Theoret. chim. Acta (Berl.) 8, 1—7 (1967)

Commentationes

Study of the Non-Adiabatic Transitions with Application to NO*

Sheng Hsien Lin

Department of Chemistry Arizona State University, Tempe, Arizona

Received January 2, 1967

An expression for the non-adiabatic transition probability is derived from the viewpoint of the non-stationary character of the adiabatic approximation. A numerical calculation has been made for the free NO molecule. The non-adiabatic transition probability for the transition $(B^2\pi\ v = 0) \rightarrow (a^4\pi\ v = 9)$ is estimated to be 10^{-6} $\sec^{-1}$ by using the wave functions proposed by Moser et al.

Für die nicht adiabatische Übergangswahrscheinlichkeit wurde aus dem nicht-stationären Charakter der adiabatischen Näherung ein Ausdruck hergeleitet, der für den Fall des NO-Moleküls numerisch ausgewertet wurde. Dabei ergab sich unter Verwendung der Wellenfunktionen von Moser u. Mitarb. eine Wahrscheinlichkeit für den Übergang $(B^2\pi\ v = 0) \rightarrow (a^4\pi\ v = 9)$ von der Größenordnung von 10^{-6} $\sec^{-1}$.

Une expression pour la probabilité de la transition non adiabatique est obtenue du point de vue du caractère non stationnaire de l'approximation adiabatique. Un calcul numérique a été effectué pour la molécule NO isolée. La probabilité de transition non adiabatique pour la transition $(B^2\pi\ v = 0) \rightarrow (a^4\pi\ v = 9)$ est évaluée à 10^{-6} $\sec^{-1}$ en utilisant les fonctions d'onde proposées par Moser et al.

1. Introduction

Recently, many investigations on the approximation of the Born-Oppenheimer separation have been carried out [*1*, *2*, *3*]. Fisk and Kirtman [*4*], and Jepsen and Hirschfelder [*5*] respectively evaluated the energy corrections to the Born-Oppenheimer approximation for the H_2 and H_2^+ molecules. Chiu [*6*] discussed the rotation-electronic interactions of diatomic molecules from the nonadiabatic viewpoint of the Born-Oppenheimer approximation. Wu and Bhatia [*7*], and Dalgarno and McCarroll [*8*] respectively studied the interactions of hydrogen and helium atoms in the ground and excited states, and found that the diagonal terms of the coupling between electronic and nuclear motion are not negligible at large separations. In the present investigation, we shall discuss the non-stationary character of the adiabatic approximation [*9*]. It will be shown that there is always a definite transition probability for the system to oscillate from one electronic state to another accompanied by a change in the quantum states of nuclear motion to make energy conserved. In the next section we shall estimate the non-adiabatic transition probability for the transition $B^2\pi \rightarrow a^4\pi$ of the free NO molecule.

Consider a system of N electrons with coordinates $\vec{r}_i$, $i = 1, 2 \,.\,.\, N$, and L nuclei with coordinates $\vec{r}_\alpha$, $\alpha = 1, 2 \,.\,.\, L$. The quantum mechanical motion of the system is then given by the Schrödinger equation

$$H\Phi = \left[\sum_{i=1}^{N} \frac{1}{2m} \vec{p}_i^{\,2} + \sum_{\alpha=1}^{L} \frac{1}{2M_\alpha} \vec{p}_\alpha^{\,2} + V(r,R)\right]\Phi = i\hbar \frac{\partial \Phi}{\partial t} \qquad (1)$$

---

* This work was supported by The Faculty Grant of Arizona State University.

where the electron mass is denoted by m, and the nuclear masses by M_α. It is possible to expand the wave function of the system of electrons and nuclei in the following form:

$$\Phi = \sum_{nv} c_{nv}(t)\,\chi_{nv}(R)\,\psi_n(r, R)\exp\left(-\frac{i\,W_{nv}\,t}{\hbar}\right) \tag{2}$$

where W_{nv} and χ_{nv} are the solution of the Schrödinger-type equation for the nuclear motion

$$\left[\sum_{\alpha=1}^{L}\frac{1}{2M_\alpha}\vec{p}_\alpha^{\,2} + E_n^{(e)}(R) + \sum_{\alpha=1}^{L}\frac{1}{M_\alpha}B_{nn}^{(\alpha)}(R)\right]\chi_{nv}(R) = W_{nv}(R)\,\chi_{nv}(R) \tag{3}$$

and

$$H_e\,\psi_n(r, R) = E_n^{(e)}(R)\,\psi_n(r, R) \tag{4}$$

with $B_{nn}^{(\alpha)}(R)$ defined by

$$B_{nn}^{(\alpha)}(R) = \tfrac{1}{2}\langle\psi_n \,|\, \vec{p}_\alpha^{\,2} \,|\, \psi_n\rangle\,. \tag{5}$$

Substituting Eq. (2) in Eq. (1), multiplying both sides of the resulting equation by $\psi_n(r, R)\,\chi_{nv}(R)$, and integrating over the electronic and the nuclear coordinates, we obtain the following set of coupled equations for the coefficients $c_{nv}(t)$:

$$i\hbar\,\dot{c}_{nv}(t) = \sum_{n'v'}{}'\,\langle\chi_{nv} \,|\, C_{nn'}(R) \,|\, \chi_{n'v'}\rangle\exp\left[\frac{i(W_{nv} - W_{n'v'})t}{\hbar}\right]c_{n'v'}(t) \tag{6}$$

where $C_{nn'}(R)$ is

$$C_{nn'}(R) = \sum_{\alpha=1}\frac{1}{M_\alpha}\left(\vec{A}_{nn'}^{(\alpha)}\cdot\vec{p}_\alpha + B_{nn'}^{(\alpha)}\right), \quad \text{and} \quad \vec{A}_{nn'}^{(\alpha)} = \langle\psi_n \,|\, \vec{p}_\alpha \,|\, \psi_{n'}\rangle\,. \tag{7}$$

The coordinate system usually used for the electrons in the integrals $\vec{A}_{nn'}^{(\alpha)}$, and $B_{nn'}^{(\alpha)}$ is fixed to the nuclear skeleton, hence some of the nuclear coordinates will not appear as parameters in the electronic wave function. It is usually easier to transform the derivatives to a coordinate system moving with the nuclei than to carry out the differentiation on the complicated function obtained when the electronic wave function is expressed in fixed coordinates. The non-diagonal matrix elements $\vec{A}_{nn'}^{(\alpha)}$, and $B_{nn'}^{(\alpha)}$ were calculated by Jepsen and Hirschfelder [*6*] for H_2^+ between the two electronic states $1s\sigma$ and $2s\sigma$. If $C_{nn'} \neq 0$, there is a definite transition probability for the system to make non-adiabatic transitions from one electronic state to another. This non-adiabatic transition from one electronic state to another is accompanied by transitions in the quantum states of the nuclear motion.

The experimental evidence shows that the influence of the coupling terms $C_{nn'}(R)$ is very small. Thus, we may use time-dependent perturbation theory to determine the transition probability which is

$$P(n'v' \to n\,v) = \frac{2\pi}{\hbar}\,|\,\langle\chi_{nv} \,|\, C_{nn'}(R) \,|\, \chi_{n'v'}\rangle\,|^2\,\varrho(W_{nv}) \tag{8}$$

where $\varrho(W_{nv})$ represent the density of states. We shall apply Eq. (8) to calculate the non-adiabatic transition probability for the transition $B^2\pi \to a^4\pi$ of the NO molecule.

2. Application to Nitric Oxide

Instead of directly performing the derivation of $P(n'v' \to nv)$ in the fixed coordinate system as already outlined, it is possible to separate off the motion of the center of mass from the Schrödinger equation before performing the derivation. Jepsen and Hirschfelder [*10*] pointed out that the two approaches give quite different Born-Oppenheimer separations, with somewhat different accuracy and somewhat different coupling terms between the electronic and nuclear motions. In the following treatment of diatomic molecules, we shall ignore the distinction between the center of gravity of the nuclei, and the center of gravity of the molecule and use the rotating coordinate system associated with the nuclei for the motion of the electrons. In this case, the coupling matrix elements $C_{nn'}(R)$ takes the following form:

$$\begin{aligned} C_{nn'}(R) = & -\frac{\hbar^2}{2\mu}\Big\{\langle\psi_n\Big|\frac{1}{R^2}\frac{\partial}{\partial R}\Big(R^2\frac{\partial}{\partial R}\Big)+\frac{\cot\theta}{R^2}\Big(\frac{\partial}{\partial\theta}-i\hat{M}_\xi\Big)+ \\ & +\frac{1}{R^2}\Big(\frac{\partial}{\partial\theta^2}-2i\hat{M}_\xi\frac{\partial}{\partial\theta}-\hat{M}_\eta^2-\hat{M}_\xi^2\Big)+ \\ & +\frac{1}{R^2\sin^2\theta}\Big[\frac{\partial^2}{\partial\varphi^2}-2\sin\theta\hat{M}_\eta\frac{\partial}{\partial\theta}-2i\cos\theta\hat{M}_\zeta\frac{\partial}{\partial\varphi}- \\ & -\sin\theta\cos\theta(\hat{M}_\eta\hat{M}_\zeta+\hat{M}_\zeta\hat{M}_\eta)\,|\psi_{n'}\rangle+ \\ & +2\langle\psi_n\Big|\frac{\partial}{\partial R}\Big|\psi_{n'}\rangle\frac{\partial}{\partial R}+\frac{2}{R^2\sin^2\theta}\langle\psi_n\Big|\frac{\partial}{\partial\varphi}- \\ & -i\sin\theta\hat{M}_\eta\Big|\psi_{n'}\rangle\frac{\partial}{\partial\varphi}+\frac{2}{R^2}\langle\psi_n\Big|\frac{\partial}{\partial\theta}-i\hat{M}_\xi\Big|\psi_{n'}\rangle\frac{\partial}{\partial\theta}\Big\} \end{aligned} \tag{9}$$

where ζ_i represents the coordinate whose axis is directed along the line joining the nuclei, and $(\hat{M}_\xi, \hat{M}_\eta, \hat{M}_\zeta)$ denote the operators of the components of the total angular momentum of the electrons. Next we want to calculate the coupling matrix element between the two electronic states $B^2\pi$ and $a^4\pi$ of the NO molecule. The qualitative molecular orbital description of nitric oxide was originally given by MULLIKEN [*11*]. Recently, a complete self-consistent LCAO treatment of NO has been carried out by MOSER et al. [*12*]. We shall use their wave functions to estimate $C_{a^4\pi, B^2\pi}(R)$. For convenience, their molecule orbitals and wave functions for nitric oxide are tabulated in Tab. 1 and 2 respectively.

Table 1. *Molecular Orbitals of Nitric Oxide*

$$\phi_{1\sigma} = (1s)_0 \qquad \phi_{2\sigma} = (1s)_n$$
$$\phi_{3\sigma} = 0.3700\,(2s)_n + 0.6561\,(2s)_0 + 0.1927\,(2p_\sigma)_n + 0.1994\,(2p_\sigma)_0$$
$$\phi_{4\sigma} = 0.8084\,(2s)_n - 0.7766\,(2s)_0 + 0.0461\,(2p_\sigma)_n + 0.2679\,(2p_\sigma)_0$$
$$\phi_{5\sigma} = 0.4847\,(2s)_n + 0.2505\,(2s)_0 - 0.6387\,(2p_\sigma)_n - 0.5392\,(2p_\sigma)_0$$
$$\phi_{6\sigma} = 0.7036\,(2s)_n - 0.7300\,(2s)_0 + 1.0618\,(2p_\sigma)_n - 1.0313\,(2p_\sigma)_0$$
$$\phi_{1\pi} = 0.5050\,(2p_\pi)_n + 0.7649\,(2p_\pi)_0$$
$$\phi_{2\pi} = 0.8887\,(2p_\pi)_n - 0.6780\,(2p_\pi)_0$$

If the rotation-electronic interactions are neglected, then the rotational angular momentum is conserved in the system. With this and the orthogonality of the electronic wave functions, we can see from Eq. (9) that the main contribution to the calculation of $C_{nn'}(R)$ comes from $\langle\psi_n\Big|\frac{\partial}{\partial R}\Big|\psi_{n'}\rangle$ and $\langle\psi_n\Big|\frac{1}{R^2}(\hat{M}_\eta^2+\hat{M}_\xi^2)\Big|\psi_{n'}\rangle$. Furthermore, since $B^2\pi \to a^4\pi$ is spin-forbidden, to calculate $C_{a^4\pi, B^2\pi}(R)$, we have to calculate the matrix elements of spin-orbit coupling, vibronic coupling and

Table 2. *Wave Functions of Nitric Oxide*[a]

$$\psi(x^2\pi\, 1\tfrac{1}{2}) = |\,(1\pi^+)_+(1\pi^-)_+(1\pi^+)_-(1\pi^-)_-(2\pi^+)_+\,|$$

$$\psi(a^4\pi\, 1\tfrac{3}{2}) = |\,(1\pi^+)_+(1\pi^-)_+(1\pi^+)_-(2\pi^+)_+(2\pi^+)_-\,|$$

$$\psi(a^4\pi\, 1\tfrac{1}{2}) = \frac{1}{\sqrt{3}}(|\,(1\pi^+)_+(1\pi^-)_+(1\pi^-)_-(2\pi^+)_+(2\pi^+)_-\,| + |\,(1\pi^+)_+(1\pi^-)_+(1\pi^+)_-(2\pi^-)_+(2\pi^+)_-\,| + \\ |\,(1\pi^+)_+(1\pi^-)_+(1\pi^+)_-(2\pi^+)_+(2\pi^-)_-\,|)$$

$$\psi_1(B^2\pi\, 1\tfrac{1}{2}) = |\,(1\pi^+)_+(1\pi^+)_-(1\pi^-)_-(2\pi^+)_+(2\pi^-)_+\,|$$

$$\psi_2(B^2\psi\, 1\tfrac{1}{2}) = \frac{1}{\sqrt{2}}(|\,(1\pi^+)_+(1\pi^-)_+(1\pi^+)_-(2\pi^+)_+(2\pi^-)_-\,| - |\,(1\pi^+)_+(1\pi^-)_+(1\pi^-)_-(2\pi^+)_+(2\pi^+)_-\,|)$$

$$\psi_3(B^2\pi\, 1\tfrac{1}{2}) = \frac{1}{\sqrt{6}}|\,(1\pi^+)_+(1\pi^-)_+(1\pi^-)_-(2\pi^+)_+(2\pi^+)_-\,| -2\,|\,(1\pi^+)_+(1\pi^-)_+(1\pi^+)_-(2\pi^-)_+(2\pi^+)_-\,| + \\ + |\,(1\pi^+)_+(1\pi^-)_+(1\pi^+)_-(2\pi^+)_+(2\pi^-)_-\,|)$$

---

[a] For simplicity, the configuration $(1\sigma)^2\,(2\sigma)^2\,(3\sigma)^2\,(4\sigma)^2\,(5\sigma)^2$ has been omitted.

spin-vibronic coupling. These matrix elements calculated by the conventional procedures [*13, 14, 15, 16*] using the wave functions of Tab. 2 are, at equilibrium positions.

$$\begin{aligned} \langle\psi_2(B^2\pi\, 1\tfrac{1}{2})\left|\frac{\partial}{\partial R}\right|\psi(a^4\pi\, 1\tfrac{1}{2})\rangle &= -\,8.76\times 10^{-3}\left(\frac{1}{a_0}\right) \\ \langle\psi(x^2\pi\, 1\tfrac{1}{2})\left|\frac{\partial}{\partial R}\right|\psi_1(B^2\pi\, 1\tfrac{1}{2})\rangle &= -\,1.54\left(\frac{1}{a_0}\right) \\ \langle\psi(x^2\pi\, 1\tfrac{1}{2})\,|\,H'_{s0}\,|\,\psi(a^4\pi\, 1\tfrac{1}{2})\rangle &= 1.32\times 10^{-4}\left(\frac{e^2}{a_0}\right) \\ \langle\psi_2(B^2\pi\, 1\tfrac{1}{2})\,|\,H'_{s0}\,|\,\psi(a^4\pi\, 1\tfrac{1}{2})\rangle &= 0.591\times 10^{-4}\left(\frac{e^2}{a_0}\right). \end{aligned} \tag{10}$$

In Eq. (14), H'_{s0} represents the spin-orbit coupling:

$$H'_{s0} = \frac{1}{2m^2c^2}\sum_i \vec{s}_i\cdot(\vec{\nabla}_i V\times\vec{p}_i) + \frac{e}{m^2c^2}\sum_i\sum_i{}' \vec{s}_i\cdot\frac{(\vec{r}_{ij}\times\vec{p}_j)}{r_{ij}^3} \tag{11}$$

where $\vec{s}_i$ are electron spin operators. The detailed calculation of the matrix elements in Eq. (10) is discusses elsewhere [*17*].

In order to evaluate the integrals involving the vibrational wave functions between two electronic states, we assume that the potential curves of the two electronic states are in the form of the Morse potential [*18*]

$$U_n(R) = D_n[1 - e^{-\alpha_n(R-R_{en})}]^2\,. \tag{12}$$

Then the vibrational wave functions $\chi_{nv}^{(\mathrm{vib})} = 1/R\;\phi_{nv}$ take the following form [*18, 19*]:

$$\phi_n = \left[\frac{\alpha_n(K_n-2v-1)}{v!\,\Gamma(K_n-v)}\right]^{1/2} e^{-Z_n/2}\, Z_n^{\frac{K_n-2v-1}{2}} \sum_{k=0}^{v}(-1)^{k+v}\binom{v}{k}\frac{\Gamma(K_n-v)}{\Gamma(K_n-v-k)}\, Z_{\mathrm{n}}^{v-k} \tag{13}$$

where $\Gamma(x)$ is the gamma function, $Z_n = K_n e^{-\alpha_n(R-R_{en})} = \lambda_n e^{-\alpha_n R}$ and K_n and D_n are related to the constants in the expression for the vibrational energy

$$W_{nv}^{(\mathrm{vib})} = \omega_n(v+\tfrac{1}{2}) - (\omega_n x_n)\,(v+\tfrac{1}{2})^2\,, \tag{14}$$

$$K_n = \frac{\omega_n}{(\omega_n x_n)}\,,\; D_n = \frac{\omega_n^2}{4(\omega_n x_n)}\,,\; (\omega_n x_n) = \frac{h}{4\pi c\mu}\,\alpha_n^2\,. \tag{15}$$

Thus, for example, the overlap integral of the vibrational wave functions between two electronic states is given by

$$\langle \chi_{nv}^{(\text{vib})} \mid \chi_{n'v'}^{(\text{vib})} \rangle = \langle \frac{1}{R}\, \phi_{nv} \mid \frac{1}{R}\, \phi_{n'v'} \rangle = (-1)^{v+v'}\, N_{nv} N_{n'v'} \lambda_n^{\frac{K_n - 1}{2}}\, \lambda_{n'}^{\frac{K_{n'} - 1}{2}}$$

$$\sum_{k=0}^{v} \sum_{k'=0}^{v'} (-1)^{k+k'} \binom{v}{k} \binom{v'}{k'} \frac{1}{\lambda_n^k \lambda_{n'}^{k'}} \cdot \frac{\Gamma(K_n - v)\, \Gamma(K_{n'} - v')}{\Gamma(K_n - v - k)\, \Gamma(K_{n'} - v' - k')}\, J(k\, k') \tag{16}$$

where

$$N_{nv} = \left[\frac{\alpha_n (K_n - 2v - 1)}{v!\, \Gamma(K_n - v)} \right]^{1/2} \tag{17}$$

and

$$J(k, k') = \int_{\infty -}^{\infty} dR \left[-\tfrac{1}{2} (\lambda_n e^{-\alpha_n R} + \lambda_{n'} e^{-\alpha_{n'} R}) \right] \times$$

$$\times \exp \left[-\left(\tfrac{1}{2} K_n - k - \tfrac{1}{2}\right) \alpha_n R - \left(\tfrac{1}{2} K_{n'} - k' - \tfrac{1}{2}\right) \alpha_{n'} R \right] \tag{18}$$

since $\alpha_n \neq \alpha_{n'}$, the integral $J(k, k')$ in general cannot be evaluated exactly, and if it is desired to obtain a general analytical formula for an overlap integral, it is necessary to resort to a valid approximation. The approximation method proposed by FRASER and JARMAIN [*20*] is to replace $U_n(R)$ and $U_{n'}(R)$ by the two new potentials $U'_n(R)$ and $U'_{n'}(R)$. The new potentials have their α-values equal to some mean value of the original α_n and $\alpha_{n'}$. It is easiest to take the arithmetic mean $\alpha = (\alpha_n + \alpha_{n'})/2$ though it is sometimes convenient to choose another α that will make final computations easier and yet not affect the result. Compensating adjustments are made in the constants of the two states that depend on the α-value for the state. Thus, normalization and closure properties are maintained. The molecular constants adjusted to correspond to the new α, and indicated by primes, are

$$K'_n = K_n \left(\frac{\alpha_n}{\alpha} \right)^2, \qquad K'_{n'} = K_{n'} \left(\frac{\alpha_{n'}}{\alpha} \right)^2, \qquad \lambda'_n = K'_n\, e^{\alpha R_{en}}, \qquad \lambda'_n = K'_{n'}\, e^{\alpha R_{en}'} \,. \tag{19}$$

With these adjustments, the integral $J(k, k')$ can be carried out easily and is given by

$$J(k\, k') = \frac{1}{\alpha} \left(\frac{1}{\lambda} \right)^{K-1-(k+k')} \Gamma(K - 1 - k - k') \tag{20}$$

where $K = \frac{1}{2}(K'_{n'} + K'_{n'})$ and $\lambda = \frac{1}{2}(\lambda'_n + \lambda'_{n'})$. Other vibrational integrals like $\langle 1/R\, \phi_{nv} \mid R^k\, \phi_{nv} \rangle$, $\langle 1/R\, \phi_{nv} \mid 1/R \frac{\partial \phi_{n'v'}}{\partial R} \rangle$ etc., can be evaluated similarly. By using the molecular constants [*21*] $\omega = 1038$ cm^{-1}, $\omega x = 7.601$ cm^{-1}, $R_e = 1.385$ Å for the $B^2\pi$ state [*22*], and $\omega = 1019$ cm^{-1}, $\omega x = 12.8$ cm^{-1}, $R_e = 1.4$ Å for the $a^4\pi$ state. We obtain, for example,

$$\langle \chi_0^{(\text{vib})}(B^2\pi) \mid \chi_9^{(\text{vib})}(a^4\pi) \rangle = -\,0.674 \times 10^{-9} \tag{21}$$

$$\langle \frac{1}{R}\, \phi_0(B^2\pi) \left| \frac{1}{R} \frac{\partial}{\partial R}\, \phi(a^4\pi) \right\rangle = -\,1.33 \times 10^{-8}/a_0 \,.$$

These values agree to the order of magnitude with those obtained by the harmonic oscillator approximation [*24*]. It should be noticed that the vibrational integrals of diatomic molecules between two electronic states depend very greatly on the modifications in equilibrium distances and vibrational frequencies of the two electronic states. The larger the modifications in equilibrium distances and vibrational frequencies of the two electronic states, the larger will be the vibrational integrals.

To calculate the non-adiabatic transition probability for the transition $B^2\pi \rightarrow a^4\pi$, we further assume that the intervals of the rotational energy are so small in comparison with those of the vibrational energy that the rotational energy may be approximately regarded as forming a continuum spectrum, and also that the electronic-rotation couplings are negligible. In this case, we have $\varrho(W_{nv}) = \frac{2\mu Re^2}{\hbar^2}$ [*24*]. Actually this is also equivalent to assume that the non-adiabatic transitions originate from a Boltzmann distribution of rotational levels at rather high temperatures so that the summation over rotational states can be replaced by an integration.

Substituting the matrix elements of spin-orbit coupling, vibronic coupling, spin-vibronic coupling, and the vibrational integrals listed respectively in Eqs. (10) and (21), into Eq. (8), and using the Franck-Condon approximation, we obtain the non-adiabatic transition probability for the transition from the state $B^2\pi(v' = 0)$ to the state $a^4\pi(v = 9)$ as

$$\begin{aligned} P(B^2\pi v' = 0 \rightarrow a^4\pi v = 9) &= \frac{2\pi}{\hbar} \left| \langle \chi_9^{(\mathrm{vib})}(a^4\pi) \mid C_{a^4\pi, B^2\pi} \mid \chi_0^{(\mathrm{vib})}(B^2\pi)\rangle \right|^2 \varrho(W^{a^4\pi}) \\ &= \frac{2\pi}{\hbar} \left| \frac{\hbar^2}{2\mu} \left[2 \left\langle \psi_2(B^2\pi\, 1\tfrac{1}{2}) \left| \frac{\partial}{\partial R} \right| \psi(a^4\pi\, 1\tfrac{1}{2}) \right\rangle \left\langle \chi_9^{(\mathrm{vib})}(a^4\pi) \left| \frac{\partial}{\partial R} \right| \chi_0^{(\mathrm{vib})}(B^2\pi) \right\rangle - \right.\right. \\ &\quad \left.\left. - \langle \psi_2(B^2\pi\, 1\tfrac{1}{2}) \mid \hat{M}_\eta^2 + \hat{M}_\xi^2 \mid \psi(a^4\pi\, \tfrac{1}{2})\rangle \left\langle \chi_9(a^4\pi) \left| \frac{1}{R^2} \right| \chi_0(B^2\pi) \right\rangle \right] \right|^2 \varrho(W^{a^4\pi}) \\ &= 1 \times 10^{-6}\ \mathrm{sec}^{-1}\,. \end{aligned} \tag{22}$$

This is indeed a small value. However, this value cannot be taken too seriously in view of the crudity of the wave functions used, and the uncertainty of the equilibrium distance of the $a^4\pi$ state. These dependences may easily change the order of magnitude estimated above. Eq. (22) gives us the spontaneous rate for an isolated NO molecule to make radiationless transition from the initial state $(B^2\pi, v' = 0)$ to the state $(a^4\pi, v = 9)$.

Although the non-adiabatic transition $B^2\pi \rightarrow X^2\pi$ is spin-allowed, because of the large electronic energy gap involved in the transition, it will not be more favorable than the non-adiabatic transition $B^2\pi \rightarrow a^4\pi$ we have discussed. The calculation of the non-adiabatic transition probability $P(B^2\pi \rightarrow X^2\pi)$ will not be attempted here. Because, in this case, even the Fraser and Jarmain's method for estimating the vibrational integrals between two electronic states becomes impractical due to the strong cancellation property of the Laguerre polynomials. Finally, it should be pointed out that the non-adiabatic transition probability calculated here is for a free molecule, and it can be greatly enhanced [*3*, *17*], when the molecule is embeded in a crystalline solvent of another species.

Acknowledgement. The author is indebted to Professor R. BERSOHN of Columbia University for some helpful discussions.

References

1. KOLOS, W., and L. WOLNIEWICZ: J. chem. Physics **41**, 3663 (1964).
2. LONGUET-HIGGINS, H. C.: Adv. in Spectroscopy **2**, 429 (1961).
3. LIN, S. H.: J. chem. Physics **44**, 3759 (1966).

4. Fisk, G. A., and B. Kirtman: J. chem. Physics **41**, 3516 (1964).
5. Jepsen, D. W., and J. O. Hirschfelder: J. chem. Physics **32**, 1323 (1960).
6. Chiu, Y. N.: J. chem. Physics **41**, 3235 (1964).
7. Wu, T. Y., and A. B. Bhatia: J. chem. Physics **24**, 48 (1956).
8. Dalgarno, A., and R. McCorroll: Proc. Roy. Soc. (London) **A 237**, 383 (1956); **A 239**, 413 (1957).
9. Born, M., and K. Huang: Dynamical theory of crystal lattice, p. 166 and p. 406 (Oxford Press, 1954). Also Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, The Molecular theory of gases and liquids, p. 925 (vohn Wiley, 1954).
10. Jepsen, D. W., and J. O. Hirschfelder: Proc. Natl. Acad. Sci. U.S. **45**, 249 (1959).
11. Mulliken, R. S.: Rev. mod. Physics **4**, 1 (1932).
12. Moser, C., H. Brion, and M. Yamasaki: J. chem. Physics **30**, 673 (1959).
13. Albrecht, A. C.: J. chem. Physics **38**, 354 (1963); **33**, 156 (1960).
14. Murrell, J. N., and J. A. Pople: Proc. physic. Soc. (London) **A 69**, 245 (1956); also Pople, J. A., and J. W. Sidman: J. chem. Physics **27**, 1270 (1957).
15. Sidman, J. W.: J. chem. Physics **29**, 644 (1958).
16. Hameka, H. F., and L. J. Oosterhoff: Mol. Physics **1**, 358 (1958).
Lin, S. H.: J. chem. Physics **44**, 2810 (1966).
17. Lin, S. H.: J. chem. Physics **46**, 279 (1967).
18. Morse, P. M.: Physic. Rev. **34**, 57 (1929).
19. Pekeris, C. L.: Physic. Rev. **45**, 98 (1934).
20. Fraser, P. A., and W. R. Jarmain: Proc. physic. Soc. (London) **66A**, 1145, 1153 (1953),
21. Herzberg, G.: Molecular spectra and molecular structure, I. Spectra of diatomic molecules, p. 560 (D. Von Nostrand, 1950).
22. Frosch, R. P., and G. W. Robinson: J. chem. Physics **41**, 357 (1964).
23. Hutchisson, E.: Physic. Rev. **36**, 410 (1930).
24. Fowler, R. H.: Statistical mechanics, p. 40 (Cambridge Press, 1955).

Dr. Sheng Hsien Lin
Department of Chemistry
University of Arizona
Tempe, Arizona 85281 USA