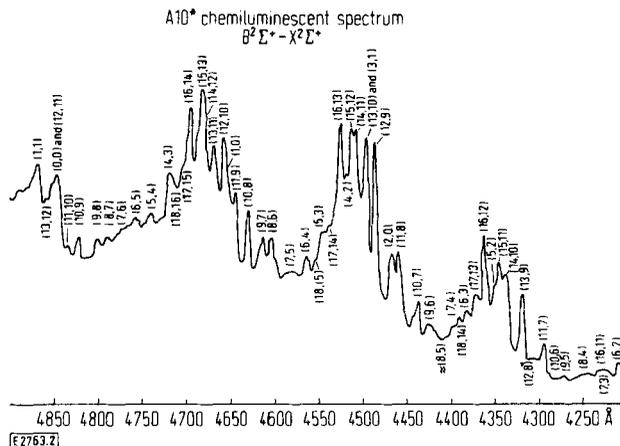


Fig. 2

$\text{AlO } B^2\Sigma^+ - X^2\Sigma^+$ chemiluminescence resulting from the reaction $\text{Al} + \text{O}_3$

a slower scan (50 Å/min) of the $\text{AlO}-X$ system between 4200 Å and 4900 Å. Here we have identified transitions from $0 \leq v' \leq 18$ of the B state to $0 \leq v'' \leq 16$ of the X state. Of prime importance to the determination of $D_0^0(\text{AlO})$ is the positive identification that the level $v' = 18$ is populated by the reaction



We now turn to the calculation of a lower bound to $D_0^0(\text{AlO})$ based on this spectroscopic observation. In the above reaction, the energy liberated in the formation of the strong Al–O bond of aluminum monoxide is considerably in excess of the energy required to rupture the weak O–O₂ bond of ozone. This reaction exoergicity must appear as internal excitation of the AlO molecules, as internal excitation of the O₂ molecules, and as relative final translational energy of the products.

Conservation of energy requires that all forms of energy on the righthand side of Equation (3) exactly balance all forms of energy on the lefthand side of Equation (3). With the choice of $\text{Al}(^2\text{P}) + \text{O}(^3\text{P}) + \text{O}_2(X^3\Sigma_g^-, v'' = 0, J'' = 0)$ as the reference energy, we may write the equality

$$-D_0^0(\text{O}-\text{O}_2) + E_{\text{int}}(\text{O}_3) + E_t(\text{reactants}) = -D_0^0(\text{AlO}) + E_{\text{int}}(\text{AlO}) + E_{\text{int}}(\text{O}_2) + E_t(\text{products}) \quad (4)$$

where $E_{\text{int}}(\text{O}_3)$, $E_{\text{int}}(\text{AlO})$, and $E_{\text{int}}(\text{O}_2)$ are the internal energies (electronic, vibrational, rotational) of O₃, AlO, and O₂, respectively, measured from the lowest energy level of each species, and $E_t(\text{reactants})$ and $E_t(\text{products})$ are respectively the center-of-mass translational energy of the reactants and products.

The energy sum, $E_{\text{int}}(\text{O}_2) + E_t(\text{products})$, is unknown and cannot be found from the chemiluminescent spectrum. By neglecting this sum we obtain the inequality

$$D_0^0(\text{AlO}) \geq E_{\text{int}}(\text{AlO}) + D_0^0(\text{O}-\text{O}_2) - E_{\text{int}}(\text{O}_3) - E_t(\text{reactants}). \quad (5)$$

The value of $E_{\text{int}}(\text{AlO})$ is calculated from the expression

$$\begin{aligned} E_{\text{int}}(\text{AlO}) &= E(\text{AlO } B^2\Sigma^+ v' = 18) \\ &\quad - E(\text{AlO } X^2\Sigma^+ v'' = 0) \\ &= 34947 \pm 50 \text{ cm}^{-1} (4.33 \text{ eV}). \end{aligned} \quad (6)$$

The value for $E_{\text{int}}(\text{O}_3)$ is estimated as $\frac{3}{2}RT = 0.04 \text{ eV}$, where account is taken of the rotational energy of the O_3 molecule but where the possible excitation of the ν_2 bending mode is ignored. The value of $D_0^0(\text{O}-\text{O}_2)$ is taken as $1.05 \pm 0.02 \text{ eV}$, where the uncertainty reflects the uncertainty in the calorimetric determination of the standard heat of formation of ozone [5]. Finally, the quantity $E_t(\text{reactants})$ can be only crudely estimated. We start from the expression

$$\begin{aligned} E_t(\text{reactants}) &= \frac{\frac{1}{2}m(\text{Al})m(\text{O}_3)}{m} v_{\text{rel}}^2 \\ &= \frac{\frac{1}{2}m(\text{Al})m(\text{O}_3)}{m} [v^2(\text{Al}) + v^2(\text{O}_3) - 2v(\text{Al}) \cdot v(\text{O}_3)] \end{aligned} \quad (7)$$

where $m = m(\text{Al}) + m(\text{O}_3)$ is the total mass of the reactants, and $v(\text{Al}) - v(\text{O}_3)$ is the relative velocity of the reactants in the center-of-mass reference frame. For the purposes of obtaining a *lower bound*, we generously estimate $E_t(\text{reactants})$ by taking the velocity of the collision partners as opposed in direction. With the additional assumptions [6] that $v(\text{Al})$ may be taken as the most probable velocity of an effusive beam, $v(\text{Al}) = [3RT(\text{Al})/m(\text{Al})]^{1/2}$, and that $v(\text{O}_3)$ may be taken as the most probable velocity of O_3 inside a volume, $v(\text{O}_3) = [2RT(\text{O}_3)/m(\text{O}_3)]^{1/2}$, we obtain the expression

$$\begin{aligned} E_t(\text{reactants}) &= \frac{3}{2}RT(\text{Al})m(\text{O}_3)/m \\ &\quad + RT(\text{O}_3)m(\text{Al})/m \\ &\quad + (6)^{1/2}R[T(\text{Al})T(\text{O}_3)]^{1/2}[m(\text{Al})m(\text{O}_3)]^{1/2}/m \\ &= 0.215 \pm 0.04 \text{ eV}. \end{aligned} \quad (8)$$

Here the uncertainty placed on $E_t(\text{reactants})$ represents the spread of values in E_t if we had used the root mean square velocity rather than the most probable velocity for the Al beam and the O_3 gas.

Substituting the above numerical values into Equation (5) we obtain

$$D_0^0(\text{AlO}) \geq 5.13 \pm 0.06 \text{ eV}. \quad (9)$$

This limit differs insignificantly from the limit of $D_0^0(\text{AlO}) \geq 5.13 \pm 0.05 \text{ eV}$ previously given by Gole and Zare [5] where the translational energy was calculated somewhat differently. Note that Equation (9) would be an equality if the products depart with zero translational energy in the center-of-mass system (an untenable condition) and the O_2 molecule is unexcited (a quite possible condition). If we assume for the purposes of making a more reasonable estimate that the products separate at right angles with a common translational temperature of 600°K , then the estimate of $D_0^0(\text{AlO})$ must be increased by 0.08 eV , i.e., $D_0^0(\text{AlO}) \geq 5.21 \pm 0.06 \text{ eV}$.

However, the largest uncertainty in this procedure remains the question whether $E_t(\text{reactants})$ has been correctly estimated. As Thrush [7] has pointed out, chemiluminescent reactions are usually rare reaction pathways and there may exist an activation energy to the process. If appreciable

relative translational energy is necessary to overcome this activation barrier, then our estimate of $E_t(\text{reactants})$ will be too low, and our estimate for a lower bound to $D_0^0(\text{AlO})$ will be correspondingly too high.

III. Determination of a Lower Bound to $D_0^0(\text{AlO})$ from the Elementary Reaction $\text{Al} + \text{O}_2$

Most chemical reactions are not as exothermic as $\text{Al} + \text{O}_3$, and one does not expect to observe visible chemiluminescence from the products. Consequently, one seeks another method for characterizing the internal states of the products of an elementary reaction process. Molecular beam studies traditionally have relied on surface ionizers or electron-impact-ionizer-massfilters to detect the reaction products [8]. However, both these techniques essentially are "blind" to the internal state of excitation of the products. We have developed a new technique for overcoming this blindness by utilizing "a search light" as part of the detection scheme [9, 10]. Here, a tunable dye laser is scanned in wavelength and the fluorescence of the reaction products is detected. Whenever the wavelength of the laser beam coincides with a molecular absorption line, corresponding to a specific $(v, J) \rightarrow (v', J')$ transition, those molecules in the (V, J) level are excited and subsequently fluorescence. By measuring the intensity of the fluorescence signal as a function of laser wavelength, it is possible to deduce the relative (v, J) population distribution from a knowledge of Franck-Condon factors and photomultiplier wavelength response factors.

Clearly the development of such a sensitive and selective molecular-beam product detector promises to advance our fundamental understanding of the dynamics of elementary reactions. However, from the viewpoint of dissociation energies, what is important is that we have a means of determining the highest (v'', J'') level populated in a given reaction. With this knowledge we can once again set a lower bound on the dissociation energy of the newly-formed product molecule, as in the case of the chemiluminescent data.

Note that the laser-induced fluorescence technique requires that the products have fluorescence bands conveniently accessible in the range of a tunable dye laser. Free radical products with their low-lying electronic states are particularly

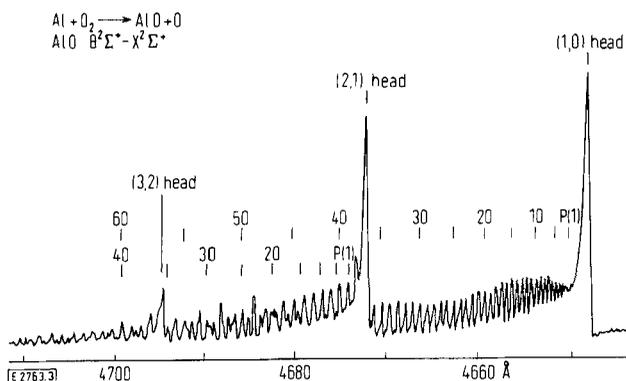


Fig. 3
Excitation spectrum ($\Delta v = 1$ sequence) of AlO formed in the reaction of $\text{Al} + \text{O}_2$

well-suited for the application of this technique. Successes using a tunable dye laser to carry out kinetic studies have already been reported for the alkaline earth oxides [9], the alkaline earth halides [10], and CN [11]. We report here the first preliminary results on AIO obtained by Cruse and Dagdigian in our laboratory.

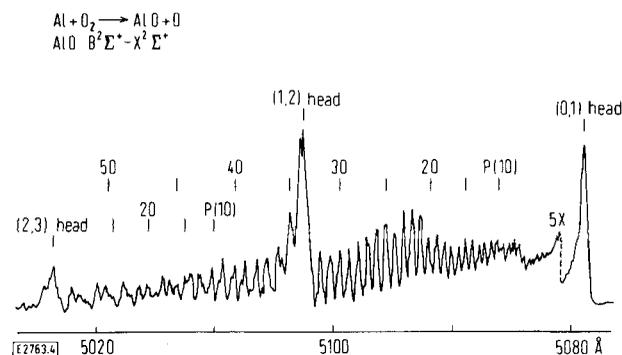


Fig. 4

Excitation spectrum ($\Delta v = -1$ sequence) of AIO formed in the reaction $\text{Al} + \text{O}_2$

Fig. 3 and 4 show the excitation spectra obtained when a beam of aluminum atoms passes through a scattering chamber filled with O_2 molecules at pressures between $2 \cdot 10^{-5}$ and $8 \cdot 10^{-5}$ Torr. The band heads formed in the R branch are clearly apparent as are the well-resolved P-branch members. Fig. 3 shows parts of the scan of the $\Delta v = 1$ sequence. The (1,0) band is most intense and its P-branch members extend past the other band heads. Although the (3,2) band head is discernible, the (4,3) band (not shown in the figure) is difficult to distinguish from the P-branch background. Fig. 4 gives part of the scan of the $\Delta v = -1$ sequence. Here the (2,3) band head is clearly visible although the (3,4) head, which has about the same calculated Franck-Condon factor [12] as (2,3), is absent. From this figure we have direct evidence that the $v'' = 3$ level of AIO is populated in the reaction



If we neglect the relative translational energy of the products, we may by analogy to Equation (5) write the inequality

$$D_0^0(\text{AIO}) \geq D_0^0(\text{O}_2) + E_{\text{int}}(\text{AIO}) - E_{\text{int}}(\text{O}_2) - E_t(\text{reactants}). \quad (11)$$

For $D_0^0(\text{O}_2)$ we use the value [13] 5.116 ± 0.004 eV, for $E_{\text{int}}(\text{AIO})$ the value $G(v = 3) - G(v = 0) = 2854.0$ cm^{-1} (0.353 eV), for $E_{\text{int}}(\text{O}_2)$ the value $\frac{3}{2}RT(\text{O}_2) = 0.04$ eV and for $E_t(\text{reactants})$ the value 0.195 ± 0.035 eV, which is obtained in the same manner as Equation (8) except that $M(\text{O}_3)$ is replaced by $M(\text{O}_2)$, $m = m(\text{Al}) + m(\text{O}_2)$, and $T(\text{Al}) = 1650^\circ\text{K}$. Hence we arrive at the result

$$D_0^0(\text{AIO}) \geq 5.23 \pm 0.04 \text{ eV}. \quad (12)$$

If the neglect of the rotational excitation of AIO in the $v'' = 3$ level is nearly counterbalanced by the neglect of the relative translational energy of the product, then (12) should be almost an equality.

IV. Discussion

Table 1 presents a summary of past efforts to derive $D_0^0(\text{AIO})$ from spectroscopic and thermodynamic data. A cursory glance at this table reveals that the best value for $D_0^0(\text{AIO})$ has long been a subject of some controversy. Most of the early and often tortuous history has been reviewed by Gole and Zare in their 1972 article and thus will not be repeated here. Since 1972, there have been two new developments of importance: (1) Hildenbrand has revised the earlier mass spectrometric determination of $D_0^0(\text{AIO})$ upwards and (2) Drowart has reinterpreted the long wavelength limit data of Tyte to set a higher upper bound than that of McDonald and Innes. If one accepts the upper bound of Drowart and the lower bound reported here [see Equation (12)], then the value for $D_0^0(\text{AIO})$ would seem at last to be certain to better than 0.1 eV as a conservative estimate.

Table 1
Values for and limits to $D_0^0(\text{AIO})$

Investigator	Method	$D_0^0(\text{AIO})$
Lessheim and Samuel ^{a)}	Birge-Sponer Extrapolation	4.15 eV
Roy ^{b)}	Birge-Sponer Extrapolation	4.03 eV
Coheur-Dehalu ^{c)}	Predissociation	≤ 3.75 eV
Rosen ^{d)}	Predissociation	≤ 0.93 eV
Gurvitch and Viets ^{e)}	Flame Photometry	5.95 ± 0.17 eV
Newman and Page ^{f)}	Flame Photometry	6.30 ± 0.26 eV
Drowart, De Maria Burns, and Inghram ^{g)}	Mass. Spec.	5.00 ± 0.21 eV
Hildenbrand ^{h)}	Mass Spec.	5.14 ± 0.11 eV
Tyte ⁱ⁾	Long Wavelength Limit of Absorption Continuum	$\leq 4.54 \pm 0.01$ eV
McDonald and Innes ^{j)}	Long Wavelength Limit of Absorption Continuum	≤ 5.20 eV
Drowart ^{k)}	Long Wavelength Limit of Absorption Continuum	$\leq 5.296 \pm 0.025$ eV
Gole and Zare ^{l)}	Chemiluminescence	$\geq 5.13 \pm 0.06$ eV
Cruse, Dagdigian, and Zare ^{m)}	Laser-Induced Fluorescence	$\geq 5.23 \pm 0.04$ eV

^{a)} H. Lessheim and R. Samuel, *Z. Physik* 84, 637 (1933).

^{b)} D. Roy, *Indian J. Physics*, 231 (1939).

^{c)} F. Coheur-Dehalu, *Bull. Acad. Roy. Belg.* 23, 604 (1937).

^{d)} B. Rosen, *Physic. Rev.* 68, 124 (1945).

^{e)} L. V. Gurvitch and I. V. Viets, *Bull. Acad. Sci. USSR Physical Series* 22, 670 (1958). See also L. V. Gurvitch and I. V. Viets, *Dokl. Akad. Nauk SSR* 108, 659 (1956).

^{f)} R. N. Newman and F. M. Page, *Combustion and Flame* 15, 317 (1970).

^{g)} J. Drowart, G. De Maria, R. P. Burns, and M. G. Inghram, *J. chem. Physics* 32, 1366 (1960). See also G. De Maria, J. Drowart, and M. G. Inghram, *J. chem. Physics* 30, 318 (1959).

^{h)} D. L. Hildenbrand, *Chem. Physics Letters* 20, 127 (1973).

ⁱ⁾ D. C. Tyte, *Proc. Phys. Soc. (London)* 92, 1134 (1967).

^{j)} J. K. McDonald and K. K. Innes, *J. Mol. Spectry.* 32, 501 (1969).

^{k)} J. Drowart (private communication), Vrije Universiteit Brussel.

^{l)} J. L. Gole and R. N. Zare, *J. chem. Physics* 57, 5331 (1972). (See text for discussion of error estimate).

^{m)} Preliminary work described herein.

It is particularly pleasing to us that the lower bound to $D_0^0(\text{AIO})$ derived from our chemiluminescence studies and from our laser-induced fluorescence studies are so close to each other. Since it seems unlikely that there is a large activation energy for the ground state reaction $\text{Al} + \text{O}_2 \rightarrow \text{AIO} + \text{O}$, we are able to conclude that the interpretation of the $\text{Al} + \text{O}_2$

chemiluminescent data seems to be free of the doubt raised by Thrush [7]. In either method, the most inaccurate step is the estimation of the reactant and product relative translational energies. Indeed it may be argued that the error estimates given here are too small by perhaps as much as a factor of two. However, with the use of velocity selectors, either to pre-select the velocities of the reactants or to measure the velocities of the products, the way seems clear, at least in principle, to refine both these techniques for determining dissociation energies. It would seem then that the characterization of product internal states in elementary gasphase reactions will permit the determination of dissociation energy limits for an increasingly larger class of simple molecules.

V. Acknowledgments

I wish to thank J. Drowart and B. A. Thrush for their comments, criticisms, and suggestions, which have greatly assisted me in the preparation of this paper. I also wish to thank P. J. Dagdigian who checked the numerical calculations of the dissociation energy.

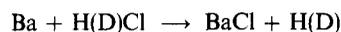
This work has been supported, in part, by the Advanced Research Projects Agency through grant DA-ARO-D-31-124-73-G82 and the Air Force Office of Scientific Research through grant AFOSR-72-2275. The costs of travel to the XI International Symposium on Free Radicals was provided by a grant from the National Science Foundation.

Discussion

K. W. Michel: Is the absence of isotope effects in vibrational distributions of products a hint for using classical models for its description?

R. D. Levine: Very much so. The fact that using the reduced variable $f_v = E_v/E$ (the fraction of the total energy in vibration) leads to distributions of final vibrational energy which is independent of isotopic variant shows that quite clearly. One can understand this "classical-like" behaviour by realizing that a given vibrational level corresponds to a large number of vibrational states. The probability of any final vibrational state is thus the sum of the probabilities of formation of the different states within the vibrational manifold. One can thus expect that quantum effects would be quenched by the extensive summation.

J. P. Simons: The isotope effect observed in the relative cross-sections for the reactions



could be explained in the following simple way: For the system in which a heavy atom approaches HCl in the entry channel while the light H-atom separates in the exit channel, conservation of angular momentum requires $\mu g b \approx p_{\text{H(D)Cl}}$, where $p_{\text{H(D)Cl}}$ is the rotational angular momentum of the H(D)Cl, and $\mu g b$ is the initial orbital angular momentum of the collision (μ is the reduced mass of the Ba + H(D)Cl system, g is the relative velocity, and b is the impact parameter). Thus $b_{\text{D}}/b_{\text{H}} = (g_{\text{H}}/g_{\text{D}}) \cdot (p_{\text{D}}/p_{\text{H}})$. Experimentally the rotational energies in the

HCl and DCl reactions are the same: thus $(p_{\text{H}}/p_{\text{D}}) = (\mu_{\text{DCl}}/\mu_{\text{HCl}})^{1/2}$. Also the relative velocity $g_{\text{H}} \approx g_{\text{D}}$, therefore $(b_{\text{D}}/b_{\text{H}})^2 = \sigma_{\text{D}}/\sigma_{\text{H}} \approx \frac{1}{2}$. Of course, in the limit of a colinear collision, no isotope effect would be predicted by this argument*).

W. M. Jackson: By narrowing the bandwidth of the laser even further one can, in principle, measure the translational energy of the fragment in addition to the vibrational and rotational energy of the molecular fragment.

N. Zare: I believe this "Doppler spectroscopy" is technologically feasible presently. However, such studies may encounter all the joys and sorrows of having to disentangle first all the fine and hyperfine structure (if any) of the molecule.

D. A. Ramsay: I would like to report that Dr. Marvin Kroll has recently excited the resonance fluorescence of two polyatomic free radicals, BO_2 and NH_2 , by means of an argon ion laser and a tunable dye laser, resp.

N. Zare: I thank Dr. Ramsay for this information. As lasers are extended into the UV region of the spectrum, I believe many more examples of laser-induced polyatomic fluorescence will be discovered.

*) R. D. Levine, this discussion.

References

- [1] A. G. Gaydon, *Dissociation Energies* (Chapman and Hall, London 1968), 3rd ed.
- [2] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Co., Princeton, New Jersey 1950), pp. 437–444; *Electronic Spectra and Electronic Structure of Polyatomic Molecules* (D. Van Nostrand Co., Princeton, New Jersey 1966), pp. 482–487.
- [3] Ch. Ottinger and R. N. Zare, *Chem. Physics Letters* 5, 243 (1970).
- [4] C. D. Jonah, R. N. Zare, and Ch. Ottinger, *J. chem. Physics* 56, 263 (1972).
- [5] J. L. Gole and R. N. Zare, *J. chem. Physics* 57, 5331 (1972).
- [6] N. F. Ramsey, *Molecular Beams* (Oxford University Press, 1956), pp. 21–22.
- [7] B. A. Thrush, "Gas Reactions Yielding Electronically Excited Species", *Annual Review of Physical Chemistry* 19, 371 (1968); B. A. Thrush, *J. chem. Physics* 58, 5191 (1973).
- [8] For a recent review, see J. L. Kinsey, in: *Chemical Kinetics*, ed. J. C. Polanyi (M.T.P. International Review of Science; Medical and Technical Publishing Co./Butterworths Co., Oxford 1972), *Physical Chemistry, Series One, Vol. 9, Chapter 6*.
- [9] A. Schultz, W. H. Cruse, and R. N. Zare, *J. chem. Physics* 57, 1354 (1972).
- [10] H. W. Cruse, P. J. Dagdigian, and R. N. Zare, *Faraday Discuss. Chem. Soc.* 55 (1973).
- [11] W. M. Jackson, *J. chem. Physics* 59, 960 (1973).
- [12] D. C. Tyte and R. W. Nicholls, *Identification Atlas of Molecular Spectra 1: The $\text{AlO A } ^2\Sigma - \text{X } ^2\Sigma$ Blue-Green System* (The University of Western Ontario, London, Ontario, Canada 1964).
- [13] B. de B. Darwent, *Bond Dissociation Energies in Simple Molecules*, NSRDS-NBS 31 (U.S. Government Printing Office, Washington, D.C., 1970).