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# On the Relation between Non Adiabatic Unimolecular Reactions and Radiationless Processes

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In this paper we present the results of a theoretical study of non adiabatic unimolecular dissociation processes with applications to the decomposition of $N_2O(^1\Sigma)$ to yield $N_2(^1\Sigma_g)$ and $O(^3P)$. Such unimolecular reactions which involve a change in the electronic state can be handled by the theory of thermally excited intramolecular radiationless decay processes in analogy to molecular predissociation and electronic relaxation in the statistical limit. General criteria were advanced for describing the decay probability of a single vibronic level in terms of Fermi's golden rule and for specifying the (high pressure) unimolecular rate constant in terms of a thermally averaged transition probability. The quantum mechanical rate constant for the non adiabatic reaction is characterized by a preexponential factor determined by the interstate coupling matrix element and by a temperature dependent activation energy. At low temperatures the activation energy is equal to the continuum onset, and the reaction involves a tunnelling process. In the high temperature limit a general demonstration of the Franck Condon principle for thermal reactions was provided, whereupon the non radiative transition occurs at the intersection of the potential surfaces. Numerical calculations for a one dimensional model system for the thermal decomposition of $N_2O$ were performed utilizing the semiclassical approximation and confirm our general conclusions. A two dimensional linear model has been developed representing the rate constant in terms of a convolution of two generalized line shape functions, which enabled us to study the distribution of vibrational energy among the diatomic $N_2$ molecules resulting from the thermal decomposition of $N_2O$. Some predictions concerning the determination of single level decay probabilities and vibrational distribution of the molecular products are presented.

In dieser Arbeit werden die Ergebnisse einer theoretischen Untersuchung nicht adiabatischer unimolekularer Zerfallsreaktionen mitgeteilt und auf den Zerfall von $N_2O(^1\Sigma)$ zu $N_2(^1\Sigma_g)$ und $O(^3P)$ angewandt. Solche unimolekularen Reaktionen, bei denen sich der Elektronenzustand ändert, können mit der Theorie thermisch angeregter intramolekularer strahlungsloser Zerfallsprozesse in Analogie zu molekularer Prädissoziation und elektronischer Relaxation im statistischen Limit behandelt werden. Kriterien zur Beschreibung der Zerfallswahrscheinlichkeiten eines einzelnen Vibrationszustands unter Berücksichtigung von Fermis Golden Rule werden entwickelt sowie die unimolekulare Geschwindigkeitskonstante (im Hochdruckbereich), wobei thermisch gemittelte Übergangswahrscheinlichkeiten berücksichtigt werden, mitgeteilt. Die quantenmechanische Geschwindigkeitskonstante für die nicht adiabatische Reaktion wird durch einen präexponentialen Faktor, der durch die Matrixelemente der Kopplung beider Zustände bestimmt ist und durch eine temperaturabhängige Aktivierungsenergie charakterisiert. Bei tiefer Temperatur stimmt die Aktivierungsenergie mit der Energie der Kontinuumsgrenze überein, die Reaktion verläuft über einen Tunneleffekt. Für hohe Temperaturen wurde ein allgemeiner Beweis des Franck-Condon-Prinzips für thermische Reaktionen gegeben, wonach der strahlungslose Übergang beim Schnittpunkt der Potentialflächen auftritt. Rechnungen für ein eindimensionales Modell des $N_2O$ Zerfalls wurden in der semiklassischen Näherung durchgeführt und bestätigen unsere Folgerungen. Ein zweidimensionales Modell wurde entwickelt, das die Geschwindigkeitskonstante als Faltungsintegral zweier verallgemeinerter Linienformintegrale wiedergibt. Dadurch wurde es ermöglicht, die Verteilung der Vibrationsenergie auf die zweiatomigen $N_2$ Moleküle, die bei dem thermischen Zerfall von $N_2O$ enstehen, zu studieren. Einige Voraussagen über die Bestimmung der Zerfallswahrscheinlichkeiten eines Vibrationszustandes und die Vibrationsverteilung der molekularen Produkte werden mitgeteilt.

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## 1. Introduction

The key physical idea underlying recent theoretical studies [1] of intramolecular radiationless transitions in large molecules is that electronically excited zero order molecular states are non stationary (or metastable) being degenerate with and irreversibly coupled to a quasi-continuum of zero order levels corresponding to lower electronic configurations. This work has established the formal analogy between electronic relaxation processes (i.e. internal conversion and intersystem crossing) and radiationless molecular decomposition processes (i.e. predissociation and autoionization). Forty years ago, Rosen [2], Langer [3] and Rice [4] proposed that thermal unimolecular decomposition reactions can be considered as an Auger process, in complete analogy to predissociation and autoionization. This approach has been revived lately in the work of Mies and Kraus [5–7] who stress the point that the "activated state" in chemical kinetics is equivalent to the concept of a resonance state in scattering theory, and is thus amenable to theoretical treatment by the Fano configuration scheme. Mies and Kraus [5–7] consider the activated molecule in unimolecular decomposition in terms of a vibrationally excited zero order molecular state located above the threshold dissociation energy. A different class of unimolecular decomposition process involve a change in the electronic state. The best documented reactions of this type [8–12] (see Table 1) pertain to the thermal decomposition of some linear triatomics to yield an oxygen atom and a closed shell diatomic molecule.

$$\mathrm{XYO}(^1\Sigma) \rightarrow \mathrm{XY}(^1\Sigma) + \mathrm{O}\,.$$

The dissociation energy, $D$ of the ground state molecule $\mathrm{XYO}(^1\Sigma)$ yielding $\mathrm{XY}(^1\Sigma)$ and an excited $\mathrm{O}(^1D)$ oxygen atom, usually exceeds the experimental Arrhenius [13] activation energy, $E_A$. There exists, however, a non bonding triplet state [8–12] dissociating into $\mathrm{XY}(^1\Sigma)+\mathrm{O}(^3P)$ yielding a ground state oxygen atom. The repulsive potential surface intersects the bound ground state potential curves at energies well below the dissociation limit, providing a proper rationalization for the low activation energy. The intramolecular interstate coupling is envisaged to be induced by weak spin-orbit interaction [8–12], so that following the usual conventional nomenclature adopted in chemical kinetics [11] (which semantically is not quite appropriate) one refers to such a process as a non adiabatic reaction. In this context the Landau-Zener [14, 15] formalism for non adiabatic processes (such as predissociation) was applied by Stearn and Eyring [8] for the thermal decomposition of $N_2O$. The predissociation probability calculated by the Landau-Zener formula was identified with the transmission coefficient $\kappa$ in the absolute reaction theory, so that the high pressure rate constant, $k$, is given by [8] $k=(\kappa k_B T/h)(Z^{\neq}/Z)\exp(-E_A/k_B T)$. The ratio $Z^{\neq}/Z$ of the partition functions for the activated complex and for the bound molecule is close to unity. An application of the unimolecular reaction rates theories of Hinshelwood, Kassel, Rice and Ramsperger [16–18] to the thermal decomposition of $N_2O$ was given by Gill and Laidler [9]. A useful review of these theories is presented by Troe and Wagner [12]. In an interesting recent work, Gilbert and Ross [19] have proposed that the formalism of intramolecular radiationless processes can be applied for the study of non adiabatic unimolecular decomposition processes,

Table 1. Experimental data for nonadiabatic unimolecular rate constants of some triatomic molecules (Ref. [12])

| $\Delta H_0$[kcal/mole] | $D$(XY–O) or $D$(XY–S) [kcal/mole] | $T$[°K] | $k_\infty\left[\frac{1}{\text{sec}}\right]$ expt | $k\left[\frac{1}{\text{sec}}\right]$ theory[a] |
|---|---|---|---|---|
| Reaction: $N_2O(^1\Sigma^+) \to N_2(^1\Sigma^+) + O(^3P)$ | | | | |
| $38.6 \pm 0.1$ | $N_2(^1\Sigma^+) \to N_2(^1\Sigma^+) + O(^1D)$ | 888 | $7.47\ 10^{-4}$ | $2.8 \times 10^{-3}$ |
| | $83.9 \pm 0.1$ | 1400–2000 | $1.6 \times 10^{11} \exp\left(-\frac{60}{RT}\right)$ | $4.1 \times 10^{11} \exp\left(-\frac{59}{RT}\right)$ |
| Reaction: $CO_2(^1\Sigma^+) \to CO(^1\Sigma^+) + O(^3P)$ | | | | |
| | $CO_2(^1\Sigma^+) \to CO(^1\Sigma^+) + O(^1D)$ | | | |
| $125.8 \pm 0.6$ | $171.1 \pm 0.6$ | 2800–3700 | $2.10^{11} \exp\left(-\frac{110}{RT}\right)$ | |
| Reaction: $CS_2(^1\Sigma^+) \to CS(^1\Sigma^+) + S(^3P)$ | | | | |
| | $CS_2(^1\Sigma^+) \to CS(^1\Sigma^+) + S(^1D)$ | | | |
| $91.5 \pm 5$ | $118 \pm 5$ | 1950–2800 | $8.10^{12} \exp\left(-\frac{89}{RT}\right)$ | |
| Reaction: $COS(^1\Sigma^+) \to CO(^1\Sigma^+) + S(^3P)$ | | | | |
| | $COS(^1\Sigma^+) \to CO(^1\Sigma^+) + S(^1D)$ | | | |
| | $97.6 \pm 1$ | 1550–2700 | $3.7 \times 10^{11} \exp\left(-\frac{68.3}{RT}\right)$ | |

[a] Theoretical value for a one dimensional system characterized by a Morse type $N_2$–O potential for the initial state and the crossing of the band and repulsive potentials occurring at $E_0 = 21023\ \text{cm}^{-1}$.

performing some approximate numerical calculations for the thermal decomposition of $N_2O$. In the present paper, we shall pursue further the formal analogy between non adiabatic high pressure unimolecular decomposition reactions and molecular radiationless processes. The main goals and accomplishments of the present work are:

a) The theory of predissociation [20–24] will be applied for the study of non adiabatic unimolecular processes. The only difference between the two types of processes involves the excitation mode of the decaying states, which is optical in the case of predissociation and thermal for unimolecular decomposition.

b) Microscopic rate constant for the decay of individual zero order vibronic levels cannot be handled by the Landau-Zener formula [14, 15] which provides an averaged level, neglecting the oscillatory nature of these transition probabilities [19]. The *WKB* semi-classical approximation which was successfully applied by Child [23] for predissociation will be adopted by us to derive analytic expression for the microscopic rate constant for simple model systems.

c) Quantum mechanical rate expression will be derived for the decay in a two electronic level system without invoking the concept of an activated complex.

d) The general features of the rate expression for non adiabatic unimolecular decomposition will be elucidated. In the low temperature limit the process corresponds to tunnelling between two zero order states, being completely analogous to the common situation encountered for electronic relaxation in large aromatic molecules. In the high temperature limit, a semi-classical approximation for nuclear motion can be adopted and the major contribution to the rate constant originates from the vicinity of the crossing of the potential surface.

e) The nature of the activation energy and its temperature dependence will be established.

f) From the practical point of view numerical calculations will be performed for a model system pertaining to the unimolecular decomposition of $N_2O$.

g) From the point of view of general methodology, we shall establish the conditions for the application of the Fermi golden rule to the study of unimolecular decomposition processes.

## 2. A Physical Model for Non Adiabatic Unimolecular Decay

To describe a unimolecular decomposition process, which involves a change in the electronic state of a triatomic molecule, we shall proceed in a manner completely analogous to the treatment of electronic relaxation [1] and decomposition processes [20–24]. We shall specify an appropriate zero order basis set to describe the approximate vibronic levels of the physical system. The choice of this basis set is in principle arbitrary, being just a matter of convenience. The total Hamiltonian $\boldsymbol{H}$ can be dissected in the form

$$\boldsymbol{H} = \boldsymbol{H}_0 + V \tag{2.1}$$

where the zero order basis set of $\boldsymbol{H}_0$ corresponds to pure spin states (of different spin configurations) in the Born-Oppenheimer approximation (see Fig. 1). The eigenfunctions of $\boldsymbol{H}_0$ can be represented as a product of electronic wave functions, $\varphi$, and vibrational wave functions, $\chi$,

$$\begin{aligned} |i\alpha\rangle &= \varphi_i(\boldsymbol{r}, \boldsymbol{R})\, \chi_{i\alpha}(\boldsymbol{R}) \\ |\mathrm{f}\beta\rangle &= \varphi_f(\boldsymbol{r}, \boldsymbol{R})\, \chi_{f\beta}(\boldsymbol{R}) \end{aligned} \tag{2.2}$$

where the indices $i$ and $f$ represent the initial and the final electronic states, respectively. The vibrational wavefunctions $\chi_{i\alpha}(\boldsymbol{R})$ and $\chi_{f\beta}(\boldsymbol{R})$ in the initial and final electronic states correspond (approximately) to the eigenvalues of the adiabatic potentials $V_i(\boldsymbol{R}) = \langle\varphi_i|\boldsymbol{H}_0|\varphi_i\rangle$ and $V_f(\boldsymbol{R}) = \langle\varphi_f|\boldsymbol{H}_0|\varphi_f\rangle$. Finally $\boldsymbol{r}$ and $\boldsymbol{R}$ represent the electronic and the nuclear coordinates respectively. The potential $V_i(\boldsymbol{R})$ is bound and the eigenstates $|i\alpha\rangle$ are discrete. The final state potential $V_f(\boldsymbol{R})$ is repulsive at least for one degree of freedom, so that the eigenstates $|f\beta\rangle$ are continuous. The corresponding energies of the zero order states will be denoted by $E_{i\alpha}$ and by $E_{f\beta}$.

The intramolecular coupling term consists of two parts

$$V = \boldsymbol{T}_R + \boldsymbol{H}_{so} \tag{2.3}$$

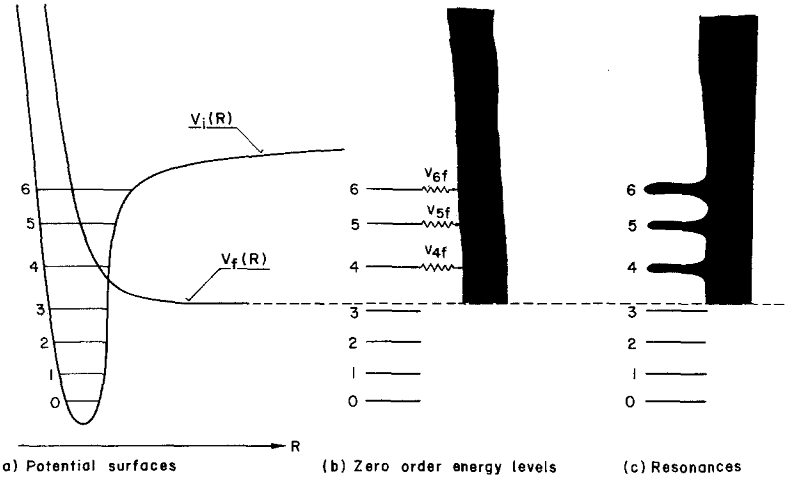


Fig. 1. A schematic description of the resonance states involved in unimolecular decomposition. a One dimensional potential surfaces. b Zero order energy levels corresponding to the two electronic states. Near resonance coupling between discrete and continuum zero order levels is designated by arrows. c Non overlapping resonances appear above the continuum threshold. These states diagonalize the total molecular Hamiltonian

where $T_R$ is the nuclear kinetic energy operator and $H_{so}$ is the spin orbit coupling operator. Now we assert that:

(A) Relaxation within a two electronic level system can be considered, whereupon off resonance second order coupling of $|i\alpha\rangle$ and $|f\beta\rangle$ with higher electronic states can be disregarded [25].

As the non adiabatic coupling term $T_R$ conserves spin states, the relevant coupling term between near resonance states $|i\alpha\rangle$ and $|f\beta\rangle$ involves just the spin orbit coupling and second order mixed type terms involving coupling via $T_R$ and $H_{so}$ with higher electronic states are neglected. Thus the relevant interstate coupling terms are

$$\begin{aligned} V_{i\alpha,f\beta} &= \langle i\alpha| T_R + H_{so} |f\beta\rangle \\ &= \int dR\, \chi_{i\alpha}(R) \left[\int dr\, \varphi_i(r,R)\, H_{so}\, \varphi_f(r,R)\right] \chi_{f\beta}(R)\,. \end{aligned} \tag{2.4}$$

To simplify this result we assume that

(B) The electronic matrix element of the spin orbit coupling operator

$$\langle H_{so}(R)\rangle = \int dr\, \varphi_i(r,R)\, H_{so}\, \varphi_f(r,R) \tag{2.5}$$

is assumed to be a slowly varying function of the nuclear coordinates $R$ and will be taken as a constant $\langle H_{so}(R)\rangle \equiv \langle H_{so}\rangle$ in the double integral (2.4).

This assumption is equivalent to the Condon approximation in the calculation of molecular optical transition moments. Recent studies [25] have indicated that for the case of non adiabatic coupling between two electronic states of the same spin via $T_R$ the application of the Condon approximation is not justified. However, for the case of coupling via $H_{so}$ between two different spin states this approximation seems to be reasonable. Thus Eq. (2.4) is recast in the form

$$V_{i\alpha,f\beta} = \langle \boldsymbol{H}_{so} \rangle \int d\boldsymbol{R}\, \chi_{i\alpha}(\boldsymbol{R})\, \chi_{f\beta}(\boldsymbol{R}) \tag{2.4a}$$

which takes the simple form of an electronic matrix element multiplied by a vibrational overlap Franck Condon factor [26].

The zero order states $|i\alpha\rangle$ which are quasidegenerate with the continuum states $|f\beta\rangle$, are metastable. Thus we encounter the extreme case of the statistical limit [1] where the density of states in the dissipative channel $|f\beta\rangle$ is a continuous function of the energy, and the physical situation is completely analogous to that of predissociation [21, 22]. Invoking assumption (A) the width $\Gamma_{i\alpha}$ of a zero order state $|i\alpha\rangle$ is given in terms of time dependent perturbation theory by the Fermi golden rule

$$\Gamma_{i\alpha} = 2\pi \sum_{\beta} |V_{i\alpha,f\beta}|^2\, \delta(E_{i\alpha} - E_{f\beta}) \tag{2.6}$$

and making use of assumption (B) (Eq. 2.4a) we get

$$\Gamma_{i\alpha} = 2\pi |\langle \boldsymbol{H}_{so} \rangle|^2 \sum_{\beta} |\int d\boldsymbol{R}\, \chi_{i\alpha}(\boldsymbol{R})\, \chi_{f\beta}(\boldsymbol{R})\, \delta(E_{i\alpha} - E_{f\beta}) . \tag{2.6a}$$

It is important to note at this point that the decay probability of an "initially prepared" zero order state $|i\alpha\rangle$ can be expressed in terms of the width (2.6) by $\Gamma_{i\alpha}/\hbar$, only provided that it is justified to consider the decay of a single resonance. We thus invoke the basic assumption.

(C) The spacing between the resonances considerably exceeds their widths. Denoting by $E_{i\alpha} - E_{i(\alpha+1)}$ the energy spacing between the adjacent order states $|i\alpha\rangle$ and $|i(\alpha+1)\rangle$ we imply that

$$\Gamma_{i\alpha} \ll |E_{i\alpha} - E_{i(\alpha+1)}| \tag{2.7}$$

for all $\alpha$. Condition (2.7) provides us with the basic relation necessary for describing the decay process in terms of the perturbation theoretical results (2.6), so that the decay probability $W_{i\alpha}$ of the zero order state $|i\alpha\rangle$ is then given by

$$W_{i\alpha} = \Gamma_{i\alpha}/\hbar = 2\pi/\hbar\, |\langle \boldsymbol{H}_{so} \rangle|^2 \sum_{\beta} \int d\boldsymbol{R}\, \chi_{i\alpha}(\boldsymbol{R})\, \chi_{f\beta}(\boldsymbol{R})\, \delta(E_{i\alpha} - E_{f\beta}) . \tag{2.8}$$

Thus, when interference effects between resonances can be disregarded, each zero order state can be described as an independently decaying resonance, its decay pattern being exponential and being characterized by the reciprocal decay time (2.8). The applicability of restriction (2.7) will imply that the thermally averaged rate constant will invoke a preexponential factor which involves the interstate coupling matrix element. This physical situation is often referred to in chemical kinetics as a non adiabatic transition [11]. The usual semiclassical description of a non adiabatic transition is provided [11] by implying that the splitting of the zero order potential surfaces at the intersection point is "small". Levich and Dogonadze [27] in their beautiful theoretical study of electron transfer processes in solution have provided a complete semiclassical criterion for the applicability of the non adiabatic kinetic scheme in terms of the Landau Zener theory, and similar conditions were also provided by Nikitin [28]. Considering unimolecularily decaying states as resonances, Eq. (2.7) provides a necessary and sufficient quantum mechanical condition for the applicability of the non adiabatic limit. To the best of our knowledge a complete quantum mechanical formulation of the adiabatic case was not yet provided. In this context, Mies and Kraus [5] have provided a simpliefied model (equal resonance spacings and widths) which exhibits the transition from the adiabatic to the non adiabatic case. For the physical case under consideration, which involves a spin forbidden transition between two different electronic states of a triatomic molecule the resonance widths are $\Gamma_{i\alpha} \sim 1$–$10\,\mathrm{cm}^{-1}$ (see Sect. 4), while the spacing between adjacent resonances corresponds to the vibrational frequency $\sim 1000\,\mathrm{cm}^{-1}$, thus the non adiabacity condition (2.7) is fulfilled.

Up to this point we have been concerned with the decay of an initially prepared isolated resonance, without referring to the "preparation" of the decaying states. We now focus attention on thermal excitation by collisions with inert molecules (which do not modify the zero order molecular levels or the intramolecular spin orbit coupling). Two further assumptions are introduced at this point:

(D) Thermal vibrational excitation (and relaxation) rates considerably exceed the non radiative decay probabilities, whereupon

$$\Gamma_{i\alpha}/\hbar \ll \frac{1}{\tau_v} \tag{2.9}$$

where $\tau_v$ is the vibrational relaxation time.

(E) The width of each resonance is considerably lower than the thermal energy $k_B T$, in the temperature range of interest [5–7]:

$$\Gamma_{i\alpha} \ll k_B T. \tag{2.10}$$

Condition (2.9) provides us with the conventional basic assumption for the applicability of unimolecular rate theory in the high pressure limit. Eq. (2.10) implies that the thermal population of all molecular eigenstates (of $\boldsymbol{H}$) which correspond to the same resonance is equal.

The high pressure thermally averaged rate constant, $k$, is now given in the form

$$k = \sum_{\alpha} \exp(-E_{i\alpha}/k_B T)\, W_{i\alpha} / \sum_{\alpha} \exp(-E_{i\alpha}/k_B T) \tag{2.11}$$

where the microscopic rate constants $W_{i\alpha}$ (Eq. (2.8)) represent the predissociation probability for the zero order $|i\alpha\rangle$ state.

## 3. A One Dimensional Model

To pursue the formal analogy between decomposition of a thermally activated zero order vibrational level of a triatomic linear molecule XYO($^1\Sigma$) and predissociation we shall first limit ourselves to a one dimensional model, considering only the displacement $R$ along the Y–O linear coordinate. We thus assume that only this single $R$ coordinate is reactive while all the other modes remain unchanged. This "diatomic molecule model" for the decomposition of a triatomic

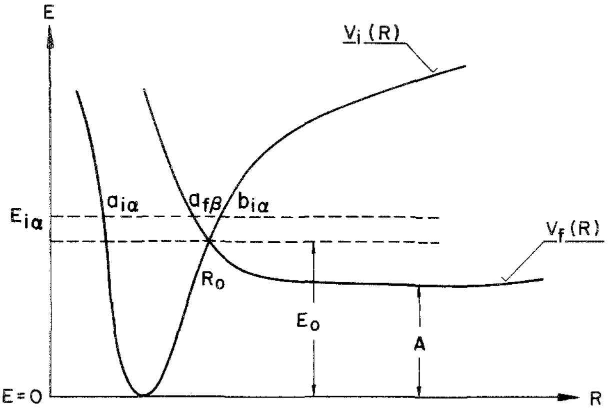


Fig. 2. Relevant parameters for the semiclassical calculation of vibrational overlap integrals between two one dimensional potential surfaces

linear molecule implies that: a) the X–Y separation is the same in the triatomic molecule XYO($^1\Sigma$) and in the resulting dissociation product XY($^1\Sigma$). This approximation can be relaxed as demonstrated in Sec. 4. b) The linear predissociation process along the XYO axis of the linear molecule is considered. This assumption neglects the role of the bending modes of the XYO molecules which can lead to predissociation off the linear axes.

Considering the one dimensional model the microscopic rate constant (or transition probability) (2.8) takes the simple form

$$W_{i\alpha} = 2\pi/\hbar\,|\langle \boldsymbol{H}_{so}\rangle|^2\,|\langle \chi_{i\alpha}(R)\,|\,\chi_{f\beta}(R)\rangle|^2 \tag{3.1}$$

where $\chi_{i\alpha}(R)$ (characterized by the energy $E_{i\alpha}$) and $\chi_{f\beta}(R)$ (characterized by the energy $E_{f\beta}$) are now the eigenfunctions belonging to the one dimensional (bound) potential $V_i(R)$ and to the (repulsive) potential $V_f(R)$, respectively. We are essentially left with the calculation of the square of the Franck Condon vibrational overlap integral between the bound vibrational state $\chi_{i\alpha}(R)$ and the continuum states $\chi_{f\beta}(R)$ which are quasidegenerate with it [20, 23]. It will be convenient for the sake of bookkeeping to set $\chi_{i\alpha}(R)$ to be normalized to unity and to choose $\chi_{f\beta}(R)$ as a continuum state of $V_f(R)$ which is normalized by the delta function of energy. Thus Eq. (3.1) then takes the form

$$W_{i\alpha} = 2\pi/\hbar\,|\langle \boldsymbol{H}_{so}\rangle|^2\,|\textstyle\int \chi_{i\alpha}(R)\,\chi_{f\beta}(R)\,dR|^2\,. \tag{3.1a}$$

We will evaluate Eq. (3.1a) with the help of the *WKB* method recently utilized by Child [33] for the case of predissociation of $O_2$. In the semiclassical approximation the wave functions are (see Fig. 2):

$$\chi_{i\alpha}(R) = \left(\frac{2\mu\omega}{\pi P_{i\alpha}(R)}\right)^{1/2} \sin\left(\frac{1}{\hbar}\int\limits_{R}^{a_{i\alpha}} P_{i\alpha}(r)\,dr + \frac{\pi}{4}\right) \tag{3,2a}$$

$$\chi_{f\beta}(R) = \left(\frac{2\mu}{\pi\hbar P_{f\beta}(R)}\right)^{1/2} \sin\left(\frac{1}{\hbar}\int\limits_{a_{f\beta}}^{R} P_{f\beta}(r)\,dr + \frac{\pi}{4}\right). \tag{3.2b}$$

Here $P_\gamma(R) = [2\mu(E_\gamma - V_\gamma(R)]^{1/2}$; $\gamma = i\alpha$, $f\beta$ are the momenta associated with the two states. $\omega$ is the classical oscillation frequency

$$\frac{2\pi}{\omega} = 2\hbar\left(\frac{\partial\beta}{\partial E}\right) = 2\mu\int_{a_{i\alpha}}^{b_{i\alpha}}\frac{dr}{P_{i\alpha}(r)} = (2\mu)^{1/2}\int_{a_{i\alpha}}^{b_{i\alpha}}\frac{dr}{[E_{i\alpha} - V_i(r)]^{1/2}} \tag{3.3}$$

taken at the energy $E = E_{i\alpha}$. $\beta$ assumes the values $(v + 1/2)\pi$ for the bound states by the Bohr quantization condition. In the region of the intersection point $R = R_0$ (characterized by the energy $E_0$) of the potential curves $V_i(R)$ and $V_f(R)$, the wavefunctions (3.2) are replaced by the corresponding Airy functions

$$Ai(\xi) = \frac{1}{\pi}\int_0^\infty \cos\left(\frac{u^3}{3} + u\xi\right)du \tag{3.4}$$

where the parameter $\xi$ is defined by

$$\xi = \left(R + \frac{E}{F}\right)(2\mu F/\hbar^2)^{1/2} \tag{3.5}$$

while the force is

$$F = -\left(\frac{\partial V}{\partial R}\right)_{R=R_0} \tag{3.6}$$

and $V$ can take either the value of $V_i(R)$ (and then we shall take (3.6) as $F_i$ and (3.5) as $\xi_{i\alpha}$) or the value of $V_f$ (whereupon we shall denote (3.6) by $F_f$ and (3.5) by $\xi_{f\beta}$). In the vicinity of the crossing point $R_0$ we have

$$\chi_{i\alpha}(R) = (\pi\hbar\omega)^{1/2}\,(2\mu/\sqrt{F_i}\,\hbar^2)^{1/2}\,Ai(-\xi_{i\alpha})\,, \tag{3.7a}$$

$$\chi_{f\beta}(R) = (2\mu/\sqrt{F_f}\,\hbar^2)^{1/2}\,Ai(-\xi_{f\beta})\,. \tag{3.7b}$$

The major contribution to the integral (3.1) originates from the region $R = R_0$ around the energy of the crossing point $E \simeq E_0$. Utilizing (3.4) the predissociation decay probability can then be recast in the form

$$W_{i\alpha} = \frac{\pi K}{\sqrt{E^*}\,(\partial\beta/\partial E)}\,|Ai(t)|^2 \tag{3.8}$$

where

$$K = \frac{2\pi^2\,(2\mu)^{1/2}\,|\langle \boldsymbol{H}_{so}\rangle|^2}{\hbar^2(F_i - F_f)} \tag{3.9}$$

and

$$E^* = |\hbar F_i F_f/(2\mu)^{1/2}(F_i - F_f)|^{2/3} \tag{3.10}$$

while the linear parameter

$$t = -(E_{i\alpha} - E_0)/E^* \tag{3.11}$$

represents the deviation of the energy of the zero order level $|i\alpha\rangle$ from the intersection point. Eqs. (3.8)–(3.11) are based on the linear extrapolation $V_j(R) = E_0 - F_j(R)$ $(j = i, f)$, thus well above the crossing point we have to apply

Eq. (3.2) and the transition probability takes the form

$$W_{i\alpha} = \frac{K}{(E_{i\alpha} - E_0)^{1/2}\,(\partial\beta/\partial E)} \sin^2\left[\Phi(E_{i\alpha}) + \frac{\pi}{4}\right] \tag{3.12}$$

$\Phi(E)$ is the phase integral

$$\Phi(E_{i\alpha}) = \frac{1}{\hbar} \int_{a_{f\beta}}^{b_{i\alpha}} [2\mu(E_{i\alpha} - V_+(R))]^{1/2} dR \tag{3.13}$$

and $V_+(R) = V_f(R)$ for $R < R_0$ and $V_+(R) = V_i(R)$ for $R > R_0$. In the region of the crossing point $\Phi = 2/3|t|^{3/2}$ and Eq. (3.12) reduces to (3.8). Thus Eq. (3.8) was used for the calculation of the predissociation probability of zero order states characterized by energy $E_{i\alpha} \leqq E_0$ while Eq. (3.12) was utilized in the energy region $E_{i\alpha} > E_0$.

## 4. Numerical Calculations for $N_2O$

To provide a numerical estimate of the reaction rate $N_2O(^1\Sigma) \rightarrow N_2(^1\Sigma_g) + O(^3P)$ we have chosen one dimensional surfaces similar to those given by Stearn and Eyring [8] and by Gilbert and Ross [19]. We took only a single coordinate corresponding to the $N_2$–O mode to be reactive, and described the bound state by a Morse potential and alternatively by a harmonic potential. The parameters for these potentials are given in Fig. 3. The repulsive state was specified in terms

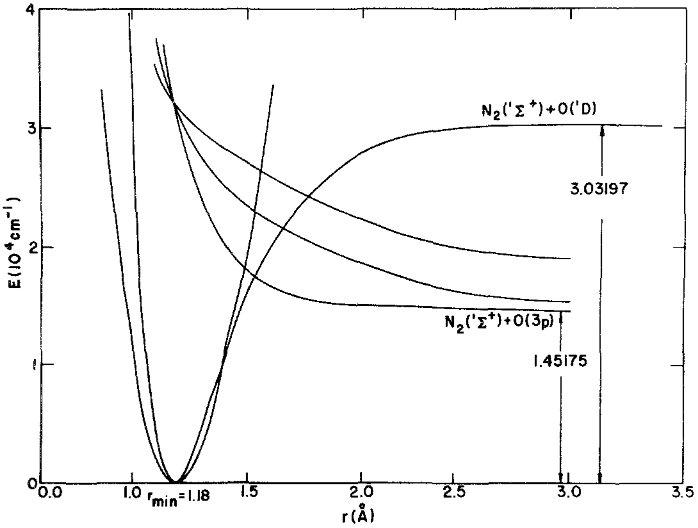


Fig. 3. Morse and harmonic potentials for $N_2O(^1\Sigma)$ and repulsive potentials for $N_2(^1\Sigma^+) + O(^3P)$. The formulas are (see text) $V_i(R) = 30319.7\,(1 - e^{-4\cdot(1.18)})^2$ for the Morse potential and $V_i(R) = \frac{1}{2}210425\,(r - 1.18)^2$ for the ground state Harmonic potential. The three repulsive potentials have the form $V_f(R) = A + \frac{B}{r^n}$ with $A = 14517.5$ [cm$^{-1}$], $B_1 = 54000$, $B_2 = 29700$, $B_3 = 22600$, $n_1 = 6.72$, $n_2 = 3.12$, $n_3 = 1.45$. The crossing points for the Morse potential are $E_0^{(1)} = 17523$ cm$^{-1}$, $E_0^{(2)} = 21023$ cm$^{-1}$, $E_0^{(3)} = 24524$ cm$^{-1}$ while for the harmonic potential we took $E_0^{(1)} = 16995$ cm$^{-1}$, $E_0^{(2)} = 21022$ cm$^{-1}$, $E_0^{(3)} = 25262$ cm$^{-1}$

of a $R^{-n}$ potential

$$V_f(R) = A + \frac{B}{R^n}. \tag{4.1}$$

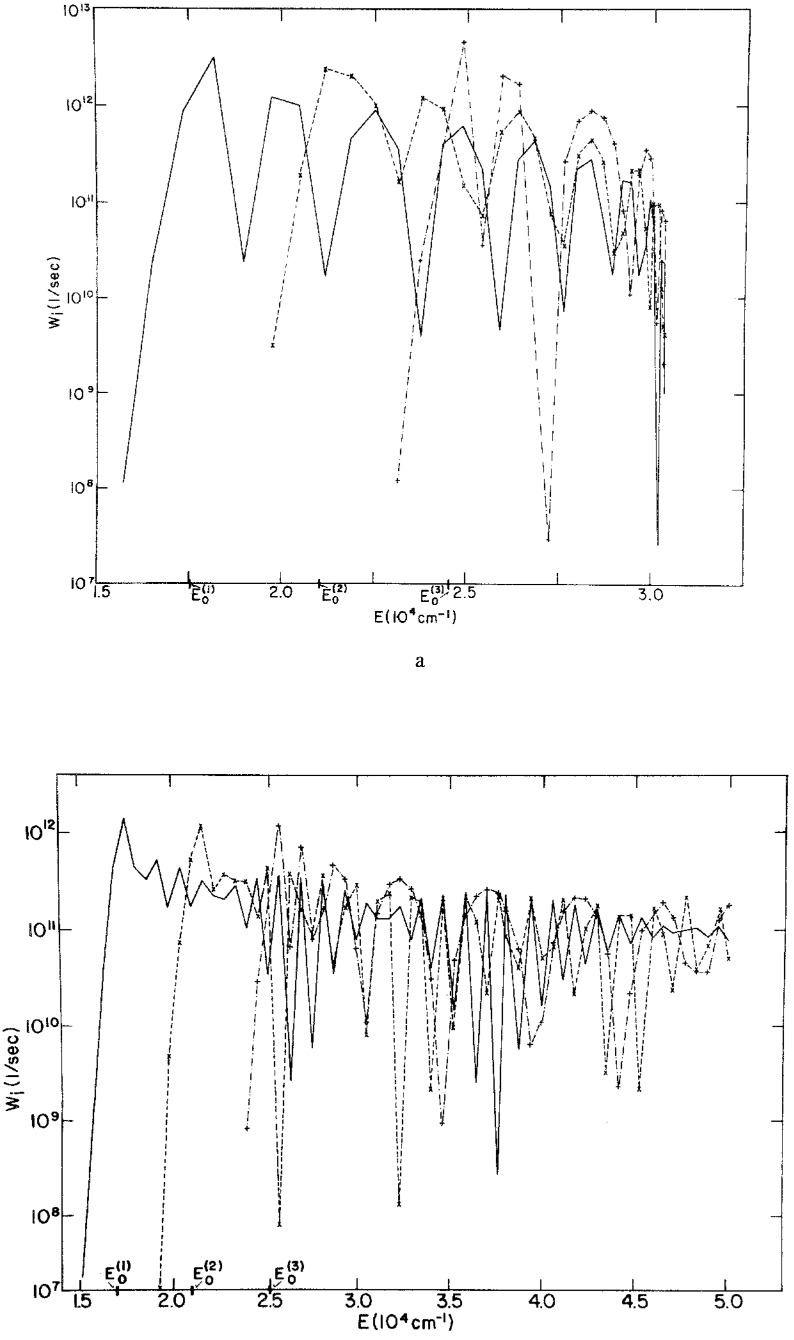
The value of $A = 14517\,\mathrm{cm}^{-1}$ was taken from the known thermochemical data (Table 1). The value of $B$ and $n$ (Fig. 3) were determined by: a) Taking the crossing point $E_0$ of the two potential curve to be located at 50, 60 or 70 kcal/mole. b) Using the observed onset for the optical dissociation continuum for the transition $N_2O(^1\Sigma) \rightarrow N_2(^1\Sigma) + O(^3P)$, located by Sponer and Bonner [29] at 4.0 eV, to correspond to the repulsive potential at the equilibrium distance of the N–O bond of $N_2O(^1\Sigma)$. Finally, the spin orbit coupling term was taken to be $|\boldsymbol{H}_{so}| \simeq 100\,\mathrm{cm}^{-1}$.

In Fig. 4 we present the microscopic rate constants Eq. (3.1) for different $|i\alpha\rangle$ levels calculated by the semiclassical approximation. It is apparent that this is not a smooth function of the energy, but rather a strongly oscillation function, as expected for the case of predissociation [23, 24]. The detailed features of the relative and absolute widths of different vibronic levels depend on the nature of the potential surfaces. The most important qualitative conclusion originating from these results is that it is not justified to use the Landau Zener formalism for the calculation of the thermally averaged rate constant, which is based on a "coarse graining" procedure assuming that $W_{i\alpha}$ is a smoothly varying function of the energy $E_{i\alpha}$. In Table 2, we display our numerically calculated thermally

Table 2. Calculated rate constants for the unimolecular decomposition of $N_2O$ at different temperatures. [Units of $k$ are $\mathrm{sec}^{-1}$].

| $T$[°K] | $k_1$ | $k_2$ | $k_3$ | $k_4$ | $k_5$ | $k_6$ |
|---|---|---|---|---|---|---|
| 100 | 9.33(−84) | 7.74(−102) | 1.98(−131) | 6.77(−86) | 7.73(−101) | 3.72(−132) |
| 200 | 2.69(−39) | 1.52(−50) | 2.42(−62) | 1.69(−39) | 3.05(−51) | 1.41(−65) |
| 300 | 2.32(−23) | 1.09(−30) | 4.11(−38) | 1.85(−38) | 1.13(−31) | 7.60(−41) |
| 400 | 4.74(−15) | 1.75(−20) | 6.66(−26) | 3.33(−15) | 1.87(−21) | 3.09(−28) |
| 500 | 5.40(−10) | 2.62(−14) | 1.43(−18) | 3.38(−10) | 3.07(−15) | 1.24(−20) |
| 600 | 1.33(−6) | 3.50(−10) | 1.09(−13) | 7.59(−7) | 4.49(−11) | 1.47(−15) |
| 700 | 3.60(−4) | 3.14(−7) | 3.31(−10) | 1.92(−4) | 4.32(−8) | 6.20(−12) |
| 800 | 2.46(−2) | 5.20(−5) | 1.36(−7) | 1.24(−2) | 7.61(−6) | 3.25(−9) |
| 900 | 6.69(−1) | 2.81(−3) | 1.48(−5) | 3.23(−1) | 4.30(−4) | 4.27(−7) |
| 1000 | 9.53(0) | 6.93(−2) | 6.35(−4) | 4.43(0) | 1.10(−2) | 2.14(−5) |
| 1500 | 9.53(0) | 6.93(−2) | 6.35(−4) | 4.43(0) | 1.10(−2) | 2.14(−5) |
| 1500 | 2.85(+4) | 1.11(+3) | 5.51(+1) | 1.13(+4) | 1.90(+2) | 2.85(0) |
| 2000 | 1.81(+6) | 1.58(+5) | 1.78(+4) | 6.70(+5) | 2.87(+4) | 1.16(+3) |
| 2500 | 1.35(+7) | 2.05(+6) | 3.98(+5) | 4.66(+6) | 3.76(+5) | 2.97(+4) |
| 3000 | 7.41(+7) | 1.57(+7) | 4.22(+6) | 2.46(+7) | 2.93(+6) | 3.45(+5) |
| 4000 | 6.87(+8) | 2.16(+8) | 8.48(+7) | 2.20(+8) | 4.15(+7) | 7.89(+6) |
| 5000 | 2.68(+9) | 1.06(+9) | 5.22(+8) | 8.52(+8) | 2.11(+8) | 5.37(+7) |
| 6000 | 5.41(+9) | 2.49(+9) | 1.41(+9) | 1.71(+9) | 5.07(+8) | 1.56(+8) |
| 8000 | 1.61(+10) | 9.07(+9) | 6.21(+9) | 5.15(+9) | 1.96(+9) | 7.82(+8) |
| 10000 | 3.21(+10) | 2.04(+10) | 1.55(+10) | 1.06(+10) | 4.69(+9) | 2.18(+9) |

$k_1$ = Morse potential $E_0 = 17523\,\mathrm{cm}^{-1}$, $k_2$ = Morse potential $E_0 = 21022\,\mathrm{cm}^{-1}$, $k_3$ = Morse potential $E_0 = 24524\,\mathrm{cm}^{-1}$, $k_4$ = Harmonic potential $E_0 = 16995\,\mathrm{cm}^{-1}$, $k_5$ = Harmonic potential $E_0 = 21022\,\mathrm{cm}^{-1}$, $k_6$ = Harmonic potential $E_0 = 25262\,\mathrm{cm}^{-1}$.



a

b

Fig. 4. a Microscopic rate constants for Morse potentials. —— $E_0 = 17523\ \mathrm{cm}^{-1}$; – – – $E_0 = 21023\ \mathrm{cm}^{-1}$ — · — $E_0 = 24524\ \mathrm{cm}^{-1}$. b Microscopic rate constants for the harmonic potential. —— $E_0 = 16995\ \mathrm{cm}^{-1}$ – – – $E_0 = 21022\ \mathrm{cm}^{-1}$; — · — $E_0 = 25262\ \mathrm{cm}^{-1}$

averaged unimolecular rate constants (Eq. (2.11)) for $N_2O$. The following points are pertinent:

a) The energy at the crossing point $E_0$ determines the high temperature activation energy (see Fig. 5 and subsequent discussion), thus at a constant temperature the rate constant (for a given $V_i(R)$ potential) increases with decreasing the crossing point energy $E_0$.

b) Anharmonicity effects tend to increase the rate constant. For a given value of $E_0$ and constant temperature the rate constant calculated for a Morse potential exceeds the value calculated for the harmonic potential by a numerical factor 3–10. the deviation increases with increasing $E_0$. These anharmonicity effects on the vibrational overlap Franck-Condon integrals are well documented in the theory of electronic relaxation processes [30].

c) In the temperature region 1400°–2000° K the experimental [31] high pressure rate constant for the decomposition of $N_2O$ is

$$k_\infty(\text{expt}) = 1.6 \times 10^{11} \exp\left(-\frac{(60/\text{kcal})}{k_B T}\right).$$

The theoretical value for the Morse potential and $E_0 = 60$ kcal/mole is

$$k(\text{calc}) = 4.1 \times 10^{11} \exp\left(-\frac{59/\text{kcal}}{k_B T}\right)$$

in the same temperature region. This almost perfect agreement between theory and experiment should not be taken too seriously in view of the approximation involved in the oversimplified one dimensional theoretical model.

The activation energy, defined in the conventional manner, turns out from our theoretical calculations to be temperature dependent. The apparent activation energy $\tilde{E}_A$, was defined in the conventional manner

$$\tilde{E}_A = -\partial \ln k / \partial (1/k_B T) \tag{4.2}$$

where $k$ is the theoretical rate constant. Utilizing Eq. (2.11) one easily obtains the formula previously given by Gilbert and Ross [19]

$$\tilde{E}_A = \frac{\sum\limits_\alpha W_{i\alpha} E_{i\alpha} \exp(-E_{i\alpha}/k_B T)}{\sum\limits_\alpha W_{i\alpha} \exp(-E_{i\alpha}/k_B T)} - \frac{\sum\limits_\alpha E_{i\alpha} \exp(-E_{i\alpha}/k_B T)}{\sum\limits_\alpha \exp(-E_{i\alpha}/k_B T)} = \frac{\langle WE \rangle}{k} - \langle E \rangle \tag{4.3}$$

where the square brackets represent averaged mean values.

In Fig. 5 we present the temperature dependence of the activation energy. The following points should be noted:

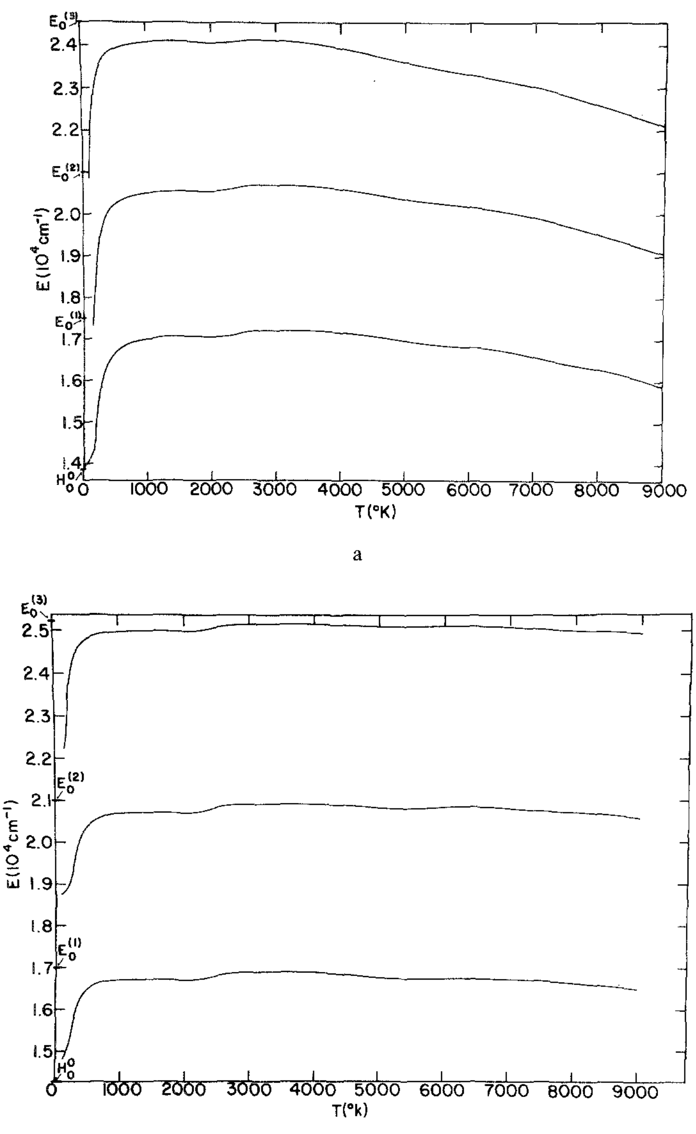
a) At low temperature where $k_B T \ll \hbar\omega$ ($\omega$ representing the vibrational frequency, as discussed in Section 5) the activation energy takes the value

$$\tilde{E}_A = A; \quad k_B T \ll \hbar\omega \tag{4.4a}$$

corresponding to the onset of the dissipative continuum (see Eq. (4.1)).

b) At higher temperatures the activation energy increases monotonously until it flattens up at high temperatures.

c) The constant value of the activation energy reached at high temperatures, i.e. when $k_B T \gg \hbar\omega$ (see Section 5) is very close to the energy $E_0$ of the crossing



a

b

Fig. 5. a Activation energy derived for the Morse potential defined in Fig. 4a. b Activation energy derived for the harmonic potential defined in Fig. 4b

point of the potential surfaces, so that

$$\tilde{E}_A \approx E_0\,; \qquad k_B T \gg \hbar\omega\,. \tag{4.4b}$$

To be more precise, we may utilize the general formula for the high temperature rate constant (see Section 5) which reads

$$k = k_0 T^{-\gamma} \exp(-E_0/k_B T) \tag{4.5}$$

where $k_0$ is a numerical constant and $\gamma$ is a half integer determined by the number, $n$, of the vibrational degrees of freedom in the initial states, $\gamma = n/2$. Thus, the high temperature activation energy obtained from (4.5) is

$$\tilde{E}_A = E_0 - \gamma k_B T . \tag{4.6}$$

Thus the apparent high temperature activation energy is expected to be somewhat lower than the crossing point energy $E_0$ in accordance with the behavior exhibited in Fig. 5.

d) The decrease of the apparent activation energy at very high temperature (see Fig. 5) has no physical significance and is attributed to arise from the truncation of the basis set of the initial vibrational levels including a finite number of vibrational levels in the present calculations. Indeed, there is a pronounced effect of the number of vibrational states taken into account. In the case of a Morse potential, the number ($\sim 50$) of the vibrational levels is not very high, the decrease of the activation energy with temperature at very high temperatures is faster than in the case of a harmonic potential, where we have included 200 levels in our calculations. These mathematical artifacts can be improved but not completely removed by extending the size of the zero order basis set corresponding to the initial vibronic levels. It should, however, be pointed out that for a real life situation at extremely high temperature when $k_B T$ is of the order of the ${}^1\Sigma$ ground state dissociation energy, $D$, direct thermally induced dissociation $N_2O \rightarrow N_2({}^1\Sigma) + O({}^1D)$ will become the dominant decompositions mechanism.

The most important conclusions arising from the present discussion of the activation energy involve the distinction between the low temperature case $\hbar\omega \gg k_B T$ and the high temperature case $\hbar\omega < k_B T \ll D$. In the low temperature limit the unimolecular decomposition of the triatomic $N_2O$ molecule occurs by quantum mechanical decay of very few bound zero order states which are located just above the continuum threshold, $A$, into the continuum. On the other hand, in the high temperature limit, the major contribution to the decay rate originates from the contribution of the intersection point of the two zero order potential surfaces. These conclusions are identical with the theory of radiationless processes in solid state [32] and molecular physics [33].

## 5. Comments on the High Temperature Activation Energy

The general expression for the non radiative thermally averaged decay probability, which under the conditions specified in Section 2 is equal to the unimolecular rate constant, can be displayed in the general form

$$k = \frac{2\pi}{\hbar Z} |\langle \boldsymbol{H}_{so} \rangle|^2 \sum_{\alpha} \sum_{\beta} \exp(-E_{i\alpha}/k_B T)\, |S_{i\alpha, f\beta}|^2\, \delta(E_{i\alpha} - E_{f\beta}) \tag{5.1}$$

where $S_{i\alpha, f\beta}$ is the (multidimensional) vibrational overlap integral with the continuum wavefunction being volume normalized), while $Z = \sum_{\alpha} \exp(E_{i\alpha}/k_B T)$ being the partitition function. Eq. (5.1) can in general be handled by recasting the thermally averaged transition probability in terms of a Fourier transform of a generating function [32–34]. Following the general methods developed by

Kubo and Toyozawa [32] and by Lax [34] one can represent (5.1) in the form

$$k=\frac{|\langle \boldsymbol{H}_{so}\rangle|^2}{\hbar^2}\sum_{\alpha}\frac{\exp(-E_{i\alpha}/k_BT)}{Z}\int_{-\infty}^{\infty}dt\left\langle \chi_{i\alpha}\left|\exp\left(\frac{i}{\hbar}\boldsymbol{H}_ft\right)\exp\left(-\frac{i}{\hbar}\boldsymbol{H}_it\right)\right|\chi_{i\alpha}\right\rangle \tag{5.2}$$

where $\boldsymbol{H}_i$ and $\boldsymbol{H}_f$ represent the molecular nuclear Hamiltonians $\boldsymbol{H}_j=\boldsymbol{T}_R+V_j(\boldsymbol{R})$ ($j=i,f$) in the initial and in the final states. This expression can be written in a closed analytical form only for the case of two harmonic potentials, which is not very useful for the problem at hand. However, it was previously demonstrated that in the high temperature limit a closed expression of (5.2) can be derived for a general form of the nuclear potentials [32, 34]. The high temperature limit is realized [32, 34] when the variation of the potential energy in the initial state within the averaged De Broglie wavelength $\hbar/(\mu k_BT)^{1/2}$ is negligible relative to the thermal energy $k_BT$, so that [32]

$$\left(\hbar/(\mu k_BT)^{1/2}\frac{\partial}{\partial\boldsymbol{R}}\right)^n V_i(\boldsymbol{R})\ll k_BT\,. \tag{5.3}$$

For all integer values of $n$ note that for $n=2$ Eq. (5.3) yields the well known condition

$$\hbar\omega\ll k_BT \tag{5.4}$$

for the validity of the high temperature limit, which was utilized in the qualitative discussion in Section 4. When condition (5.3) is satisfied, one can neglect the commutator $[\boldsymbol{T}_R, V_i(\boldsymbol{R})]$ in the exponent of the matrix element of (5.2), whereupon

$$\begin{aligned}&\frac{1}{\hbar}\int_{-\infty}^{\infty}\left\langle\chi_{i\alpha}\left|\exp\left(\frac{i}{\hbar}\boldsymbol{H}_ft\right)\exp\left(-\frac{i}{\hbar}\boldsymbol{H}_it\right)\right|\chi_{i\alpha}\right\rangle dt\\&=\frac{1}{\hbar}\int_{-\infty}^{\infty}\left\langle\chi_{i\alpha}\left|\exp\left[\frac{i}{\hbar}(V_f-V_i)t\right]\right|\chi_{i\alpha}\right\rangle dt=\int d\boldsymbol{R}|\chi_{i\alpha}|^2\,\delta(V_f(\boldsymbol{R})-V_i(\boldsymbol{R}))\,.\end{aligned} \tag{5.5}$$

Furthermore, we can replace the summation over $\alpha$ states by the classical expression

$$\begin{aligned}\frac{1}{Z}\sum_{\alpha}|\chi_{i\alpha}|^2\exp(-E_{i\alpha}/k_BT)&=\exp(-V_i(\boldsymbol{R})/k_BT)/Z\\&=\exp(-V_i(\boldsymbol{R})/k_BT)/\int d\boldsymbol{R}\exp(-V_i(\boldsymbol{R})/k_BT)\,.\end{aligned} \tag{5.6}$$

Eq. (5.2) with the aid of Eqs. (5.5) and (5.6) takes the following limiting form at high temperatures

$$k=\frac{|\langle\boldsymbol{H}_{so}\rangle|^2}{\hbar}\,\frac{\int d\boldsymbol{R}\exp(-V_i(\boldsymbol{R})/k_BT)\,\delta(V_f(\boldsymbol{R})-V_i(\boldsymbol{R}))}{\int d\boldsymbol{R}\exp(-V_i(\boldsymbol{R})/k_BT)}\,. \tag{5.7}$$

The following comments should be made at this point:

a) The high temperature rate constant is valid for any form (and dimension) of the potential surfaces for the initial and final states.

b) This rate constant was derived for the case of interstate coupling which is independent of the nuclear coordinates. When the zero order states are coupled by the nuclear kinetic energy operator, $\langle \boldsymbol{H}_{so} \rangle$ in (5.7) is replaced by the matrix elements of the nuclear momentum and by a temperature dependent factor.

c) Eq. (5.7) provides the most general proof that in the high temperature limit the non radiative transition takes place in the configuration where the two potential surfaces intersect, i.e. along the hypersurface where

$$V_i(\boldsymbol{R}) = V_f(\boldsymbol{R}) . \tag{5.7}$$

d) Condition (5.7) is usually referred to as the Franck-Condon principle for thermal reaction which involve a change in the electronic states. This principle played a crucial role in the understanding of electron transfer processes in solution [36, 37, 27]. However, from the present discussion it is obvious that this argument is much more general.

For the sake of comparison with the results of the numerical calculations of Section 4, let us specialize to the one dimensional case setting $\boldsymbol{R} = R$. Recasting the high temperature partition function in the approximate form corresponding to a harmonic potential characterized by a force constant $\kappa$,

$$\int dR \exp(-V_i(R)/k_B T) \approx (\pi k_B T/\kappa)^{1/2}$$

and utilizing the well known properties of the delta function, Eq. (5.7) is reduced to the simple form

$$\begin{aligned} k &= \frac{|\langle \boldsymbol{H}_{so} \rangle|^2}{\hbar} \left( \frac{\kappa}{4\pi k_B T} \right)^{1/2} \frac{\exp(-V_i(R_0)/k_B T)}{\left| \frac{\partial}{\partial R} (V_f(R) - V_i(R)) \right|_{R=R_0}} \\ &= \frac{|\langle \boldsymbol{H}_{so} \rangle|^2}{\hbar} \left( \frac{\pi \mu \omega^2}{k_B T} \right)^{1/2} \frac{\exp(-E_0/k_B T)}{\left| \frac{\partial}{\partial R} (V_f(R) - V_i(R)) \right|_{R=R_0}} \end{aligned} \tag{5.8}$$

where $E_0$ and $R_0$ correspond again to the distance and energy of the crossing point of the one dimensional potential surfaces. Thus in this high temperature limit the activation energy in the one dimensional model is just $E_0$ while the apparent activation energy being $E_0 - k_B T/2$. Finally, it is worthwhile to notice that the high temperature unimolecular rate constant is determined by $|(F_f - F_i)|^{-1}$ in a manner analogous to the result of the semiclassical approximation (Eq. (3.12)), and also to the Landau Zener formula.

## 6. A Two Dimensional Linear Model for the Unimolecular Decomposition of $N_2O$

The one dimensional model for the unimolecular decomposition of $N_2O$ can be extended to include the role of the N–N vibration, still maintaining that the dissociation in the final state occurs along the N–N–O ($^1\Sigma$) axes. Gilbert and Ross [19] have performed approximate numerical calculations for a two dimensional model. In what follows we shall present some general results for such a model, which may be of interest for the understanding of the nature of the distribution vibrational energy among the $N_2$ molecules resulting from the thermal decomposition of $N_2O$. This problem, which cannot be handled by the simple one dimensional model, is of considerable theoretical and experimental interest.

Denoting by $R$ the N–O and by $X$ the N–N distance, the two dimensional potentials representing the initial and the final states are

$$V_i(R, X) = f_1(R) + f_2(X) \tag{6.1}$$

$$V_f(R, X) = A + \frac{B}{R^n} + \tilde{f}_2(X) \tag{6.2}$$

where $f_1(R), f_2(X)$ and $\tilde{f}_2(X)$ can be chosen to be either Morse or harmonic potentials. The ground state potential (6.1) is similar to that previously used for some triatomic molecules. $f_1(R)$ corresponds to the bound N–O potential in the ground state. It should be noted that the bound N–N potentials $f_2(X)$ and $\tilde{f}_2(X)$ in the initial and final states may differ both in their equilibrium distance, in the vibrational frequency (for a harmonic potential) or in the characteristic reciprocal length and the effective dissociation energy (for a Morse Potential). In this approximate representation the $X$ and $R$ modes are independent and the vibrational wave functions are

$$\chi_{i\alpha\alpha'}(R, X) = \chi_{i\alpha}(R)\, \chi_{i\alpha'}(X)\,, \tag{6.3a}$$

$$\chi_{f\beta\beta'}(R, X) = \chi_{f\beta}(R)\, \chi_{f\beta'}(X)\,, \tag{6.3b}$$

while the corresponding energies are given by

$$E_{i\alpha\alpha'} = E_{i\alpha} + E_{i\alpha'}\,, \tag{6.4}$$

$$E_{f\beta\beta'} = E_{f\beta} + E_{f\beta'}\,, \tag{6.5}$$

We now require two indices to specify each vibrational state. Note that as before $\chi_{f\beta}(R)$ represents an unbound state.

The unimolecular rate constant is now given by

$$k = \frac{2\pi}{\hbar} |\langle \boldsymbol{H}_{so} \rangle|^2 \tag{6.6}$$

$$\cdot \frac{\sum\limits_{\alpha}\sum\limits_{\alpha'}\sum\limits_{\beta}\sum\limits_{\beta'} \exp\left(-\frac{E_{i\alpha}+E_{i\alpha'}}{k_B T}\right) |\langle \chi_{i\alpha} | \chi_{f\beta} \rangle|^2 |\langle \chi_{i\alpha'} | \chi_{f\beta'} \rangle|^2 \delta(A + E_{f\beta} + E_{f\beta'} - E_{i\alpha} - E_{i\alpha'})}{\sum\limits_{\alpha}\sum\limits_{\alpha'} \exp\left(-\frac{E_{i\alpha}+E_{i\alpha'}}{k_B T}\right)}\,.$$

Rewriting the delta function in (6.6) in terms of a convolution integral involving two delta functions we have

$$k = \frac{2\pi}{\hbar Z_\alpha Z_{\alpha'}} |\langle \boldsymbol{H}_{so} \rangle|^2 \int d\varepsilon \sum_{\alpha}\sum_{\beta} \exp\left(-\frac{E_{i\alpha}}{k_B T}\right) \tag{6.7}$$

$$\cdot |\langle \chi_{i\alpha} | \chi_{f\beta} \rangle|^2\, \delta(A + E_{f\beta} - E_{i\alpha} + \varepsilon) \sum_{\alpha'}\sum_{\beta'} \exp\left(-\frac{E_{i\alpha'}}{k_B T}\right) |\langle \chi_{i\alpha'} | \chi_{f\beta'} \rangle|^2\, \delta(E_{f\beta'} - E_{i\alpha'} - \varepsilon)$$

where $Z_\alpha Z_{\alpha'}$ is the product of the two partition functions in the denominator of (6.6).

It will be convenient at this stage to define two auxiliary functions.

$$F(\varepsilon)=\frac{1}{Z_\alpha}\sum_\alpha \exp\left(-\frac{E_{i\alpha}}{k_BT}\right)|\langle\chi_{i\alpha}|\chi_{f\beta}\rangle|^2\,\delta(A+E_{f\beta}-E_{i\alpha}+\varepsilon)\,, \tag{6.8}$$

$$G(\varepsilon)=\frac{1}{Z_{\alpha'}}\sum_{\alpha'} \exp\left(-\frac{E_{i\alpha'}}{k_BT}\right)|\langle\chi_{i\alpha'}|\chi_{f\beta'}\rangle|^2\,\delta(E_{f\beta'}-E_{i\alpha'}-\varepsilon) \tag{6.9}$$

and to rewrite (6.7) in the concise form

$$k=\frac{2\pi}{\hbar}|\langle H_{so}\rangle|^2\int d\varepsilon F(\varepsilon)\,G(\varepsilon)\,. \tag{6.10}$$

Thus the quantum mechanical rate constant for the present model can be expressed in terms of a convolution integral involving two generalized line shape functions. The line shape functions $F(\varepsilon)$ (Eq. (6.8)) can be evaluated by the numerical methods described in Sections 3 and 4 which are based on the semiclassical approximation. Obviously $F(\varepsilon)$ involves the decay of the N–O zero order vibronic into the continuum, however, now the N–N modes come in and the onset energy $A$ for tunnelling can be reached by different combinations of N–O and N–N modes. Thus the metastable decaying states correspond to a combination of both N–O and N–N vibrationally excited states. The role of the N–N modes is incorporated in terms of the generalized line shape function $G(\varepsilon)$ (Eq. (6.9)). An explicit expression for $G(\varepsilon)$ can be provided assuming that the N–N vibrations in the initial and final states are harmonic both being characterized by a reduced mass $\mu_2$ and the same frequency $\omega_2$, while the origins of the N–N potentials are displaced by $(\Delta X)$ in these two electronic states. In this simple case one gets the Fourier integral [32–36]

$$G(\varepsilon)=\int dt\exp(-i\varepsilon t/\hbar)\exp\left\{-\frac{\Delta^2}{2}\Bigl[\coth\left(\frac{\hbar\omega_2}{2k_BT}\right)(1-\cos\omega_2 t)-i\sin\omega_2 t\right\} \tag{6.11}$$

where the reduced displacement is defined by

$$\Delta=\left(\frac{\mu_2\omega_2}{\hbar}\right)^{1/2}\Delta X\,. \tag{6.11a}$$

In the simple case when $\Delta=0$, thus the two N–N potentials are not displaced between the two electronic states $G(\varepsilon)=\delta(\varepsilon)$ and Eq. (6.10) is reduced to

$$k=\frac{2\pi}{\hbar}|\langle H_{so}\rangle|^2 F(0) \tag{6.12}$$

which is just the result of the one dimensional model discussed in Section 3. It is also interesting to note that in a manner completely analogous to the theoretical study of optical selection in electronic relaxation [39], the present formalism can be extended to provide the vibrational population of the $N_2$ molecules resulting from the unimolecular decomposition. We can define the rate $k_{\beta'}$ for the production of the $N_2$ in the $\beta'$ vibrational state, so that

$$k_{\beta'} = \frac{2\pi}{\hbar} |\langle \boldsymbol{H}_{so} \rangle|^2 \int d\varepsilon F(\varepsilon)\, G_{\beta'}(\varepsilon) \tag{6.13}$$

where

$$G_{\beta'}(\varepsilon) = \frac{1}{Z_{\alpha'}} \sum_{\alpha'} \exp\left(-\frac{E_{i\alpha'}}{k_B T}\right) |\langle \chi_{i\alpha'} | \chi_{f\beta'} \rangle|^2\, \delta(E_{f\beta'} - E_{i\alpha'} + \varepsilon)\,. \tag{6.14}$$

From the formal point of view the decomposition processes resulting in different vibrational levels of the $N_2$ product correspond to different decay channels and $k = \sum_{\beta'} k_{\beta'}$. Now in the simple case $\Delta = 0$ we have $G_{\beta'}(\varepsilon) = (\exp(-E_{i\alpha'}/k_B T))\, \delta(\varepsilon)/Z_{\alpha'}$ whereupon Eq. (6.13) takes the simple form

$$k_{\beta'=\alpha'} = k \frac{\exp(-E_{i\alpha'}/k_B T)}{Z_{\alpha'}} \tag{6.15}$$

so that the vibrational states of the $N_2$ product assume a Boltzmann distribution characteristic of the ground state. In real life the situation when $\Delta \neq 0$ a more complex distribution (6.13) is obtained.

## 7. Discussion

In this paper we consider a general theoretical scheme for the nonadiabatic unimolecular decomposition of some triatomic molecules, which involve a change in the electronic state, and is thus amenable to study in terms of a thermally induced intramolecular radiationless decomposition, in complete analogy to molecular predissociation (classified by Herzberg [38] as case 1 c) and to electronic relaxation in the statistical limit. We have advanced some simple general criteria (Eq. (2.7)) for describing the decay process in terms of Fermi's golden rule, and were able to present general expressions for the decay probability of a single vibronic level (Eq. (2.8)) and for the thermally averaged unimolecular rate constant (Eq. (2.11)). The general quantum mechanical rate expression (2.11) for the non adiabatic reaction (subjected to restriction (2.7)) is characterized by a pre-exponential factor which is determined by the square of the interstate coupling matrix elements, in a manner analogous to electronic relaxation process [1], and as was previously asserted on the basis of transition state theory for this class of reactions [11]. The general behavior of the rate constant at low and high temperatures is of considerable interest. At low temperatures the rate constant is determined by tunnelling from the small number of zero order vibrational levels $\{i\tilde{\alpha}\}$ just above the continuum threshold $A$, so that $E_{i\tilde{\alpha}} \gtrsim A$ whereupon

$$k \approx \frac{2\pi}{\hbar} |\langle \boldsymbol{H}_{so} \rangle|^2 \sum_{\{\tilde{\alpha}\}} \frac{|\langle \chi_{i\tilde{\alpha}} | \chi_{f\beta} \rangle|^2}{Z_\alpha} \exp(-A/k_B T) \tag{7.1}$$

while at high temperatures the general rate constant (5.7) represents non radiative transition occurring at the intersection of the two potential surfaces. Note that the notion of an activated complex does not enter into these considerations and this concept can be defined only in the high temperature limit as corresponding to the configuration satisfying Eq. (5.7).

We have then proceeded to present the results of model calculations for the unimolecular decomposition of $N_2O$ adopting one or two dimensional linear models. Applying the semiclassical approximation the microsopic rate constant calculated for the one dimensional model result in an oscillatory function of the energy and cannot be handled within the framework of the Landau-Zener [14, 15] approximate scheme. This conclusion concurs with the results of the original work of Gilbert and Ross [19], however, we believe that some of our arguments (Section 2 and 6), the physical models and the computational method employed by us are somewhat more general. The numerical results obtained herein for the one dimensional model confirm our general considerations. Similar results for thermally induced predissociation of a diatomic molecule (see appendix) also provide support to our general conclusions. In particular, it is important to notice that the calculated apparent activation energy varies from the value of $A$ corresponding to the continuum onset at low temperatures to a value close to $E_0$, which represents the intersection point of the two one dimensional surfaces, at high temperatures.

An important conclusion originating at this point is that unimolecular reaction rates which correspond to processes involving a change in the electronic states, cannot be described over a broad temperature region in terms of the Arrhenius equation, and experimental activation energies can be compared to the theoretical data only over a narrow temperature range.

The one dimensional and the two dimensional linear models employed herein are admittedly crude, but they are very helpful in the elucidation of the gross features of the physical problem at hand. In particular, it is important to notice that in describing the potential surfaces for the initial and the final states we have completely discarded the conventional notion of normal modes [8]. As the decaying resonance states involve an admixture of highly excited vibrational ground state levels and continuum states, the use of normal modes (which is only valid for a small number of low lying bond vibrational levels) is quite useless in this context. The use of vibrational modes corresponding to different bonds was utilized in the semiquantitative description of molecular ground state potential surfaces [8, 38]. It was felt for some time that the highly excited vibronic levels of a lower electronic configuration which act as a dissipative channel in intramolecular electronic relaxation processes in large molecules are inadequately described in terms of normal modes, however, the problem of an alternative description of nuclear motion in a large molecule was not yet resolved.

We were able to provide a theoretical scheme for the linear dissociation process, the inclusion of the N–N vibrational mode being of considerable interest in relation to the vibrational states of the $N_2$ molecules which result from the unimolecular dissociation of $N_2O$. In the case when the N–N coordinate remains unchanged between the initial and the final states the partition of the $N_2$ vibrational states in the final product will be the same as in the initial ground state molecule.

The most serious sin of omission involved in the present treatment is the complete disregard of the doubly degenerate ground state bending vibration which will result in non linear dissociation (i.e. to an $O(^3P)$ atom flying apart at an angle

$\Theta < \pi$ relative to the $N_2(^1\Sigma)$ molecular axes). This problem can be handled (at least within the framework of the harmonic approximation) by assigning additional out of plane imaginary frequencies for the N–O motion. This interesting problem deserves a further study.

Any theoretical study should be tested in terms of the correlations it provides for the available experimental data and, most important, in terms of the suggestions for new experiments. The following comments are now in order:

a) The activation energy for the nonadiabatic unimolecular dissociation of $N_2O, CO_2, CS_2$ and COS should vary in the range $\Delta H_0^0 \leqq A \leqq E_A \leqq E_0 \leqq D$ (see Table 1). The only exception of this general conclusion (i.e. $E_A < D$) involves the high pressure dissociation of the $CO_2$ molecule [40] where $E_A = 110$ kcal/mole while $\Delta H_0^0 = 126$ kcal/mole. As the experimental data were obtained from shock wave experiments autocatalytic effects cannot be excluded. A further experimental study of $k_\infty$ for this reaction will be desirable.

b) The thermally averaged rate constant is rather uniformative and it will be very interesting to obtain direct experimental information concerning the energy dependence of the microscopic rate constants $W_{i\alpha}$ for the decay of a single vibronic zero order ground state level. In view of anharmonicity effects these highly excited vibrational levels located above the continuum onset $A$ may be accessible to optical excitation by either one photon absorption or, alternatively, by multiphoton absorption utilizing intense high power laser light sources. Such experiments of laser induced unimolecular decay of a single vibronic level will be of considerable value. Such optical selection experiments seem to be feasible by combining modern laser techniques with sensitive mass spectrometric detection methods.

c) The distribution of vibrational energy among the diatomic molecules resulting from conventional thermal dissociation or by optical selection of a single level (above $A$) is of considerable interest for the test of the general theory outlined in Section 6. To monitor the vibrationally excited states of homonuclear $N_2$ resulting from $N_2O$ dissociation one can utilize antistokes Raman scattering from a laser. In the cases of nonadiabatic unimolecular decomposition of $CO_2$, $CS_2$ or COS one can monitor directly the infrared emission from the resulting heteronuclear molecule. In the suggested thermal experiments vibrational relaxation of the products by the buffer gas has to be taken into account.

In conclusion, we would like to state that the formalism developed for nonradiative processes can be successfully applied to nonadiabatic unimolecular reactions. The present treatment is by no means limited to triatomic molecules. In the case of large molecular systems, it might be sometimes feasible to consider a "submolecule" within a large molecule (leaving out all the vibrational modes which are unchanged between the two electronic states) and to treat unimolecular thermally induced nonadiabatic decomposition or optically excited predissociation in large molecules by the adaptation of theoretical scheme employed in the present work.

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## Appendix

## Some Calculations on the Collision Induced Predissociation of $O_2(^3\Sigma_u^-)$

In the Schumann-Runge band of $O_2$ a line broadening due to predissociation can be experimentally observed. Murrell and Taylor [24] calculated this line broadening by numerical evaluation of the Franck-Condon factors and investigated the influence of the form of the repulsive potential while Child [23] has applied the *WKB* method for this system. We repeated this calculation with the method outlined for a *RKR* potential [41, 23] a Morse-potential and a harmonic potential. From the results for the line broadening in Fig. 6, it can be seen that the pattern of the line broadening is quite sensitive to the different bound state potentials as well as to the absolute value of the crossing point. The absolute values for the line broadening were calculated with a spinorbit interaction value of 70 $\mathrm{cm}^{-1}$ as for this value the absolute line broadening is in best agreement with the experimental results. The line broadening $\Delta\nu$ is given by the formula

$$\Delta\nu_i = \hbar W_i \tag{A.1}$$

We next turn our attention to the problem of collision induced predissociation [42] of $O_2(^3\Sigma_u^-)$ electronically excited states initially excited optically in the pres-

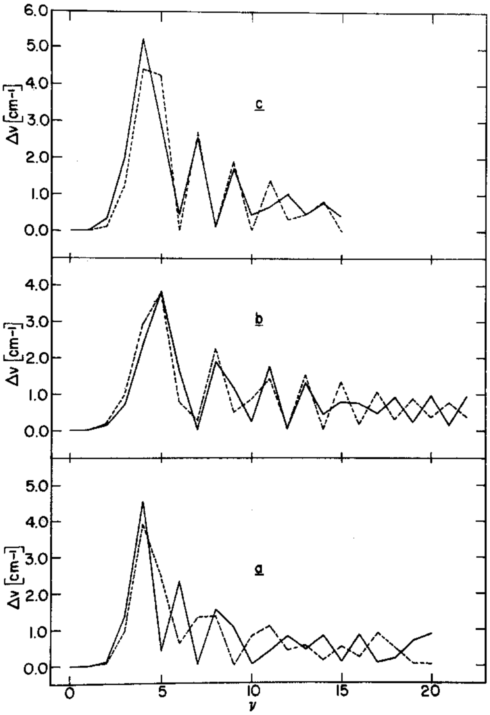

Fig. 6. Line broadening for the Schumann Runge spectrum of $O_2$. a for the RKR potential with —— $E_0 = 2359\ \mathrm{cm}^{-1}$; – – – $E_0 = 2604\ \mathrm{cm}^{-1}$; b for the harmonic potential with —— $E_0 = 2760\ \mathrm{cm}^{-1}$; – – – $E_0 = 2610\ \mathrm{cm}^{-1}$; c for the Morse potential with —— $E_0 = 2468\ \mathrm{cm}^{-1}$; – – – $E_0 = 2634\ \mathrm{cm}^{-1}$

ence of an inert gas at sufficiently high pressure to satisfy relation (2.9). Thus we can consider a decay process where the lowest vibrational level of the excited electronic state $^3\Sigma_u^-$ is optically populated and assuming that this electronically excited $^3\Sigma_u^-$ state arrives in thermal equilibrium before nonradiative (predissociated) decay. The microscopic rate constants, which are proportional to $\Delta v_i$ (Eq. A.1), were

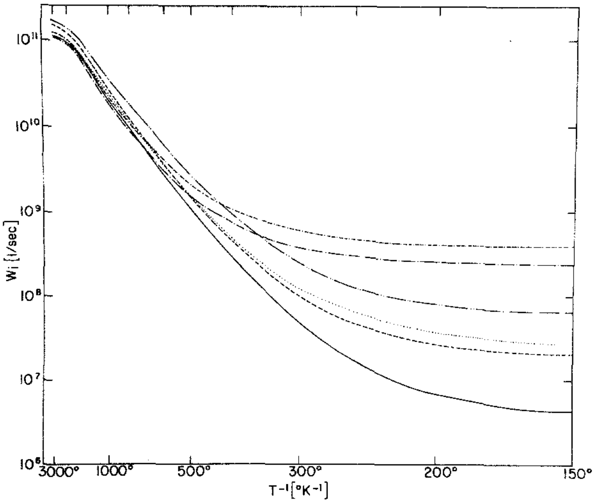

Fig. 7. Rate constants versus $T^{-1}$ for the thermally induced predissociation of $O_2(^3\Sigma_u)$. For the RKR potential —— $E_0=2604$ cm$^{-1}$; ······ $E_0=2359$ cm$^{-1}$; for the harmonic potential; —·— $E_0=2760$ cm$^{-1}$; —·—·— $E_0=2610$ cm$^{-1}$; for the Morse potential; —··— $E_0=2648$ cm$^{-1}$; ——— $E_0=2634$ cm$^{-1}$

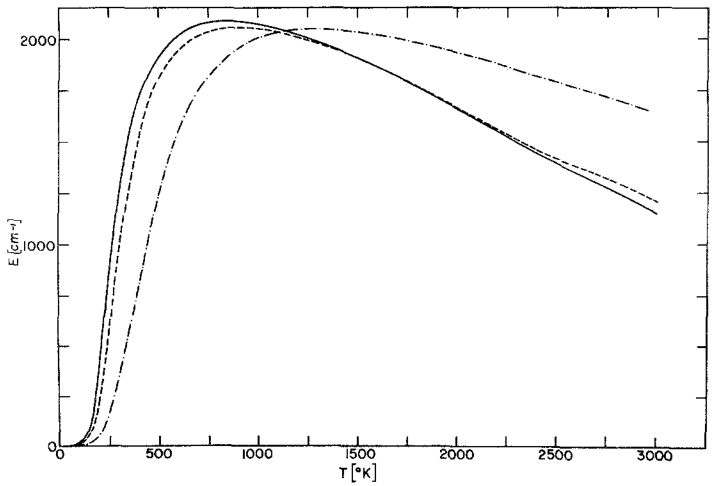

Fig. 8. Activation energy for the thermally induced predissociation of $O_2(^3\Sigma_u)$. General behaviour for —·— a harmonic potential; —— a Morse potential; ——— a RKR potential

used to calculate the thermally averaged rate constants and the activation energies. The results are given in Figs. 7 and 8. As expected, the rate constants are of the same order of magnitude for the different potentials chosen and yield zero activation energy for low temperatures while at high temperatures the energy value corresponding to the crossing point of the two potential surfaces is obtained. These results for thermally induced predissociation of an excited electronic state of a diatomic molecule concern with the results of our general analysis.

## References

1. a Robinson, G. W.: J. chem. Physics **47**, 1967 (1967).
   b Bixon, M., Jortner, J.: J. chem. Physics **48**, 715 (1960).
   c Rhodes, W.: J. chem. Physics **50**, 2885 (1969).
   d Jortner, J.: J. Chim. Physique **67**, 1 (1970).
2. Rosen, N.: J. chem. Physics **1**, 319 (1933).
3. Langer, R. M.: Physic. Rev. **34**, 92 (1929).
4. Rice, O. K.: J. chem. Physics **1**, 375 (1933).
5. Mies, F. M., Kraus, M.: J. chem. Physics **45**, 4455 (1966).
6. – J. chem. Physics **51**, 787 (1969).
7. — J. chem. Physics **51**, 798 (1969).
8. Stearn, A. E., Eyring, H.: J. chem. Physics **3**, 778 (1935).
9. Gill, E. K., Laidler, K.: Canad. J. Chemistry **36**, 13731 (1958).
10. Wieder, G. M., Marcus, R. A.: J. chem. Physics **37**, 1835 (1962).
11. Gladsstone, S., Laidler, K. J., Eyring, H.: The theory of rate processes. N. Y.: McGraw-Hill 1941.
12. Troe, J., Wagner, H.: Ber. Bunsenges. physikal. Chem. **71**, 937 (1967).
13. Arrthenius, S.: Z. physik. Chem. **4**, 226 (1889).
14. Landau, L. D.: Physics Z. Sovijet Union **1**, 88 (1932).
15. Zener, C.: Proc. Roy. Soc. (London) A **140**, 660 (1933).
16. Hinshelwood, C. N.: Proc. Roy. Soc. (London) A **113**, 230 (1927).
17. Kassel, L. S.: J. physic. Chem. **32**, 225 (1928).
18. Slater, N. B.: Theory of unimolecular reactions. Ithaca: Cornell University Press 1959.
19. a Gilbert, R. G.: Ph. D. thesis. Australia: University of Canberra 1970.
    b — Ross, I. G.: Austral. J. Chemistry **24**, 1451 (1971).
20. Landau, L. D., Lifshitz, E. M.: Quantum mechanics. London, New York: Pergamon Press 1958.
21. Coulson, C. A., Zalewsky, K.: Proc. Roy. Soc. (London), A **268**, 437 (1962).
22. Harris, R. A.: J. chem. Physics **39**, 978 (1963).
23. Child, M. S.: J. molecular Spectroscopy **33**, 487 (1970).
24. Murrell, J. N., Taylor, J. M.: Molecular Physics **16**, 609 (1969).
25. Nitzan, A., Jortner, J.: Chem. Physics Letters (in press).
26. Siebrand, W.: J. chem. Physics **46**, 440 (1967).
27. Levich, V. G.: Physical chemistry and advanced treatise, Vol. IXB, p. 985, edited by H. Eyring, Academic Press (1970).
28. Nikitin, E. E.: In: Chemische Elementarprozesse. Berlin: Springer Verlag 1968.
29. Sponer, H., Bonner, L. G.: J. chem. Physics **8**, 33 (1940).
30. Burland, D. M., Robinson, G. W.: J. chem. Physics **51**, 4548 (1969).
31. Olschewski, H. A., Troc. J., Wagner, H. Gg.: Ber. Bunsenges. physik. Chem. **70**, 450 (1966).
32. Kubo, R., Toyozawa, Y.: Progr. theoret. Physics **13**, 160 (1955).
33. Englman, R., Jortner, J.: Molecular Physics **28**, 145 (1970).
34. Lax, M.: J. chem. Physics **20**, 1752 (1952).
35. Lin, S. H.: J. chem. Physics **44**, 3759 (1966).
36. Marcus, R. A.: J. chem. Physics **24**, 966 (1956).
37. Libby, W.: J. physic. Chem. **56**, 863 (1952).

38. Herzberg, G.: Electronic spectra of polyatomic molecules. New York: D. Van Nostrand Company 1966.
39. Nitzan, A., Jortner, J.: J. chem. Physics, to be published.
40. Olschewski, H. A., Troe, J. A., Wagner, Gg.: Ber. Bunsenges. physik. Chem. N.F. **45**, 329 (1965).
41. Ackerman, M., Biounne, F.: J. molecular Spectroscopy **35**, 73 (1970).
42. Commes, F. J., Wenning, M.: Chem. Physics Letters **5**, 199 (1970).

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